

STEELS

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Microstructure and Properties

Fourth edition

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PREFACE TO THE FIRST EDITION

In this book, I have attempted to outline the principles which determine the microstructures of steels and through these the mechanical properties. At a time when our metallographic techniques are reaching almost to atomic resolution, it is essential to emphasise structure on the finest scale, especially because mechanical properties are sensitive to changes at this level. While this is not a book on the selection of steels for different uses, I have tried to include sufficient information to describe how broad categories of steels fulfil practical requirements. However, the main thrust of the book is to examine analytically how the γ/α phase transformation is utilised, and to explain the many effects that non-metallic and metallic alloying elements have, both on this transformation and on other phenomena.

This book is written with the needs of metallurgists, materials scientists and engineers in mind, and should be useful not only in the later years of the first degree and diploma courses but also in postgraduate courses. An elementary knowledge of materials science, metallography, crystallography and physics is assumed.

I am indebted to several colleagues for their interest in this book, particularly Dr D.V. Edmonds, who kindly read the manuscript, Dr P.R. Howell, Dr B. Muddle and Dr H.K.D.H. Bhadeshia, who made helpful comments on various sections, and numerous other members of my research group who have provided illustrations. I wish also to thank my colleagues in different countries for their kind permission to use diagrams from their work. I am also very grateful to Mr S.D. Charter for his careful preparation of the line diagrams. Finally, my warmest thanks go to Mrs Diana Walker and Miss Rosemary Leach for their careful and dedicated typing of the manuscript.

R.W.K. Honeycombe
Cambridge, 1980

PREFACE TO THE SECOND EDITION

This new edition retains the basic framework of the original book; however, the opportunity has been taken to introduce several additional chapters dealing with areas which have emerged or increased in significance since the book was first published in 1981. There is now a separate chapter on acicular ferrite which has become a desirable structure in some steels. The control of microstructures during welding is undoubtedly a crucial topic which now requires a chapter, while the modelling of microstructures to achieve optimum properties has emerged as an important approach justifying the inclusion of a further new chapter. The opportunity has also been taken to include a completely revised chapter on bainite transformations.

The overall aim of the book remains to introduce students to the principles determining the microstructures of steels, and through these, the mechanical properties and behaviour in service. Steels remain the most important group of metallic alloys, possessing a very wide range of microstructures and mechanical properties, which will ensure their continued extensive use far into the foreseeable future.

R.W.K. Honeycombe and H.K.D.H. Bhadeshia
Cambridge, 1995

PREFACE TO THE THIRD EDITION

Steel has the ability to adapt to changing requirements. This comes from the myriads of ways in which its structure can be influenced by processing and alloying. This is why it is the standard against which emerging materials are compared. Added to this is the commercial success, with output at record levels and a production efficiency which is uncanny. It is pleasing to see how, all over the world, iron and its alloys contribute to improving the quality of life of so many human beings. The technology is so good that most of these people rightly take it for granted.

This new edition captures developments since 1995, e.g., the extremely fine-grained alloys, steels with the ability to abnormally elongate and the properties of minute particles of iron. Questions are posed as to the theoretical limit to the finest crystals that can be manufactured on a large scale. In addition, there are major revisions in the explanations of microstructure, strengthening, kinetics and modelling.

The original aim of this book, to introduce students and technologists to the principles determining the microstructure and properties of iron and its alloys, has remained the guiding principle in the new edition.

H.K.D.H. Bhadeshia and R.W.K. Honeycombe
Cambridge, 2006

PREFACE TO THE FOURTH EDITION

Some 1.6 billion tonnes of steel is produced annually. This kind of consumption is not sustainable. A lot of the steel that is used today is not the most technologically advanced but is cheap in terms of the immediate cost, though not if the environmental deficit is accounted for. When threatened by aluminium, steel manufacturers globally created concept cars based on more capable steels and clever engineering design. This enabled them to retain their markets while enhancing safety and fuel efficiency. Some of this was driven by legislation. This approach stimulated research, development and education on the nature of steels. A similar strategy is required for commodity alloys that are used in infrastructure development, so that there is a substitution of high-quality steels that enable dramatic reductions in consumption.

The engineers and metallurgists who help in design and innovation need to understand the immense versatility of steels. Materials scientists in general need to do the same so that ridiculous claims, for example that graphene is 200 times stronger than steel, can be distinguished from fact. The best designers of the future will not simply consult material databases, but will seek imaginative solutions based on adventure and risk.

I hope that this book, apart from serving its long-standing aim of exposing the principles of microstructure and properties, helps change the way in which steels are thought of during the art of design. The present edition is a major revision, the nature of which is best understood by leafing through the pages. The book is written in a form that is self-contained and hence should appeal to any person who values the elegance of iron as a material.

H.K.D.H. Bhadeshia
Cambridge, 2016

ACKNOWLEDGMENTS

My adventure in Cambridge began when the late Professor Robert Honeycombe suggested that I should join him for research on steels. I owe him an enormous debt of gratitude for that, and for the opportunity some 21 years ago to participate in the second edition of this book.

Cambridge is a special place where discourse across disciplinary boundaries is an everyday occurrence. I am grateful to the vast numbers of students who over the years have stimulated my thoughts on some of the basic principles of metallurgy, principles that often are taken for granted until challenged by unpolluted minds.

I have had wonderful opportunities to collaborate, in one way or another, with many enlightened industries. These interactions inform about the complexity of real products and when they go well, result in tangible products. On the same lines, I have enjoyed my interactions with numerous academic institutions and national laboratories. Steels research and teaching is truly a global phenomenon.

I thank my extended family who seem to take delight in everything I publish, thus guaranteeing an audience!

H.K.D.H. Bhadeshia

ACRONYMS

bcc	Body-centred cubic
bct	Body-centred tetragonal
CE	Carbon equivalent
fcc	Face-centred cubic
P-LE	Partitioning local equilibrium
NP-LE	Negligible partitioning local equilibrium
ILS	Invariant-line strain
IPS	Invariant-plane strain
ECAP	Equal channel angular processing
FATT	Fracture assessed transition temperature
HAZ	Heat-affected zone of welded joints
hcp	Hexagonal close-packed
HREM	High-resolution electron microscopy
HSLA	High-strength low-alloy steels
HTP	High-temperature processed
HV	Vickers hardness
KN	Knoop hardness
KS	Kurdjumov-Sachs
LEFM	Linear-elastic fracture mechanics
NW	Nishiyama-Wasserman
ppm	Parts per million by weight
RE	Rare earth additions
SCR	Stress corrosion cracking resistance
SSAW	Self-shielded arc weld
TRIP	Transformation-induced plasticity
TTT	Time-temperature-transformation
CCT	Continuous cooling transformation
CHT	Continuous heating transformation
ULCB	Ultra-low carbon bainite
UTS	Ultimate tensile strength

NOMENCLATURE

α	Allotriomorphic or idiomorphic ferrite
α'	Martensite
α_1	One-dimensional parabolic thickening rate constant
α_a	Acicular ferrite
α_b	Bainite
α_{lb}	Lower bainite
α_{ub}	Upper bainite
γ	Austenite, or shear strain
γ'	Carbon-enriched austenite
γ_p	Plastic work done in creating crack surfaces, per unit area
γ_s	Surface energy per unit area
δ	Body-centred cubic iron that precipitates in liquid
$\dot{\epsilon}$	Strain rate
ϵ	Plastic strain
η	Arc energy transfer efficiency in welding
ζ	Uniaxial dilatation normal to the habit plane
θ	Cementite
θ_1	$M_{23}C_6$
θ_2	M_7C_3
κ	Mean % planar misfit between inclusion and ferrite
μ	Shear modulus
μ_i	Chemical potential of element i
ν	Poisson's ratio
ξ	Volume fraction normalised by the equilibrium volume fraction
ρ	Density
ρ_d	Dislocation density
ρ_m	Mobile dislocation density
ρ_L	Mobile dislocation density at the lower yield point
ρ_U	Mobile dislocation density at the upper yield point
σ	Applied stress
σ_0	Friction stress
σ_e	Entropy production rate
σ_g	Strengthening due to grain boundaries
σ_N	Normal stress on the habit plane
σ_p	Work of fracture, per unit area of crack surface
σ_r	Stress as a function of the distance r ahead of the crack tip
σ_s	Saturation value of σ_{iy} in a fatigue test
σ_c	Critical stress to trigger a dislocation source
σ_{Fe}	Strength of pure annealed iron
σ_r	Stress corresponding to a unit dislocation velocity
$\sigma_{\theta\alpha}$	Interfacial free energy per unit area for the boundary between θ and α
σ_{iy}	Instantaneous flow stress at any particular stage of a test

σ_{SS}	Solid solution strengthening due to substitutional solutes
σ_{UTS}	Ultimate tensile strength
σ_Y	Yield strength
τ	Incubation time before the growth of an individual particle begins during isothermal transformation, or before a detectable degree of overall transformation. Alternatively, the shear stress resolved along the shear direction
τ^*	Athermal resistance to dislocation motion
τ_0	Temperature dependent resistance to dislocation motion
A_3	$\alpha \rightleftharpoons \gamma$ transition temperature for pure iron
A_4	$\gamma \rightleftharpoons \delta$ transition temperature for pure iron
Ac_3	Temperature at which a sample becomes fully austenitic during heating
Ae_1	Temperature separating the $\alpha + \gamma$ and α phase fields for a specific alloy
Ae_3	Temperature separating the $\alpha + \gamma$ and γ phase fields for a specific alloy
Ar_1	Temperature at which austenite completes its transformation to ferrite during cooling
Ar_3	Temperature at which austenite begins to transform to ferrite during cooling
b	Magnitude of Burgers vector of dislocation
B_F	Bainite-finish temperature (not well defined)
B_S	Bainite-start temperature
B	Matrix representing the Bain deformation
$\bar{c}$	Average concentration
c	Concentration, or half the length of crack
$c^{\gamma g}$	Concentration in γ that is in equilibrium with gas (g)
$c_i^{\alpha\theta}$	Concentration of element i in phase α in equilibrium with phase θ
C_i	Constants, with $i = 1, 2, 3 \dots$
d	Displacement vector for an invariant-plane strain
$D_{C,V}^{\gamma}$	Diffusion coefficient of solute identified by subscript in phase identified by superscript. The terms V or B refer to volume or boundary diffusion
D_1	Ideal critical diameter in Grossman test
E	Young's modulus
f^*	Attempt frequency
f_N	Empirical function in nucleation theory
Δg	Free energy of formation of a single vacancy
Δg_{∞}	Free energy change per atom
ΔG	General term representing driving force
$\Delta G^{\gamma \rightarrow \alpha}$	Free energy change for transformation without composition change, $G^{\alpha} - G^{\gamma}$
ΔG_m	Molar Gibbs free energy change on transformation; alternatively, the maximum molar Gibbs free energy change accompanying nucleation
ΔG_m	Molar Gibbs free energy
ΔG_{chem}	Chemical driving force
ΔG_{mech}	Mechanical driving force
ΔG_{strain}	Coherency strain energy during nucleation
G	Growth rate
G^*	Activation free energy for nucleation, or for interfacial motion
G_S	Strain energy per mole
G_{SB}	Stored energy of Widmanstätten ferrite
G_{SW}	Stored energy of bainite

Δh	Enthalpy of formation of a single vacancy
H^*	Activation enthalpy during plastic deformation
I_V	Nucleation rate per unit volume
J	Diffusion flux
k	Boltzmann constant
k_A	Constant in the Avrami equation
k_g	Constant relating lath size to strength
k_y	Hall-Petch constant relating grain size to yield strength
K	Bulk modulus of elasticity
K_{IC}	Critical stress intensity in mode 1 loading
K_I	Stress intensity in mode 1 loading
$\bar{L}$	Mean intercept length in stereology, grain size
$\bar{L}_\gamma$	Austenite grain size
L	Average distance moved by dislocations during plastic deformation
L_S	Lower bainite start temperature
L_p	Interparticle distance
L_p	Mean spacing of neighbouring particles on plane
m	Magnitude of shape deformation
m_i	Mass fraction of element i
M_σ	Temperature below which martensite can be induced by stress
M_F	Temperature at which 95% martensite is obtained
M_S	Martensite-start temperature
M_S^0	Martensite-start temperature for infinitely large austenite grain size
n	Time exponent in the Avrami equation
N_V^γ	Martensite plates per unit volume of austenite
N_V	Martensite plates per unit volume of sample
p_{dis}	Probability of dislocations being absorbed into grain boundary
q	heat input during welding
Q	Activation energy
Q	Matrix representing an inhomogeneous lattice-invariant deformation
$\bar{r}_o$	Mean particle size
$\bar{r}_t$	Mean particle size following isothermal coarsening for a time t
r	Radius of a disc; alternatively, the distance ahead of a crack tip; alternatively the tip radius of a growing plate, particle radius, atomic radius
r^*	Critical size beyond which an embryo can grow with a reduction in free energy
r_c	Critical radius of particle at which its growth rate becomes zero
r_p	Mean particle radius intersected by plane
R	Universal gas constant
R	Matrix for rigid body rotation
Δs	Entropy of formation of a single vacancy
s	Shear component of the IPS shape deformation
s_A	Apparent shear strain
S	Interlamellar spacing in pearlite, with critical value S_C
S_V	Interfacial area per unit volume
S	Deformation matrix in the crystallographic theory of martensite
$\Delta t_{8 \rightarrow 5}$	Time required to cool from 800 to 500°C in the context of welding
t	Time; alternatively, the thickness of a disc

t_a	Time required to reach a given fraction ξ of isothermal transformation
t_c	Time required for a sub-unit to reach a limiting size
t_d	Time required to decarburise a plate of bainite
t_i	Time interval for step i in a series of isothermal heat treatments
t_p	True thickness of a plate
T	Temperature
T_0	Temperature at which γ and α of identical composition have the same free energy
T'_0	As T_0 , but accounting for the stored energy of ferrite
T_θ	Temperature at which the T_0 curve and $\gamma/\gamma + \theta$ phase boundary intersect
T_E	Eutectoid temperature
T_P	Peak temperature
T_{crit}	Temperature at which half the dislocation core sites are occupied by solute
U_i	Binding energy between solute and defect
U_O	Strain energy due to interstitial in octahedral hole
U_{Te}	Strain energy due to interstitial in tetrahedral hole
U_e	Elastic energy
U_s	Surface energy
v^*	Activation volume
v_a	Volume per atom
v_i, v_0	Interfacial velocity
v_l	Plate lengthening rate
v_P	Growth rate of pearlite
V	Volume of a sample
V^α	Volume of phase α
V_e^α	Extended volume of phase α
V_τ	Volume per particle
V_l	Plate lengthening rate
V_S	Sheaf lengthening rate
V_u	Volume of sub-unit
V_V	Volume fraction of material identified by superscript
V_m	Molar volume
w	Thickness of a bainite sub-unit
w_i	Weight percent of element i
$\bar{x}$	Average mole fraction of carbon in an alloy
$x^{\alpha\gamma}$	Mole fraction of carbon in ferrite which is in equilibrium or paraequilibrium with austenite
$x^{\gamma\alpha}$	Mole fraction of carbon in austenite which is in equilibrium or paraequilibrium with ferrite
x^α	Mole fraction of phase α
x_{Ae3}	Carbon concentration given by the Ae_3 curve
$x_{T'_0}$	Carbon concentration given by the T'_0 curve
γ_C	Ratio of carbon to all other atoms, $x/(1-x)$
z	Coordinate normal to the interface plane
z^*	Position of the interface along coordinate z
z_d	Effective diffusion distance

CHAPTER 1

Iron and Its Interstitial Solutions

Abstract

Pure iron is remarkable in its complexity, not only because of its many allotropic forms. There are hidden features related to magnetism which, for example, make the expansion coefficient of austenite greater than that of the more loosely packed ferrite – one consequence of this is that austenitic steels deteriorate when subjected to a combination of stress and thermal fluctuations. We discuss here the choreography of atoms during solid-state phase transformations together with the role and behaviour of interstitial atoms such as carbon, nitrogen and hydrogen. The mobility of substitutional solutes is described to emphasise some counterintuitive observations such as the fact that heavy atoms like molybdenum actually diffuse faster than the iron in which they are dissolved.

1.1 INTRODUCTION

Iron is created in the stars, which at first fuel themselves through the fusion of hydrogen into helium. When hydrogen is exhausted, the fusion of helium leads to the creation of carbon. This exothermic process of nuclear burning can, in sufficiently massive stars, lead to the formation of even heavier elements, the sequence ending with the creation of iron. Iron is the most stable element in the universe and further fusion to form even heavier elements does not release energy. As a consequence, the fuel supply becomes exhausted and the star collapses into states that depend on its mass. If the core becomes so heavy that it cannot support its own gravity, a giant explosion (a supernova) occurs that produces in a short time scale, most of the elements beyond iron.

Impressive as the cosmological origins of iron and carbon are, the story that truly is worth telling can be witnessed in every aspect of terrestrial life. Such is the success of iron, that steel forms the ‘gold-standard’ against which emerging materials or supreme acts of endeavour are compared. What is often not realised is that this is a moving standard, with notoriously regular and exciting discoveries being made in the context of iron and its alloys. This is why steel remains the most successful and cost-effective of all materials, with more than a billion tonnes being consumed annually in improving the quality of life. This book attempts to explain why steels continue to take this pre-eminent position, and examines in detail the phenomena whose exploitation enables the desired properties to be achieved.

One reason for the overwhelming dominance of steels is the endless variety of microstructures and properties that can be generated by solid-state transformation and processing. Therefore, in studying steels, it is useful to consider the behaviour of pure iron first, then the iron-carbon alloys, and finally the many complexities that arise when further solutes are added.

Pure iron is not an easy material to produce. It has nevertheless been made with a total impurity content less than 60 parts per million (ppm), of which 10 ppm is accounted for by non-metallic impurities such as carbon, oxygen, sulphur and phosphorus, with the remainder representing metallic impurities. Iron of this purity can be extremely weak when reasonably sized samples are tested: the resolved shear stress needed to induce slip in single crystal at room temperature can be as low as 10 MPa, while the yield stress of a polycrystalline sample at the same temperature can be well below 50 MPa. However, the shear strength of small single crystals has been observed to exceed 19,000 MPa when the size of the sample is reduced to about 2 μm . This is because the chances of finding crystal defects such as dislocations become small as the size of the crystal is reduced. The ideal tensile strength of a perfect crystal of iron pulled along $\langle 100 \rangle$ is about 14,200 MPa [1].

For comparison purposes the breaking strength of a very small carbon nanotube has been measured to be about 130,000 MPa; this number is so astonishing that it has led to misleading statements about their potential in structural applications. For example, the tubes are said to be a hundred times stronger than steel; in fact, there is no carbon tube which can match the strength of iron beyond a scale of 2 mm, because of the inevitable defects which arise as the tubes are grown [2,3].

The lesson from this is that systems which rely on perfection in order to achieve strength necessarily fail on scaling to engineering dimensions. Since perfection is thermodynamically impossible to achieve in large samples, steels must in practice be made stronger by other means which are insensitive to size. The mechanisms by which the strength can be increased will be discussed – suffice it to state here that it is possible to produce steel with a strength of 5500 MPa, with sufficient ductility to ensure safe application. Some of the methods by which such impressive combinations of properties are achieved without compromising safety will be discussed, before the wide range of complex structures which determine the properties is dealt with.

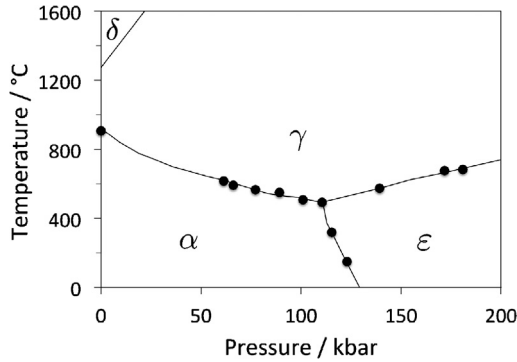


Figure 1.1 The phase diagram for pure iron (data from Bundy [5]). The triple point temperature and pressure are 490°C and 110 kbars, respectively. α , γ and ε refer to ferrite, austenite and ε -iron, respectively. δ is simply the higher temperature designation of α . However, below the Curie temperature, α -iron is slightly tetragonal with a difference in lattice parameters of just 6×10^{-15} m, determined from magnetostriction experiments [6].

1.2 ALLOTROPES OF PURE IRON

At least three allotropes of iron occur naturally in bulk form, body-centred cubic (bcc, α , ferrite), face-centred cubic (fcc, γ , austenite) and hexagonal close-packed (hcp, ε). The phase β in the alphabetical sequence α , β , γ , δ ... is missing because the magnetic transition in ferrite was at one time incorrectly thought to be the β allotrope of iron, responsible for hardening when the iron is quenched. Nevertheless, it is true that α -iron is not strictly cubic in its ferromagnetic state below the Curie temperature [4]. This is because the magnetic spins are aligned, say along the z axis, so that rotations about the x or y axes must be combined with time reversal to preserve the directions of the spins. The magnetic point group becomes tetragonal. It follows that the ferrite structure below the Curie temperature is tetragonal, but the extent of tetragonality is very small and neglected in most experiments on steels containing complex microstructures where X-ray diffraction peaks are too broad to detect small differences in lattice parameters.

In fact, there are magnetic transitions in all of the allotropes of iron. The phase diagram for pure iron is illustrated in Fig. 1.1. Each point on any boundary between the phase fields represents an equilibrium state in which two phases can coexist. The *triple point*, where the three boundaries intersect, represents an equilibrium between all three phases which coexist.

It is seen that in pure iron, the hcp form is stable only at very large pressures, consistent with its high density. The best comparison of the relative densities of the phases is made at the triple point where the allotropes are in equilibrium and where the sum of all the volume changes is zero:

$$\left. \begin{aligned} \Delta V(\text{bcc} \rightarrow \text{hcp}) &= -0.34 \\ \Delta V(\text{hcp} \rightarrow \text{fcc}) &= +0.13 \\ \Delta V(\text{fcc} \rightarrow \text{bcc}) &= +0.21 \end{aligned} \right\} \text{ cm}^3 \text{ mol}^{-1}$$

There may exist a fourth natural allotrope in the core of the earth, where the pressure reaches some three million times that at the surface and where the temperature is estimated to be about 6000°C. The core of the earth is predominantly iron, and consists of a solid inner core surrounded by a liquid outer core. Knowledge of the core is uncertain, but it has been suggested that the crystal structure of the solid core may be double hcp, although calculations which assume pure iron, indicate that the ϵ -iron remains the most stable under inner-core conditions.

1.2.1 Thin films and isolated particles

There are two further allotropes which can be created in the form of thin films. Face-centred tetragonal iron has been prepared by coherently depositing iron as a thin film on a $\{1\ 0\ 0\}$ plane of a substrate such as copper with which the iron has a mismatch. The position of atoms in the first deposited layer in this case replicates that of the substrate. A few monolayers can be forced into coherency in the plane of the substrate with a corresponding distortion normal to the substrate. This gives the deposit a face-centred tetragonal structure. Growing iron on a misfitting $\{1\ 1\ 1\}$ surface of a fcc substrate leads to trigonal iron.

Very thin films of iron retain their ferromagnetic character, but there are special effects due to the small dimensions. The magnetic moment per atom becomes very large: 3.1 Bohr magnetons compared with 2.2 for bulk α -iron. This is due to the smaller coordination number for atoms in a thin film. The second effect is that magnetic anisotropy greatly increases for thin films because the spins tend to align normal to the surface. The Curie temperature is greatly reduced, again because of the change in coordination. For a monolayer of iron the Curie temperature is just $\simeq 280^\circ\text{C}$.

Many classical studies of nucleation theory have been conducted on minute (5–1000 nm) particles of iron where the defects responsible for heterogeneous nucleation can be avoided. Such particles have acquired new

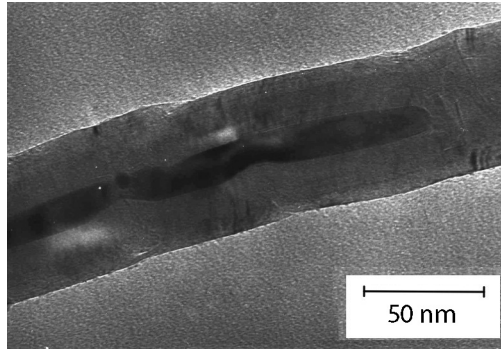


Figure 1.2 A multi-walled carbon nanotube containing a particle of iron (unpublished micrograph courtesy of I. Kinloch).

significance in that they are exploited in the manufacture of carbon nanotubes. The particles are deposited due to the decomposition of ferrocene in chemical mixtures which also contain the ingredients necessary to grow the tubes. Small particles of iron also have a role in increasing the thermal conductivity of fluids when in suspension [7].

It is expected that the coarser particles will have the bcc crystal structure of ferrite, but it has to be appreciated that a 5 nm particle has about half its atoms at the surface. Metal surfaces are prone to reconstruction into a variety of two-dimensional structures which will complicate the interpretation of the structure of the particle as a whole. The surface also plays another role, in that it alters the total free energy of the particle leading to a depression of its melting temperature. It has been estimated that a 5 nm diameter iron particle could melt at a temperature as low as 500°C. Fig. 1.2 illustrates an iron particle inside a carbon nanotube – its bulbous character has been speculated to be due to melting.

Small metal particles in the size range 1–5 nm are close to a metal/insulator transition. When observed at the tips of carbon nanotubes using scanning electron microscopy, the iron particles have shown a tendency to charge, possibly indicating a loss of metallic behaviour.

1.3 AUSTENITE TO FERRITE TRANSFORMATION

The vast majority of steels rely on just two allotropes, α and γ . Pure iron is a peculiar element in that at ambient pressure, bcc ferrite is stable from all temperatures up to 910°C (the A_3 point), when it transforms into the

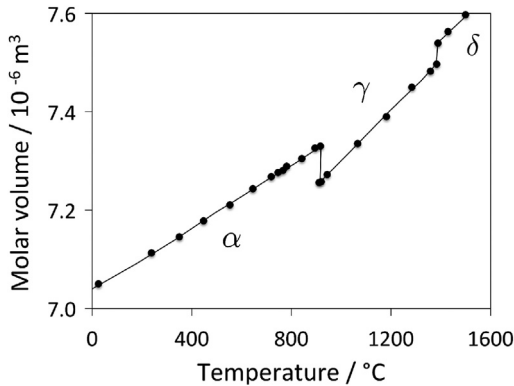


Figure 1.3 Temperature dependence of the volume per mole of atoms in iron crystals (data adapted from [8]).

fcc austenite, only to revert to ferrite at 1390°C (the A_4 point). This high-temperature ferrite is traditionally labelled δ , although it is no different in crystal structure from α . The δ -ferrite remains the stable phase until melting occurs at 1536°C.

Fig. 1.3 shows the phase changes on a plot of the mean volume per atom of iron as a function of temperature. It should be noted that the $\gamma \rightarrow \alpha$ transformation is accompanied by an atomic volume change of approximately 1–3%, which can lead to the generation of internal stresses during transformation.

The detailed geometry of unit cells of α - and γ -iron crystals is particularly relevant to, e.g., the solubility in the two phases of non-metallic elements such as carbon and nitrogen, the diffusivity of alloying elements at elevated temperatures and the general behaviour on plastic deformation. The bcc structure of α -iron is more loosely packed than that of fcc γ -iron (Fig. 1.4). The largest cavities in the bcc structure are the tetrahedral holes existing between two edge and two central atoms in the structure, which together form a tetrahedron. The second largest are the octahedral holes which occupy the centres of the faces and the $\langle 001 \rangle$ edges of the body-centred cube. The surrounding iron atoms are at the corners of a flattened octahedron. It is interesting that the fcc structure, although more closely packed, has larger holes than the bcc structure. These holes are at the centres of the cube edges, and are surrounded by six atoms in the form of an octagon, so they are referred to as octahedral holes. There are also smaller

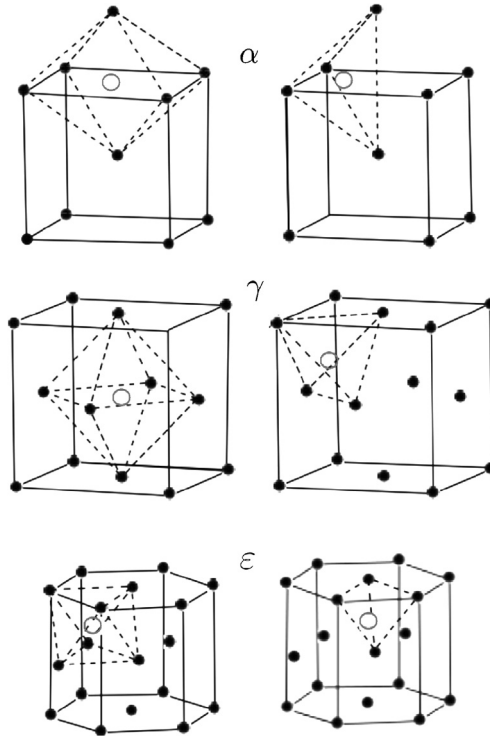


Figure 1.4 Schematic representation of the octahedral and tetrahedral interstices in ferrite (α), austenite (γ) and hexagonal iron (ϵ). The filled circles represent the positions of iron atoms whilst the interstices are represented by open circles together with their coordination polyhedra. Adapted from [9].

tetrahedral interstices. The largest sizes of spheres which will enter these interstices are given in [Table 1.1](#).

The $\alpha \rightleftharpoons \gamma$ transformation in pure iron occurs very rapidly, so it is not generally possible to retain the high-temperature fcc form at room temperature. Rapid quenching can substantially alter the morphology of the resulting α -iron, but it still retains its bcc structure. It follows that any detailed study of austenite in pure iron must be done at elevated temperatures, e.g. using X-ray or neutron diffraction. The transformation of the austenite on cooling can also be followed using diffraction based on the intense X-rays generated in a synchrotron, or using precision dilatometry. The latter technique relies on the volume change accompanying the transformation from austenite to ferrite.

Table 1.1 Size of largest spheres fitting interstices in bcc and fcc iron. r = atomic radius of iron, N is the number of interstices per iron atom. Typical coordinates of the interstices are expressed as fractions of the cell parameters. The calculations assume hard sphere models for the crystal structures

	N		Coordinates	Relative radius	Radius / Å
bcc	6	Tetrahedral	$\frac{1}{2}, 0, \frac{1}{4}$	$0.29r$	0.37
	3	Octahedral	$0, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, 0$	$0.15r$	0.19
fcc	2	Tetrahedral	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$	$0.23r$	0.28
	1	Octahedral	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$0.41r$	0.51
hcp	6	Tetrahedral	$\frac{1}{2}, \frac{1}{3}, \frac{1}{4}$ and $\frac{1}{2}, \frac{1}{3}, \frac{3}{4}$	$0.23r$	0.28
	3	Octahedral	$\frac{1}{3}, \frac{1}{2}, \frac{3}{4}$	$0.41r$	0.51

There are circumstances where it is necessary to study pure austenite at temperatures well below ambient. Pure iron can be retained in its austenitic state to very low temperatures by coherent precipitation in copper. Copper has an fcc crystal structure and hence prevents the coherent particles of austenitic iron from transforming during cooling. This technique has been used to establish the antiferromagnetic nature of the austenite with a Néel temperature of about -190°C (the austenite can also be ferromagnetic at higher temperatures, with a Curie point of some 1525°C , depending on its density).

1.3.1 Mechanisms of transformation

One of the reasons why there is a great number of microstructures in steels is because the atoms can move in a variety of ways to achieve the same allotropic transition. The transformation can occur either by breaking all the bonds and rearranging the atoms into an alternative pattern (*reconstructive* transformation), or by homogeneously deforming the original pattern into a new crystal structure, i.e. *displacive* or *shear* transformation, Fig. 1.5.

In the displacive mechanism the change in crystal structure also alters the macroscopic shape of the sample when the latter is not constrained. The shape deformation during constrained transformation is accommodated by a combination of elastic and plastic strains in the surrounding matrix. The product phase grows in the form of thin plates to minimise the strains. The atoms are displaced into their new positions in a coordinated motion. Displacive transformations can, therefore, occur at temperatures where diffusion is inconceivable within the time scale of the experiment. Some solutes may be forced into the product phase, a phenomenon known as

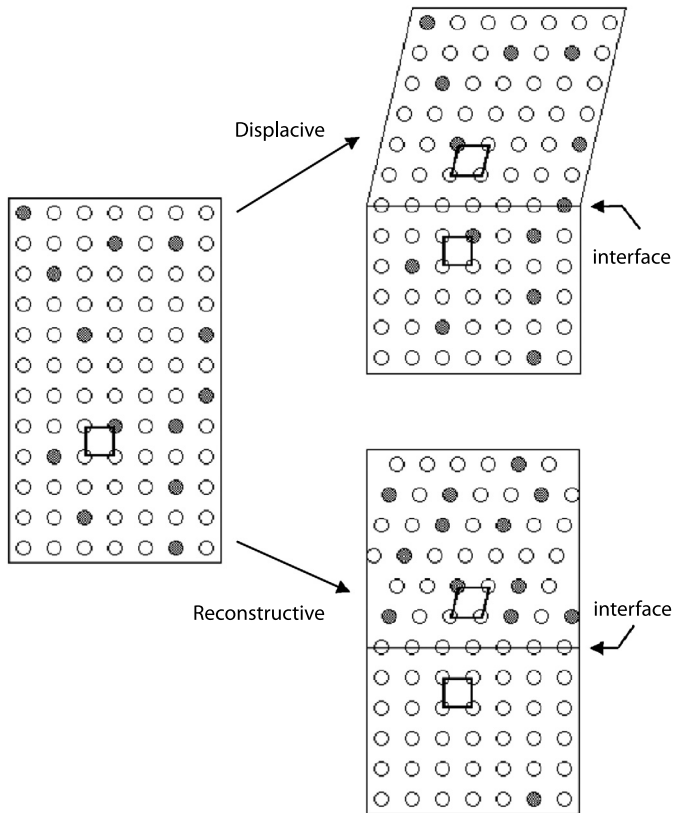


Figure 1.5 Schematic illustration of the mechanisms of transformation. The parent crystal contains two kinds of atoms. The figures on the right represent partially transformed samples with the parent and product unit cells outlined in bold.

solute trapping.¹ Both the trapping of atoms and the strains make displacive transformations less favourable from a thermodynamic point of view.

It is the diffusion of atoms that leads to the new crystal structure during a reconstructive transformation. Imagine that the transformation proceeds as by the displacive mechanism (Fig. 1.6a, b), but that the resulting shape deformation is eliminated by transporting the segment as in Fig. 1.6c to recover the overall shape shown in (d). This transport is the diffusion that is needed in order that the strain energy term is essentially eliminated as if there is fluid flow in the surrounding matrix. The flow of matter is sufficient to avoid any shear components of the shape deformation, leaving only the effects of volume change. In alloys, the diffusion process may also lead to

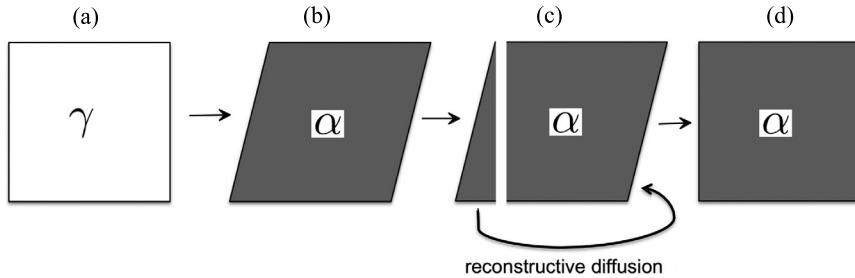


Figure 1.6 Phenomenological interpretation of reconstructive transformation. The virtual operation that eliminates the shape change is the diffusion required during a reconstructive transformation, irrespective of whether it occurs in pure iron or in an alloyed steel [10].

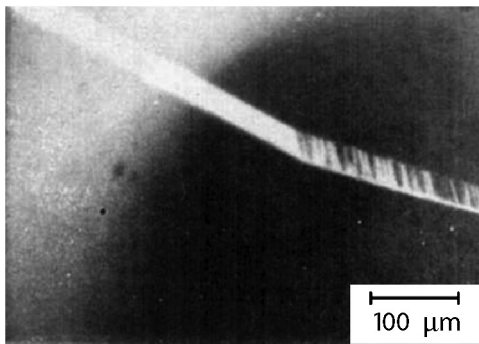


Figure 1.7 A whisker of iron, originally straight, transformed partially to austenite – the image is a frame from a movie taken to show the shape deformation due to the unconstrained $\alpha \rightarrow \gamma$ transformation. The position of the kink represents the interface between the α and the striated γ . After Zerwech and Wayman [11], reproduced with permission of Elsevier.

the redistribution of solutes between the phases in a manner consistent with a reduction in the overall free energy.

It should be emphasised that the diffusional flow is essential even in pure iron, where the reconstructive ferrite and martensite are distinguished purely by the consequences of the shape deformation in the latter case. Fig. 1.7 shows the shape deformation caused in a single crystal of pure iron when heated sufficiently rapidly to induce the $\alpha \rightarrow \gamma$ transformation by a displacive mechanism [11]. All the phase transformations in steels can be discussed in the context of these two mechanisms (Fig. 1.8). The details are presented in subsequent chapters.

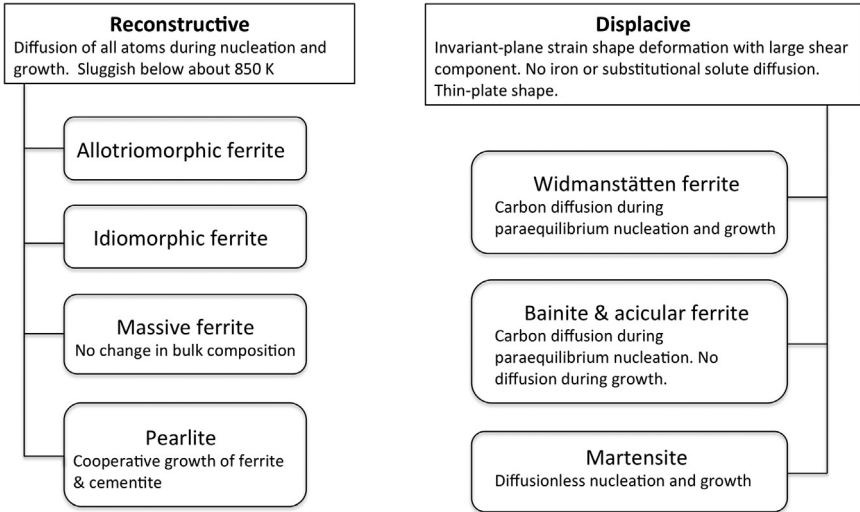


Figure 1.8 A selection of the structures generated by the decomposition of austenite. The term ‘paraequilibrium’ refers to the case where carbon partitions but the substitutional atoms do not do so. The substitutional solute to iron atom ratio is therefore unchanged by transformation.

1.4 CARBON, NITROGEN AND HYDROGEN IN SOLUTION

1.4.1 Solubility in α - and γ -iron

It is often said that ‘ferrite has a solubility for carbon of about 0.02 wt%’. However, solubility is defined by equilibrium between two or more phases. The solubility of carbon in ferrite that is in equilibrium with austenite will therefore not be the same as when it is in equilibrium with cementite, [Fig. 1.9](#). Ferrite which is in equilibrium with cementite has a particularly low solubility for carbon at low temperatures; [Fig. 1.9c](#) shows the precipitation of cementite occurring in a steel containing just 0.02 wt% of carbon, when the alloy is aged at 240°C. The solubility will depend also on external parameters such as pressure, temperature, magnetic fields and stress.

The atomic sizes of carbon and nitrogen ([Table 1.2](#)) are sufficiently small relative to that of iron to allow these elements to enter the α - and γ -iron lattices as *interstitial* solute atoms. In contrast, the metallic alloying elements such as manganese, nickel and chromium have much larger atoms, i.e. nearer in size to those of iron, and consequently they enter into *substitutional* solid solution. However, comparison of the atomic sizes of C and N with the sizes of the available interstices makes it clear that some lattice dis-

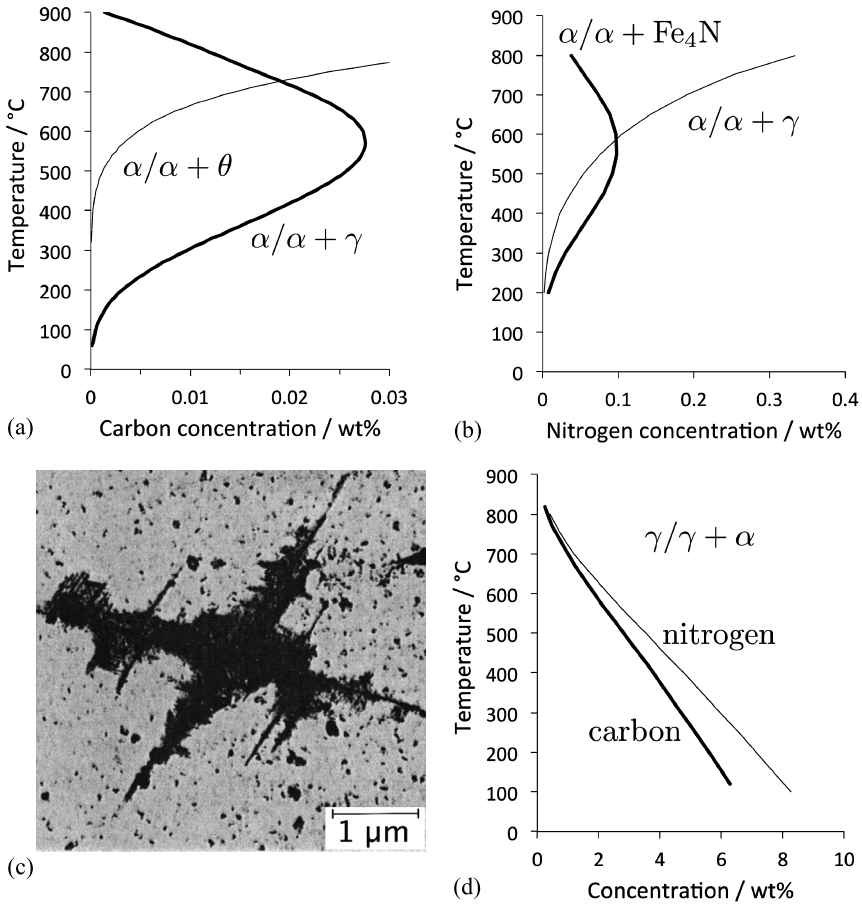


Figure 1.9 (a) The solubility of carbon in ferrite (α) when the latter is in equilibrium with austenite (γ) or cementite (θ). (b) The solubility of nitrogen in ferrite (α) when the latter is in equilibrium with austenite (γ) or a particular nitride. (c) Cementite precipitation in quench-aged iron containing just 0.02 wt% carbon, 1560 min at 240°C [12]. (d) The solubility of carbon or nitrogen in austenite that is in equilibrium with ferrite.

tortion must take place when these atoms enter the iron lattice. Indeed, it is found that C and N in α -iron occupy not the larger tetrahedral holes, but the octahedral interstices which are more favourably placed for the relief of strain, which occurs by movement of two nearest-neighbour iron atoms.

In the case of tetrahedral interstices, four iron atoms are of nearest-neighbour status and the displacement of these would require more strain energy. Consequently these interstices are not preferred sites for carbon

Table 1.2 Atomic sizes of non-metallic elements in iron

Element	Atomic radius, $r / \text{\AA}$	r/r_{Fe}
α -Fe	1.28	1.00
B	0.94	0.73
C	0.77	0.60
N	0.72	0.57
O	0.60	0.47
H	0.46	0.36

and nitrogen atoms. The strain energies for the two locations of carbon in ferrite, when Poisson's effects are neglected, are proportional to [13]:

$$U_O \propto 2(r_i - r_o)^2 E_{100} \quad (1.1)$$

where r_i is the interstitial-atom radius, r_o is the radius of the undistorted hole and E is the Young's modulus along the crystallographic direction identified in the subscript. For the tetrahedral site,

$$U_{Te} \propto 4(r_i - r_o)^2 E_{210} \quad (1.2)$$

so for $r = 0.08$ nm, $U_{Te}/U_O = 1.38$. More recent calculations suggest that there is in addition, a substantial difference in the chemical energy of solution between the octahedral and tetragonal sites, which makes the former interstice the favoured site for carbon atoms [14].

The solubility of both C and N in austenite in equilibrium with ferrite should be greater than in ferrite, because of the larger interstices available, Table 1.1. Fig. 1.9 shows that this is so for both elements, with the austenite able to accommodate concentrations in excess of 6 wt%, in contrast to the maximum that can be accommodated in α -iron. These marked differences of the solubilities of the main interstitial solutes in γ and in α are of profound significance in the heat treatment of steels, and are fully exploited to increase strength (Chapter 2).

Although the solubility of C and N in ferrite at ambient temperature can be incredibly small, the presence of solute atoms can have profound effects on the mechanical properties through their interaction with defects such as dislocations. Sensitive physical techniques allow the study of very small concentrations of interstitial solute atoms in α -iron. Snoek first showed that internal friction measurements on an iron wire oscillating in a torsional pendulum, over a range of temperature just above ambient temperature, revealed an energy loss peak (Snoek peak) at a particular

temperature for a given frequency. It was shown that the energy loss was associated with the migration of carbon atoms from randomly chosen octahedral interstices to those holes which were enlarged on application of the stress in one direction, followed by a reverse migration when the stress changed direction and made other interstices larger. This movement of carbon atoms at a critical temperature is an additional form of damping or internal friction: below the critical temperature the diffusivity is too small for atomic migration, and above it the migration is too rapid to lead to appreciable damping. The height of the Snoek peak is proportional to the concentration of interstitial atoms, so the technique can be used not only to determine the very low solubilities of interstitial elements in iron, but also to examine the precipitation of excess carbon or nitrogen during an ageing treatment.

1.4.2 Diffusion of solutes in iron

The diffusion coefficient of carbon increases by a factor of five as its concentration changes from about 0.1 to 2 wt% at 1000°C. There are several reasons for this. Diffusion is strictly driven by free energy gradients rather than concentration gradients, so there is a thermodynamic factor related to the way in which the activity of carbon depends on concentration. However, this is not the full explanation because carbon atoms in close proximity repel each other so in a concentration gradient there will be an additional factor promoting diffusion down the gradient. The atoms also cause a concentration dependent dilatation of the lattice. As a result, the diffusion coefficient is often expressed empirically as [15]:

$$D_C^{\gamma} = 4.53 \times 10^7 \left[1 + \gamma_C (1 - \gamma_C) \frac{8339.9}{T} \right] \times \exp \left\{ - \left(\frac{1}{T} - 2.221 \times 10^{-4} \right) (17767 - 26436 \gamma_C) \right\} \quad \text{m}^2 \text{s}^{-1} \quad (1.3)$$

where γ_C is the ratio of carbon atoms to all other atoms. There is more rigorous theory available to deal with the diffusion of carbon in austenite, which indicates that the activation energy for diffusion is about 150 kJ mol⁻¹ at a low carbon concentration [16,17]. Further diffusion data for which the concentration dependence is minimal are presented in Table 1.3. The activation energy reported for nitrogen diffusion in austenite is similar to that for carbon in that phase. In ferrite, where the concentrations of interstitial solutes are rather limited, so internal friction techniques

Table 1.3 Some diffusion data [22–24] conforming to the equation $D = D_0 \exp\{-Q/RT\}$ where R is the gas constant and T the absolute temperature

	$D_0/\text{m}^2\text{s}^{-1}$	$Q/\text{kJ mol}^{-1}$
Nitrogen in austenite	7.0×10^{-4}	166
Carbon in ferrite	1.67×10^{-7}	78
Nitrogen in ferrite	1.26×10^{-7}	73
Iron in austenite	7.0×10^{-5}	286
Iron in ferromagnetic ferrite	5.0×10^{-5}	240
Iron in paramagnetic ferrite	1.6×10^{-4}	240

have been used to determine the diffusivities of C and N. The activation energies for diffusion are much smaller than in austenite, Table 1.3.

Hydrogen is a pernicious solute in iron in the sense that it leads to dramatic changes in the ability of the metal to absorb energy during fracture, at concentrations which are so small that it is difficult to avoid the ingress of nascent hydrogen during, for example, corrosion reactions. The dissolution energy of hydrogen in the interstices of iron, calculated using first principles are [18]²:

Ferrite	Octahedral	0.34 eV
	Tetrahedral	0.19 eV
Austenite	Octahedral	0.07 eV
	Tetrahedral	0.51 eV

Unlike carbon, the much smaller hydrogen atom fits best within the larger tetrahedral interstice of ferrite (Table 1.1). For the same reason, the larger octahedral interstices in austenite are preferred by hydrogen. The diffusion coefficient of hydrogen in ferrite is greater than in austenite, Fig. 1.10, whereas the reverse holds for the solubility of hydrogen, which is far greater in austenite than in ferrite. The diffusion of hydrogen through both lattices is complicated by the fact that it interacts strongly with defects such as dislocations and interfaces. The strain fields of these defects are attractors for hydrogen and hence its passage through the defective lattice is retarded. The effect is pronounced in the case of ferrite because of the high intrinsic mobility of hydrogen in body-centred cubic iron, as illustrated in Fig. 1.10.

The self-diffusion of iron naturally involves much greater activation energies, Table 1.3, because they include the energies of formation and

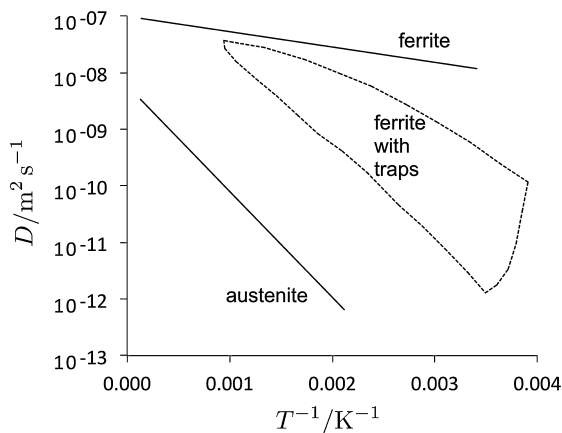


Figure 1.10 Diffusion coefficients for hydrogen in ferrite and austenite. The dashed region represents diffusion in ferrite containing strong traps. Data from [19,20].

migration of vacancies. Substitutional and self-diffusion in ferritic iron is complicated by the paramagnetic to ferromagnetic transition at the Curie temperature with both the vacancy formation and migration energies altered in the ferromagnetic state. The activation energy for migration in austenite is larger than in ferrite, presumably because the former is a more densely packed crystal structure. It is worth noting that in Table 1.3, the activation energies for diffusion are all less than 300 kJ mol^{-1} . When analysing phenomena such as grain growth or even phase transformations, the activation energy of the process should not be much greater than this. It is usually the case the very large activation energies are a consequence of the empirical methods employed to analyse the grain growth data, or because of overfitting of limited experimental data [21]. Substitutional solutes in general have activation energies for diffusion which are approximately the same as those for the self-diffusion of iron. This makes the homogenisation of steels that contain uneven distributions of such solutes difficult.

There are some remarkable empirical trends in the diffusivities of substitutional solutes in iron, illustrated in Fig. 1.11 [22]. Many of these solutes, including those that have larger atomic masses than iron, diffuse faster than the iron itself. Similar data exist for aluminium, silicon, phosphorus and sulphur, all of which diffuse faster than iron. There is no clear explanation of these observations.

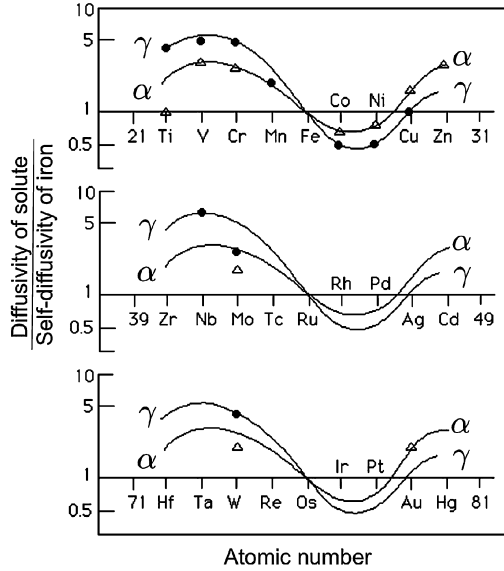


Figure 1.11 Ratio of the diffusivity of solute to that of the self-diffusivity of iron in α or γ , as a function of species. Adapted from [22].

1.4.3 Practical consequences of diffusion

Surface treatment

The rapid diffusion of carbon and nitrogen in iron compared with that of the metallic alloying elements is exploited in the processes of *carburising* and *nitriding*. Both of these surface modification processes are used extensively in the manufacture of engineering components such as bearings and gears, that require a high hardness at the surface but a tough core. Carburising can be carried out by heating a low carbon steel in contact with carbonaceous gas such as carbon monoxide, to the austenitic range, e.g. 1000°C, where the solubility of carbon in austenite that is in equilibrium with gas (g), c^{yg} , is substantial. The result is a carbon gradient in the steel, from c^{yg} at the surface in contact with the carbon, to c^y at a depth z . The solution of Fick's second diffusion law for the case where the steel initially contains a carbon concentration $\bar{c}$ is:

$$c^y = c^{yg} - (c^{yg} - \bar{c}) \operatorname{erf} \left\{ \frac{z}{2\sqrt{D_C^y t}} \right\}, \quad (1.4)$$

which defines the variation in the carbon concentration as a function of depth from the surface of the steel; t is the carburising time. As pointed out

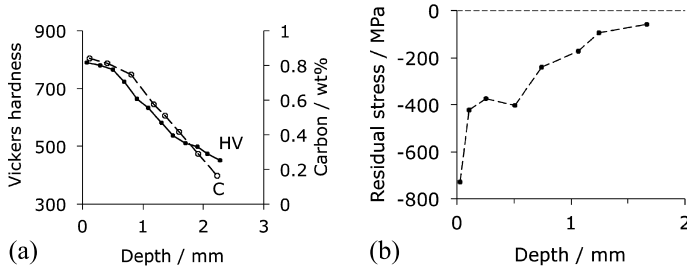


Figure 1.12 Properties of a bearing steel that has been carburised and heat-treated to produce a hard case. (a) Hardness and carbon concentration as a function of depth. (b) Residual stress pattern. Data from [25].

previously, the diffusion coefficient D_C^y varies with carbon content, so the above relationship is not rigorously obeyed. Carburising, whether carried out using carbon, or more efficiently using a carburising gas (*gas carburising*), provides a high-carbon surface on the steel, which, after appropriate heat treatment, is strong and wear resistant. Typical surface hardness values close to 800 HV can be achieved whilst preserving the structural integrity requirements of the core of the component. The heat treatment following carburising involves austenitisation, quenching and tempering at about 200°C, leaving the case in a martensitic state with some austenite retained. The phase transformation also leaves the surface in a state of compression which is useful in enhancing the resistance to surface-initiated fatigue in components such as shafts and bearings. Fig. 1.12 shows some typical data for an aeroengine bearing steel that is case carburised.

Nitriding is normally carried out in an atmosphere of ammonia, but at a lower temperature (500–550°C) than carburising, consequently the reaction occurs in the ferrite phase, in which nitrogen has a substantially higher solubility than carbon, Fig. 1.9. Nitriding steels usually contain chromium (~0.1 wt%), aluminium (~1 wt%), vanadium or molybdenum (~0.2 wt%), which are nitride-forming elements, and which contribute to the high hardness, in excess of 1100 HV of the surface layer produced. The hard layer produced is not uniform in that the region closest to the surface becomes a compound with mixtures of matrix and nitride phases underneath. The compound layer is brittle and hence is removed by grinding the component. In circumstances where the depletion of chromium by the formation of its nitrides can compromise corrosion resistance, plasma nitriding is used because it can be carried out at temperatures less than 450°C where Fe_4N and $\epsilon\text{-Fe}_{2-3}\text{N}$ nitrides predominate.

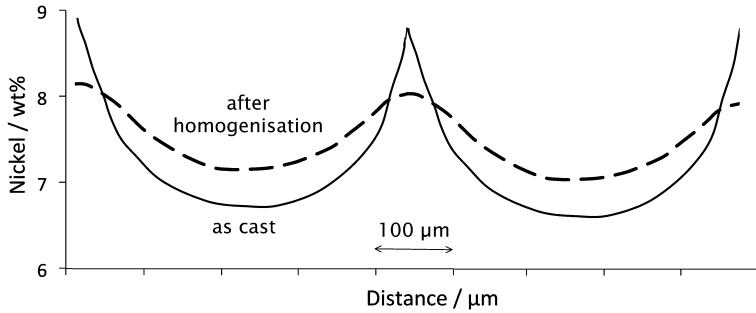


Figure 1.13 Schematic adaptation based on Jin and Purdy's unpublished work quoted in [27], but with realistic scales, to show the effect of annealing at 1220°C for 72 h on the chemical segregation pattern.

Whereas carburising can produce hardened layers that are millimetres in thickness, nitriding penetrates only a few micrometres below the surface. Duplex hardening involves the nitriding of a component that has already been carburised [26]. This results in a very high surface hardness approaching 1200 HV which then drops off to carburising levels deeper within the component.

Homogenisation

In cast steels, metallic alloying elements are usually segregated on a microscopic scale, by *coring* of dendrites. Therefore, to obtain a more uniform distribution, *homogenisation* annealing must be carried out, otherwise the inhomogeneities will persist even after large amounts of mechanical working. The much lower diffusivities of the metallic alloying elements compared with carbon and nitrogen, means that the homogenisation must be carried out at high temperatures (1200–1300°C), approaching the melting point. This may not be economically viable, but hot deformation usually greatly reduces the length scale of the segregation and enhances diffusion. The spreading of segregation during hot deformation leads to the classical banded microstructures seen in commercial steels.

Assuming that the chemical segregation pattern varies periodically with distance (Fig. 1.13), an approximation that it is sinusoidal leads to the relationship:

$$c = \bar{c} + A \sin \frac{\pi z}{z_0} \exp \left\{ -\frac{Dt\pi^2}{z_0^2} \right\} \quad (1.5)$$

where A is the amplitude, $2z_0$ the wavelength, the decay of the solute wave will occur exponentially with time [27]. The time to reach $1/e$ of the initial

amplitude is $z_0^2/\pi^2 D$. The characteristic distance defining the segregation, z_0 , features as a square and means that macroscopic segregation, of the kind that occurs in ingots, simply cannot be homogenised in any reasonable time scale [28]. A second corollary is that although the amplitude decreases with time, the length scale of the segregation does not change – this must be altered by deformation.

1.5 SUMMARY

There are a few metals that exhibit the peculiarity of allotropic and magnetic transitions that are evident in iron. Plutonium has many more (monoclinic, body-centred monoclinic, face-centred orthorhombic, fcc, bct and bcc); in fact the liquid is more dense than the first solid to form so there is a sequence of martensitic transformations to structures that lead to densification. Uranium and neptunium each have three allotropic forms. However, these elements are not strictly engineering materials, nor are they available in sufficient quantity – plutonium is essentially an artificially created element on earth. Nor are they stable relative to iron. Titanium is, however, available in quantity although it only has two allotropic forms.

And the magnetic transitions in iron are all important, they are responsible for the fact that the most stable form of iron under ambient conditions is not hexagonal close packed. Ruthenium and osmium are iron analogues in the sense that they have the same outer electronic structure (in the same column of the periodic table). They do not have the same magnetic characteristics and hence are hcp, which has limited slip systems.

Furthermore, iron undergoes remarkable changes, whether advantageous or detrimental, with the introduction of minute quantities of small atoms that dissolve in the interstices between iron atoms. The manner in which the iron atoms move during allotropic transitions has a great influence on the structures that develop, and on the influence of interstitial species when they relocate into the new structure. We shall see that alloying and processing introduce a vast variety of possibilities that will become apparent in the chapters that follow.

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BACKNOTES

1. The formal definition of ‘trapping’ is that the chemical potential of the solute concerned increases on transfer across the interface into the product phase.
2. $1\text{ eV} = 1.60217662 \times 10^{-19}\text{ J}$.

CHAPTER 2

Strengthening of Iron and Its Alloys

Abstract

The ability of a metal to sustain plastic flow without permanently disrupting its crystal structure is a testimony to the nature of the metallic bond. The forces necessary to initiate deformation can be controlled by introducing obstacles that interfere with the smooth progress of plastic deformation. These strengthening mechanisms are the tools available to metallurgists in their efforts to design strong steels without compromising other properties. One particular property that is indispensable in safe engineering design, and which distinguishes steels from materials such as glass, carbon nanotubes or graphene, is the ability to absorb energy by plastic deformation prior to failure. The yearning for strength cannot and should not therefore be considered in isolation, but rather as one component in the holistic design of materials. Some notions about carbon based materials being 100–300 times stronger than steel are shown to be false.

2.1 INTRODUCTION

Although pure iron can be weak, steels cover a wide range of the strength spectrum as illustrated in Fig. 2.1 which shows commercially available alloys that can be manufactured in large quantities. The vast majority of the billion tonnes of steel produced annually has strength levels much less than 1000 MPa, because applications require a combination of properties that cannot usually be achieved for very strong materials. For example, the construction of high-rise buildings requires beams that have sufficient cross section to be elastically rigid, which is not possible if a thinner section of a strong steel is fully loaded. Similarly, large fabrications are usually put together by welding, which becomes more difficult to implement as steels become stronger. As we will see, strength is achieved by creating particular features in the microstructure that resist plastic flow, and the heat input due to welding can disrupt the carefully engineered microstructure. Research samples can reach strength levels in excess of 10 GPa. This is not difficult to achieve but the materials are usually prepared as perfect samples, or severely deformed samples, neither of which can be scaled to quantities suitable for commercial production, even if a panoply of other design parameters could be achieved. Bearing this in mind, although Fig. 2.1 shows the strength

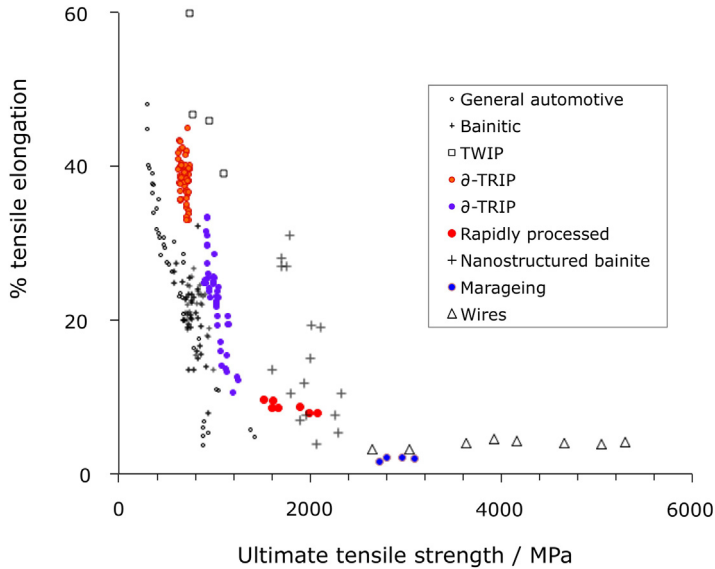


Figure 2.1 A selection of the strength and elongation of steels available commercially.

and elongation of commercially available steels, they have at the same time, many other attributes that make them useful.

There are many ways of strengthening steels and they can be exploited in combination. On the other hand, there has been limited progress in methods for mathematically modelling of properties, and hence of deconvoluting the overall strength into its components. The basic ways in which iron can be strengthened are discussed first, by reference to simple systems. These results should then be helpful in examining the behaviour of more complex alloys.

Like other metals, iron can be strengthened by several mechanisms, the most important of which are:

- Work hardening.
- Solid solution strengthening by interstitial atoms.
- Solid solution strengthening by substitutional atoms.
- Refinement of grain size.
- Dispersion strengthening, including lamellar and random dispersed structures.
- Order hardening.
- Size and shape effects.

The most distinctive aspect of the strengthening of iron is the role of the interstitial solutes carbon and nitrogen. These elements also play a vital part in interacting with dislocations, and in combining preferentially with some of the metallic alloying elements used in steels.

2.2 WORK HARDENING

Work hardening is an important strengthening process in steel, particularly in obtaining high strength levels in rod and wire, both in plain carbon and alloy steels. For example, the tensile strength of an 0.05 wt% C steel subjected to 95% reduction in area by wire drawing, is raised by no less than 550 MPa, while higher carbon steels are strengthened by up to twice this amount. Indeed, without the addition of special alloying elements, plain carbon steels can be raised to strength levels above 1500 MPa simply by the phenomenon of work hardening.

Basic work on the deformation of iron has largely concentrated on the other end of the strength spectrum, namely pure single crystals and polycrystals subjected to small controlled deformations. This approach has shown that the slip plane in α -iron is not unique. Slip occurs on several planes, $\{101\}$, $\{112\}$ and $\{123\}$, but always in the close packed $\langle 11\bar{1} \rangle$ direction which is common to each of these planes (Fig. 2.2). The diversity of slip planes leads to rather irregular wavy slip bands in deformed crystals, as the dislocations can readily move from one type of plane to another by cross slip, provided they share a common slip direction (Fig. 2.2d). The Burgers vector of the slip dislocations would thus be expected to be $\frac{a}{2}\langle 111 \rangle$, which has been confirmed by thin-foil electron microscopy.

The yield stress of α -iron single crystals is very sensitive to both temperature and strain rate, and a similar dependence has been found for less pure polycrystalline iron. Fig. 2.3 shows the flow stress σ_T at temperature T , less than that at room temperature σ_{293} , plotted against T , showing that both single crystal and polycrystalline iron of different interstitial content give values falling on the one curve. Therefore, the temperature sensitivity cannot be attributed to interstitial impurities. It is explained by the effect of temperature on the stress needed to move free dislocations in the crystal, the Peierls-Nabarro stress. Crystals are periodic and the Peierls-Nabarro stress is that required for the dislocation to move from one equilibrium position in the lattice to the adjacent equivalent position. It is larger when the slip plane is less densely packed, and therefore, is larger in bcc-iron than in fcc-iron, giving rise to the temperature sensitivity of flow stress in

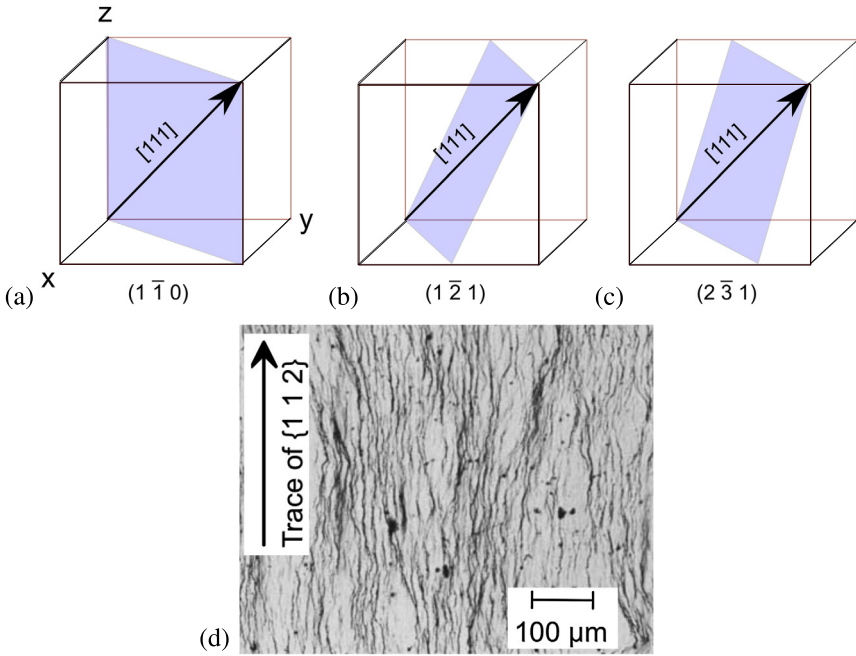


Figure 2.2 (a)-(c) The slip systems in the bcc structure. (d) Wavy slip traces on a crystal of iron following plastic deformation. Image adapted from Keh [1], with the permission of Taylor and Francis.

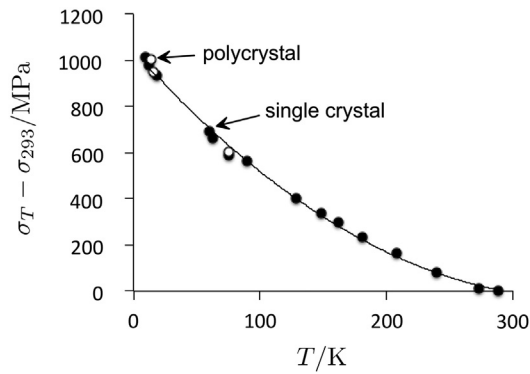


Figure 2.3 Temperature dependence of the flow stress of single crystals and polycrystals of pure bcc-iron. After Altshuler and Christian [2].

the former allotrope. Direct observation of screw dislocations in iron in the electron microscope has shown that their ease of dislocation mobility decreases strongly with decreasing temperature.

If the shear stress at any point on the stress-strain curve is considered, the measured shear stress τ for further deformation comprises two quantities:

$$-\tau = \tau_o + \tau^*. \quad (2.1)$$

The shear stress, τ_o arises from the interaction of the dislocations with short range obstacles, e.g. isolated dislocations.¹ This stress is strongly temperature dependent as thermal activation is helpful in moving dislocations around short range obstacles [3]. On the other hand, τ^* is the internal stress arising from long range obstacles such as grain boundaries, cell walls and other complex dislocation arrays [4]. In these circumstances thermal fluctuations are of no assistance. The two component stresses are defined as follows:

$$\tau_o = \frac{1}{\nu^*} \left[H^* + kT \ln \frac{l\dot{\epsilon}}{\rho_m A_s b f^*} \right], \quad (2.2)$$

$$\tau^* = C_1 \mu b \rho_d^{1/2}, \quad (2.3)$$

where ν^* = activation volume

H^* = activation enthalpy at $\tau = 0$

k = Boltzmann's constant

T = temperature

l = length of dislocation line activated

$\dot{\epsilon}$ = strain rate

ρ_m = mobile dislocation density

ρ_d = dislocation density

A_s = area of glide plane covered by dislocation

b = magnitude of Burgers vector

f^* = frequency of vibration of dislocation line length

C_1 = constant

μ = shear modulus

ρ_m = mobile dislocation density.

The initial flow stress or yield stress with its large temperature dependence arises primarily from τ_o , while the increment in flow stress resulting from work hardening is largely independent of temperature, and is caused by the increase in τ^* with increasing strain as the dislocation density ρ increases.

To summarise, work hardening in conventional materials is due largely to the creation of crystal defects, primarily dislocations, during plastic deformation. The hardening can reach saturation once the defect creation and annihilation rates balance.

Work hardening has an important consequence on ductility. During tensile testing, the sample will inevitably contain features which cause the stress to concentrate and hence to initiate necking. The reduced cross-sectional area at the neck increases the stress in the necked region. In the absence of work hardening to help resist local deformation, the neck becomes unstable and the sample fractures with poor overall ductility. To encourage uniform elongation, the work hardening must raise the yield strength at a rate greater than the increase in stress due to the reduced area at the neck.

Given the origin of work hardening, microstructures in which the dislocation density does not substantially increase during deformation should lack ductility. A pertinent example based on extremely fine grains is discussed in Section 2.5. A different mechanism in which mechanical twins partition the parent grains into ever finer compartments and hence introduce work hardening, is discussed in Section 10.5.

2.3 INTERSTITIAL SOLID SOLUTION STRENGTHENING

Carbon and nitrogen have a disproportionate influence on the strength of ferritic iron and a relatively minor effect on that of austenitic iron. The following relations between change in Vickers hardness with interstitial content illustrate this vividly [5–8]²:

$$\begin{aligned}\Delta HV_{\alpha} &\approx 950 \times w_C, \\ \Delta HV_{\gamma} &\approx 52 \times w_C, \\ \Delta HV_{\alpha} &\approx 630 \times w_N, \\ \Delta HV_{\gamma} &\approx 240 \times w_N.\end{aligned}\tag{2.4}$$

Solid solution strengthening occurs when the strain fields around misfitting solutes interfere with the motion of dislocations. Atoms which substitute for iron cause local expansions or contractions; these strains are isotropic and therefore can interact only with the hydrostatic components of the strain fields of dislocations. In contrast, an interstitial atom located in the irregular octahedral interstice in ferrite causes a tetragonal distortion

(Fig. 1.4) which has a powerful interaction with the shear that is the dominant component of a dislocation strain field. This is why interstitial solid solution strengthening is so potent in ferrite. The corresponding interstitial site in austenite is the regular octahedron. An interstitial atom in austenite therefore behaves like a substitutional solute, with only hydrostatic strains surrounding it. This is why carbon is much less effective in strengthening austenite.

Ferritic iron has such a small solubility for carbon and nitrogen (Fig. 1.9a) that there is an overwhelming tendency for these solutes to segregate to defects. This leads to another significant effect in α -iron, that carbon and nitrogen can promote heterogeneous deformation by making it difficult to initiate plastic flow. This is the yield point effect, described next.

2.3.1 The yield point

Carbon and nitrogen in iron, even in concentrations as low as 0.005 wt%, lead to a sharp transition between elastic and plastic deformation in a tensile test performed on ferritic iron. Decarburisation of the iron results in the elimination of this sharp transition or *yield point*, which implies that the solute atoms are in some way responsible for this striking behaviour. Frequently the load drops dramatically at the *upper yield point* 'a' (Fig. 2.4a) to another value referred to as the *lower yield point* 'b'. Under some experimental conditions, yield drops of about 30% of the upper yield stress can be obtained.

Following the lower yield point, there is frequently a horizontal section of the stress-strain curve 'b→c' during which the plastic deformation propagates at a front which can move uniformly along the specimen. This front is referred to as a Lüders band (Fig. 2.4b), and the horizontal portion, bc, of the stress-strain curve as the Lüders extension. The development of Lüders bands can be much less uniform; in pressings where the stress is far from uniaxial, complex arrays of bands can be observed (Fig. 2.4c). These are often referred to as *stretcher strains*, but they still are Lüders bands. Stretcher strains clearly are not desirable when making components that require a smooth surface visible to the user, e.g. an automobile body that is painted.

The concentrated deformation at the Lüders band leads to localised heating which spreads along the sample as the deformed region increases in size (Fig. 2.4d). When the whole specimen has yielded, general work hardening commences and the stress-strain curve begins to rise in the normal way. If, however, this deformation is interrupted, and the specimen allowed

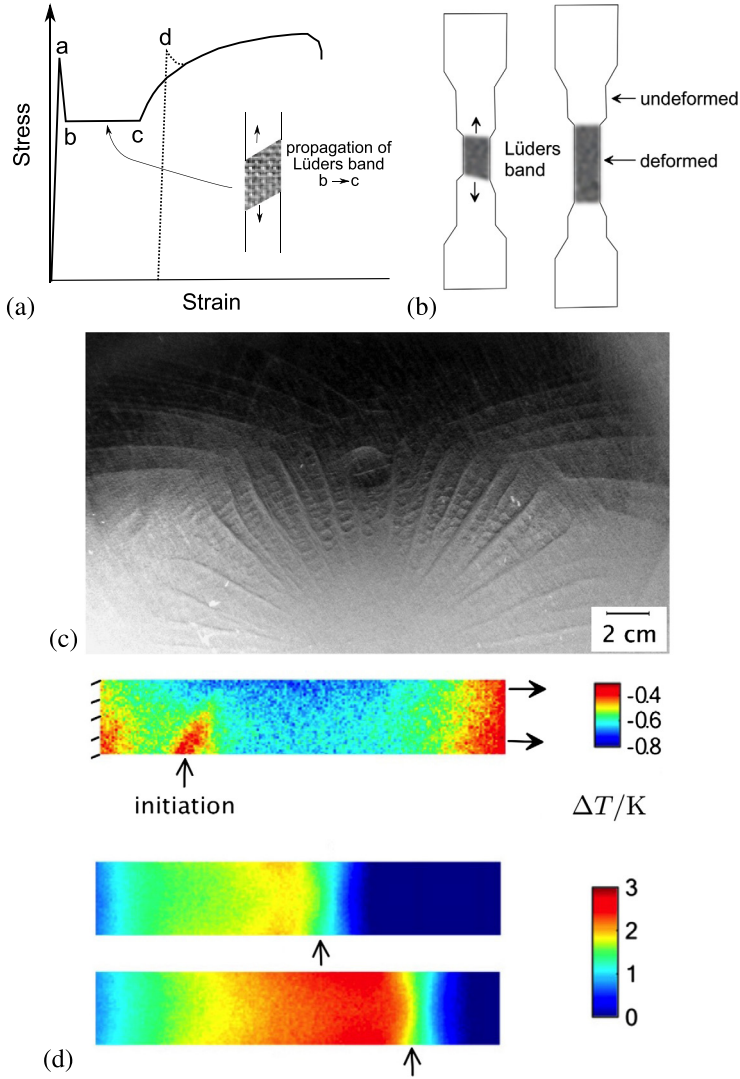


Figure 2.4 (a) Illustration of the yield phenomenon as discussed in the text. (b) Schematic illustration of the propagation of Lüders front during tensile testing. (c) Stretcher strains on a biaxially stretched component. (d) Thermal effects (change in temperature) observed on the gauge length of a tensile specimen, due to adiabatic heating of the sample during Lüders band initiation and propagation along the sample. The arrows indicate the position of the band as deformation progresses. Part (d) adapted with permission of Elsevier Masson SAS from Dumoulin et al. [9].

to rest either at room temperature or for a shorter time at 100–150°C, on reloading a new yield point is observed ('d', Fig. 2.4) due to the diffusion of interstitial atoms to dislocations which once again pins them. This return of the yield point is referred to as *strain ageing*.

2.3.2 Role of interstitial elements in yield phenomena

The sharp upper and lower yield point in iron is eliminated by annealing in wet hydrogen, which greatly reduces the concentration of carbon and nitrogen. However, substantial strain ageing can occur at carbon levels around 0.002 wt%, and as little as 0.001–0.002 wt% N can result in severe strain ageing. Nitrogen is more effective in this respect than carbon, because its residual solubility near room temperature is substantially greater than that of carbon (Fig. 1.9).

Cottrell and Bilby first showed that interstitial atoms such as carbon and nitrogen would interact strongly with the strain fields of dislocations. The interstitial atoms have strain fields around them, but when such atoms move into the dislocation strain fields, there should be an overall reduction in the total strain energy. This leads to the formation of interstitial concentrations or *atmospheres* in the vicinity of dislocations, which in an extreme case can amount to lines of interstitial atoms along the cores of the dislocations (*condensed atmospheres*), e.g. in edge dislocations at the region of the strain field where there is maximum dilation (Figs. 2.5a, b). The binding energy between a dislocation in iron and a carbon atom is typically about $\approx 10^{-19}$ J. Consequently dislocations can be locked in position by strings of carbon atoms along the dislocations, thus substantially raising the stress which would be necessary to cause dislocation movement. A particular attraction of this theory is that only a very small concentration of interstitial atoms is needed to produce locking along the whole length of all dislocation lines in annealed iron. For a typical dislocation density of 10^{12} m^{-2} in annealed iron, a carbon concentration of 10^{-6} wt% would be sufficient to provide one interstitial carbon atom per atomic plane along all the dislocation lines present, i.e. to saturate the dislocations. Consequently, this theory can explain the observation of yield phenomena at very low carbon and nitrogen concentrations.

The formation of interstitial atmospheres at dislocations requires diffusion of the solute. As both carbon and nitrogen diffuse very much more rapidly in iron than substitutional solutes, it is not surprising that strain ageing can take place readily in the range 20–150°C. The fractional occupancy

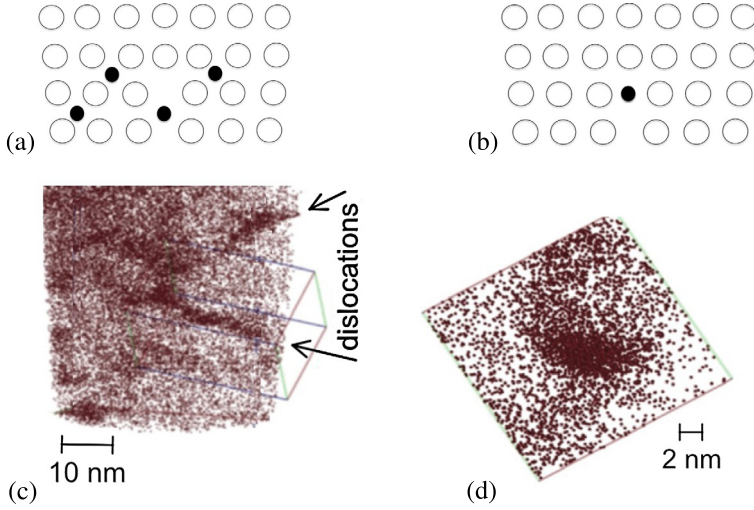


Figure 2.5 Schematic diagram of interstitial atoms (black) in the vicinity of an edge dislocation (a) random distribution, (b) condensed. (c) Atom probe image where each dot is a carbon atom, showing dislocations in ferrite, with dislocation-lines parallel to the arrows, decorated with carbon atmospheres. (d) Atom probe image showing an image plane normal to the dislocation line, illustrating the extent of the atmosphere. Figures c, d are adapted from Caballero et al. [10], reproduced with the permission of Elsevier.

x_i of interstitial sites with binding energy U_i is given by:

$$\frac{x_i}{1 - x_i} = \frac{\bar{x}}{1 - \bar{x}} \exp\left\{\frac{U_i}{kT}\right\}, \quad (2.5)$$

where $\bar{x}$ is the corresponding average occupancy of interstitial sites in the matrix far from the influence of the dislocation [11]. In general, this approach leads to a Maxwellian distribution of solute about the dislocation, but for carbon and nitrogen in steel, the elastic interaction energy U between solute and dislocation is so large that $U \geq kT$. Consequently the atmosphere condenses to form rows of interstitial atoms along the cores of the dislocations.

The maximum solute-dislocation interaction is when carbon occupies the dislocation core with $U_i = U_{\max}$. The temperature T_{crit} at which half the core sites are occupied is then given by:

$$T_{\text{crit}} = \frac{U_{\max}}{k \ln\left\{\frac{1-\bar{x}}{\bar{x}}\right\}}. \quad (2.6)$$

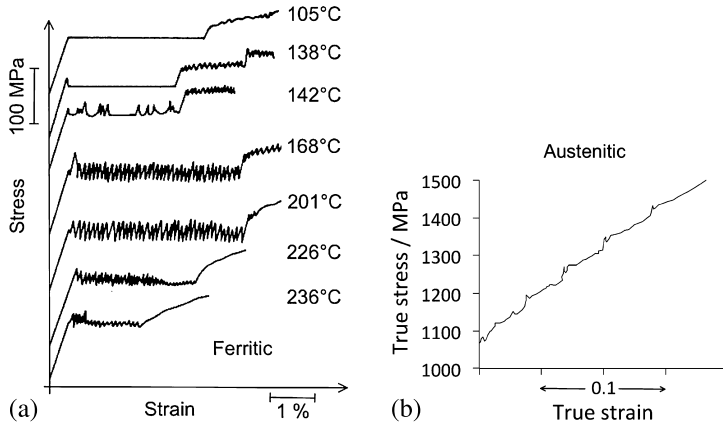


Figure 2.6 (a) Typical stress-strain curves for mild steel at elevated temperatures (adapted from Hall [12]). (b) Dynamic strain ageing in austenitic steel. Adapted from Lee et al. [13], reproduced with the permission of Elsevier.

It is therefore expected that for $\bar{x} = 10^{-4}$, $U_{\max} = 10^{-19}$ J, 10% of the dislocation core would be occupied by carbon even if the temperature is as high as 1000 K. This does not necessarily mean that the decorated dislocations would be pinned because the carbon atoms may be able to keep up with the dislocations by diffusion at high temperatures. Fig. 2.6a therefore shows that the zone of yielding is well defined at the lower testing temperatures, becoming less regular as the temperature is raised, until it is replaced by fine serrations along the whole stress-strain curve. This phenomenon is referred to as *dynamic strain ageing*, in which the serrations represent the replacement of the primary yield point by numerous localised yield points within the specimen. These arise because the temperature is high enough to allow interstitial atoms to diffuse during deformation, and to form atmospheres around dislocations generated throughout the stress-strain curve. Steels tested under these conditions also show low ductilities, due partly to the high dislocation density and partly to the nucleation of carbide particles on the dislocations where the carbon concentration is high. The phenomenon is often referred to as *blue brittleness*, blue being the interference colour of the steel surface when oxidised in this temperature range.

Dynamic strain ageing is not limited to ferritic steel. Fig. 2.6b shows how the interaction of carbon with dislocations in an austenitic steel (Fe-0.6C-18Mn wt%) causes serrated flow – a similar effect is found when nitrogen is added to this alloy.

The break away of dislocations from their carbon atmospheres as a cause of the sharp yield point became a controversial aspect of the theory because it was found that the provision of free dislocations, e.g. by scratching the surface of a specimen, did not eliminate the sharp yield point. An alternative theory was developed which assumed that, once condensed carbon atmospheres are formed in iron, the dislocations remain locked, and the yield phenomena arise from the generation and movement of newly formed dislocations (Gilman and Johnston). The velocity of movement v of these fresh dislocations is related to the applied stress as follows:

$$v = \left(\frac{\sigma}{\sigma_r} \right)^m, \quad (2.7)$$

where σ_r is the stress corresponding to a unit velocity, σ is the yield stress and m is an empirical index characteristic of the material, varying between 1 and 60. The strain rate $\dot{\epsilon}$ can be defined in terms of the movement of dislocations, as

$$\dot{\epsilon} = nvb, \quad (2.8)$$

where n is the number of mobile dislocations per unit area, v is their average velocity and b is the magnitude of the Burgers vector.

Using Equation (2.8) the strain rates at the upper yield point ($\dot{\epsilon}_U$) and the lower yield point ($\dot{\epsilon}_L$) can be defined as follows:

$$\dot{\epsilon}_U = \rho_U v_U b,$$

where ρ_U is the mobile dislocation density at the upper yield point and

$$\dot{\epsilon}_L = \rho_L v_L b,$$

where ρ_L is the mobile dislocation density at the lower yield point, so

$$\frac{v_U}{v_L} = \frac{\rho_L}{\rho_U},$$

and using Equation (2.6)

$$\frac{\sigma_U}{\sigma_L} = \left(\frac{\rho_L}{\rho_U} \right)^{\frac{1}{m}}. \quad (2.9)$$

Thus the ratio σ_U/σ_L will be large, i.e. there will be a large yield drop, where m is small, and when ρ_L is much larger than ρ_U . Consequently, if at the upper yield stress the density of mobile dislocations is small, e.g. as a result of solute atom locking, a large drop in yield stress will occur if many new dislocations are generated. Observations indicate that the dislocation

density just after the lower yield stress is much higher than that observed at the upper yield point.

To summarise, the occurrence of a sharp yield point depends on a sudden increase in the number of mobile dislocations. However, the precise mechanism by which this takes place will depend on the effectiveness of the locking of the pre-existing dislocations. If the pinning is weak, then the yield point can arise as a result of unpinning. However, if the dislocations are strongly locked, either by interstitial atmospheres or precipitates, the yield point will result from the rapid generation of new dislocations.

Under conditions of dynamic strain ageing, where atmospheres of carbon atoms form continuously on newly generated dislocations, it would be expected that a higher density of dislocations would be needed to complete the deformation, if it is assumed that most dislocations which attract carbon atmospheres are permanently locked in position. Electron microscopic observations have shown that in steels deformed at 200°C, the dislocation densities are an order of magnitude greater than those in specimens similarly deformed at room temperature.

2.3.3 Strengthening at high interstitial concentrations

Austenite can take into solid solution about 9 at% of carbon when in equilibrium with cementite (Fig. 3.2), which can then be retained in solid solution by rapid quenching. However, in these circumstances, the phase transformation takes place not to ferrite but to a body-centred tetragonal structure referred to as *martensite* (Chapter 5). This phase forms as a result of a diffusionless shear transformation leading to characteristic laths or plates, which normally appear acicular in polished and etched sections. If the quench is sufficiently rapid, the martensite is essentially a supersaturated solid solution of carbon in a tetragonal iron matrix, and as the carbon concentration can be greatly in excess of the equilibrium concentration in ferrite, the strength is raised very substantially. High carbon martensites are normally very hard but brittle, the yield strength reaching as much as 1500 MPa; much of this increase can be directly attributed to increased interstitial solid solution hardening, but there is also a contribution from the high dislocation density which is characteristic of martensitic transformations in iron-carbon alloys. Martensite will be dealt with in more detail in Chapter 5, which shows that by subjecting it to a further heat treatment known as *tempering*, at temperatures below A_{e1} , a proportion of the strength is retained, with a substantial gain in the toughness and ductility of the steel.

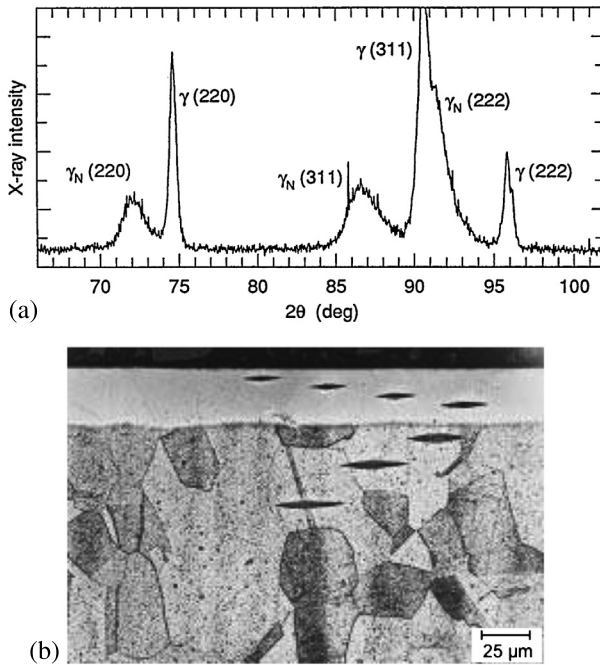


Figure 2.7 (a) X-ray diffraction pattern from a mixture of nitrogen-expanded austenite (γ_N) and the unaffected austenitic stainless steel. After [16], reproduced with the permission of Elsevier. (b) A carbon-rich layer of expanded austenite produced by low temperature plasma carburising, with indents that revealed a Knoop hardness of about 900 KN at the surface. Image reproduced from [17] with the permission of Maney Publishing.

Very large concentrations of carbon (15 at%) or nitrogen (38 at%) can be introduced into the surfaces of austenitic steels either by diffusion or using techniques such as ion implantation [14,15]. The lattice parameter of the austenite then expands dramatically by 10% in the case of the nitrogen enriched austenite and 3% for the carbon-enriched version. The resulting surface layers can be extremely hard and corrosion resistant, making the process suitable for components where wear resistance is paramount. Nano-hardness values in excess of 1100 HV have been reported. There is sharp transition observed between the lattice parameters of the expanded austenite and that of the unaffected substrate. Fig. 2.7 shows two distinct sets of X-ray diffraction peaks from the two kinds of austenite. The expanded austenite is also found to be ferromagnetic whereas the unaffected austenite is paramagnetic. It is known that the expanded austenite is crys-

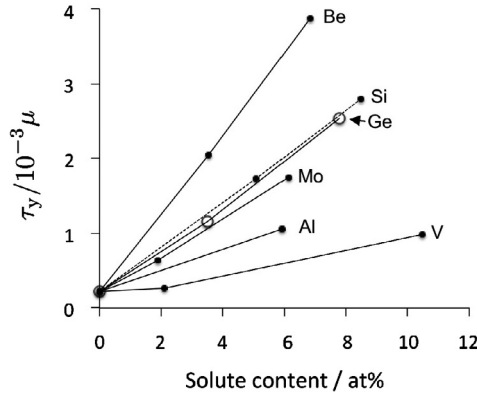


Figure 2.8 Solid solution strengthening of α -iron crystals by substitutional solutes. Ratio of the resolved shear stress τ_y at yield and at 300 K, to shear modulus μ , as a function of atomic concentration. Data from [18].

tallographically contiguous with the substrate austenite, so there is a very large dislocation density to accommodate the misfit.

2.4 SUBSTITUTIONAL SOLUTION STRENGTHENING

Many metallic elements form solid solutions in γ - and α -iron. These are invariably substitutional solid solutions, but for a constant atomic concentration of alloying elements there are large variations in strength. Using single crystal data for several metals, Fig. 2.8 shows that an element such as vanadium has a weak strengthening effect on α -iron at low concentrations (<2 at%), while silicon and molybdenum are much more effective strengtheners. Other data indicate that phosphorus, manganese, nickel and copper are also effective strengtheners. However, it should be noted that the relative strengthening may alter with the temperature of testing, and with the concentrations of interstitial solutes present in the steels.

The strengthening achieved by substitutional solute atoms will depend on the difference in atomic size of the solute from that of iron because it is the strain field around the misfitting atoms that determines some of the interaction with dislocations. However, the elastic properties and bonding within the metal are also likely to be influenced and may play a role in the potency of strengthening. Thus, the thermal component of shear stress τ^* (Equation (2.1)) may increase or decrease due to solute additions. The mechanism by which a solute atom might reduce τ^* is simply that

the local distortion helps the dislocation overcome a barrier; nickel, for example, softens iron at low temperatures. On the other hand, the athermal component τ^* always increases on alloying because of the contribution of solute atoms to long-range internal stresses [19]. These concepts apply in polycrystalline substances as long as the key deformation mechanism involves the passage of dislocations through significant lengths in individual crystals. They would be less relevant if mechanisms such as grain boundary sliding and rotation are dominant. Simulations indicate that solutes that stiffen the grain interiors are most effective in increasing the strength of nanocrystalline alloys that deform by sliding and grain rotation [20].

In practical terms, the contribution to strength from solid solution effects is superimposed on hardening from other sources, e.g. grain size and dispersions. Also it is a strengthening increment, like that due to grain size, which need not adversely affect ductility. In industrial steels, solid solution strengthening is a far from a negligible factor in the overall strength, where it is achieved by a number of familiar alloying elements, e.g. manganese, silicon, nickel, molybdenum, several of which are frequently present in a particular steel and can be additive in their effect. These alloying elements are usually added for other reasons, e.g. Si to achieve deoxidation, Mn to combine with sulphur or Mo to promote hardenability. Therefore, the solid solution hardening contribution can be viewed as a useful bonus.

2.5 GRAIN SIZE

2.5.1 Hall-Petch effect

The refinement of the grain size of ferrite provides one of the most important strengthening routes in the heat treatment of steels.

The yielding of imperfect single crystals depends largely on the orientation of the crystal relative to the applied stress, the operative slip systems and the friction provided by the lattice to the motion of dislocations. By contrast, individual crystals within a polycrystalline aggregate are constrained by their surroundings and there are discontinuities presented to the motion of dislocations at the junctions between crystals, i.e. the grain boundaries. Macroscopic yielding of a polycrystalline aggregate is therefore defined as the point where yield can be stimulated in adjacent grains when a particular crystal is induced to deform so that plasticity can be propagated. The grain size effect on the yield stress can therefore be explained by assuming that a dislocation source operates within a crystal causing dislocations to move and eventually to pile-up at the grain boundary. The pile-up represents a

concentration of stress that extends beyond the grain boundary, into the surrounding crystals.

The number of dislocations (n) that can participate in a pile up for an applied stress σ is proportional the grain size d , basically scaling with the size of the slip planes. It also scales with the stress which causes the dislocations in the pile up be closer to each other as the stress is increased. However, the stress of interest is the applied stress less the friction stress σ_0 that opposes the motion of a dislocation in a lattice. Therefore, $n \propto d(\sigma - \sigma_0)$. This pile-up of dislocations causes a concentration of the stress rather like the situation at a crack tip. The stress concentration from the pile up, at some distance in the adjacent grain is proportional to the effective stress and the number of dislocations in the pile-up, i.e., $n \times (\sigma - \sigma_0) \equiv d(\sigma - \sigma_0)^2$. When the stress in the adjacent grain reaches a constant critical value σ_c , it triggers a dislocation source in the adjacent grain and hence causes macroscopic yielding so that the applied stress σ is set to the yield strength σ_y . Therefore, $\sigma_c \propto d(\sigma_y - \sigma_0)^2$, which on rearrangement yields $(\sigma_y - \sigma_0) \propto d^{-\frac{1}{2}}$.

This analysis can be used to interpret the first study of the relationship between grain size and strength, carried out on ARMCO iron by Hall and Petch, that led to the Hall-Petch relationship between the yield stress σ_y and the grain size d ,

$$\sigma_y = \sigma_0 + k_y d^{-\frac{1}{2}}, \quad (2.10)$$

where k_y is a constant. This type of relationship holds for a wide variety of irons and steels as well as for many non-ferrous metals and alloys. A typical set of results for mild steel is given in Fig. 2.9, where the linear relationship between σ_y and $d^{-\frac{1}{2}}$ is seen.

The friction stress σ_0 represents the stress required to move free dislocations along the slip planes in the bcc crystals, and can be regarded as the yield stress of a single crystal ($d^{-\frac{1}{2}} = 0$). This stress is particularly sensitive to temperature and composition. The k_y term that is the slope of the σ_y versus $d^{-\frac{1}{2}}$ plot has been found not to be sensitive to temperature as shown in Fig. 2.9, nor to the composition and strain rate.

In line with the Cottrell-Bilby theory of the yield point involving the break away of dislocations from interstitial carbon atmospheres, k_y has been referred to as the unpinning parameter. However, the insensitivity of k_y to temperature suggests that unpinning rarely occurs, and emphasises the theory that new dislocations are generated at the yield point. This is consistent with the theories explaining the yield point in terms of the movement

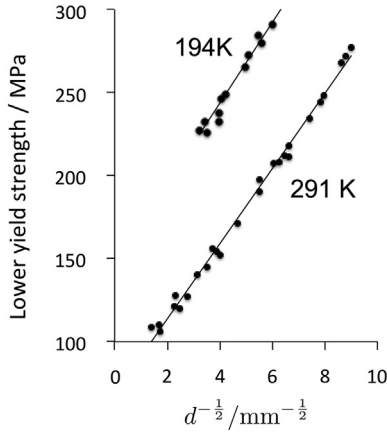


Figure 2.9 Dependence of the lower yield stress of mild steel on grain size. Data from [21].

of new dislocations, the velocities of which are stress dependent (Section 2.3.2).

In practical terms, the finer the grain size, the higher the resulting yield stress and, as a result, in modern steel working much attention is paid to the final ferrite grain size. While a coarse grain size of $d^{-\frac{1}{2}} = 2$, i.e. $d = 0.25 \text{ mm}$, gives a yield stress in mild steels of around 100 MPa, grain refinement to $d^{-\frac{1}{2}} = 20$, i.e. $d = 0.0025 \text{ mm}$, raises the yield stress to over 500 MPa, so that achieving grain sizes in the range $2\text{--}10 \mu\text{m}$ is extremely worthwhile. Over the last 40 years, developments in rolling practice and the addition of small concentrations of particular alloying elements to mild steels, have resulted in dramatic improvements in the mechanical properties of this widely used engineering material (Chapter 9).

2.5.2 Nanostructured steels

Modern technologies allow steels to be made routinely and in large quantities with grain sizes of about $2\text{--}10 \mu\text{m}$. Limited processes, generally involving severe thermomechanical processing, have been developed to achieve nanostructured ferrite grains in steel, with a size in the range $20\text{--}100 \text{ nm}$. To understand the behaviour at such incredibly small crystal sizes, it is pertinent to examine the volume fraction V_V^B of material occupied by the boundaries:

$$V_V^B \simeq 2a/\bar{L},$$

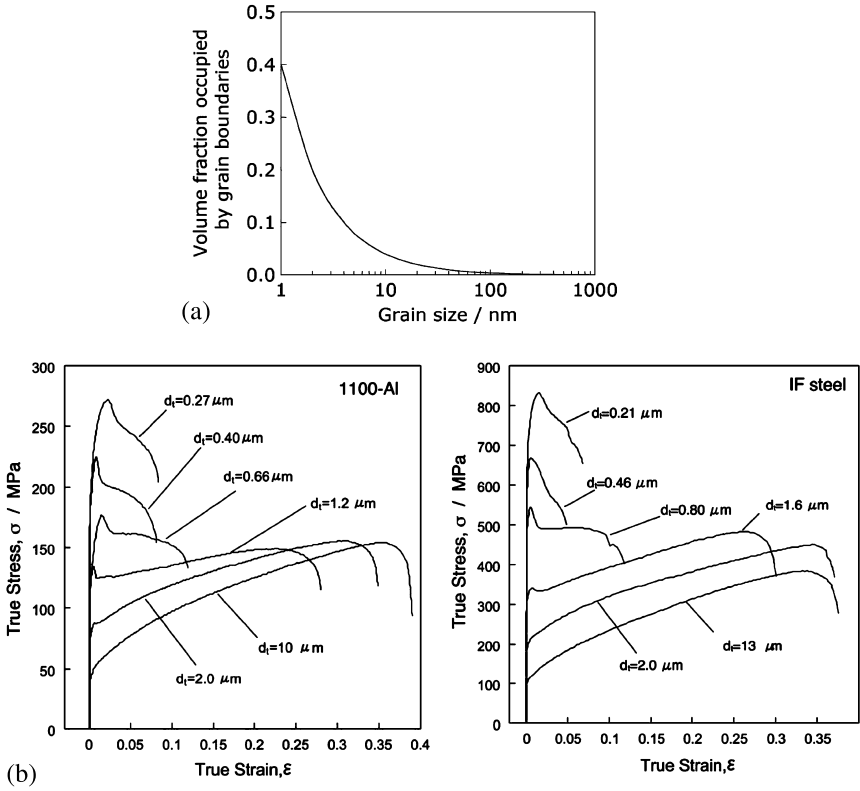


Figure 2.10 (a) The volume fraction of grain boundary within a given volume, as a function of the grain size. (b) Loss of ductility as the strength is increased by dramatically reducing the grain size in aluminium and iron alloys. After Tsuji et al. [22], reproduced with permission from Elsevier.

where $\bar{L}$ is the mean linear intercept defining the grain size and a is the thickness of the boundary layer. Clearly, the fraction of atoms located at the grain surfaces becomes very large in the nanostructured materials, facilitating diffusional processes such as dislocation absorption and grain sliding (Fig. 2.10a).

The Hall-Petch Equation (2.10) has been shown to fail (for some metals other than iron) when the equiaxed grain size reaches the nanostructure scale less than about 20 nm. Instead, an “inverse Hall-Petch” relation is observed, in which the strength decreases as the grain size is refined, Fig. 2.11. One explanation for this behaviour is that the probability (p_{dis}) of dislocations being absorbed by grain boundaries increases as the grain size is

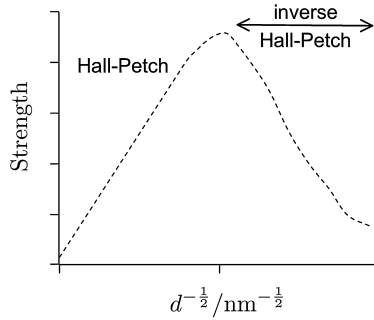


Figure 2.11 Schematic illustration of the inverse Hall-Petch effect observed in some nanostructured metals with equiaxed grain structures.

reduced. So a modified form of the Hall-Petch equation is proposed:

$$\sigma_y = \sigma_0 + \underbrace{k'_y(1 - p_{\text{dis}})}_{\text{slope}} d^{-\frac{1}{2}} \quad (2.11)$$

The absorption of the dislocations reduces the number that can participate in pile-ups and hence as p_{dis} increases, the slope of the plot of σ_y versus $d^{-\frac{1}{2}}$ becomes a function of d , with negative values when the grain size is small enough [23].

The inverse Hall-Petch equation is not encountered in practice when considering any commercial steel, but there are other significant consequences of very fine grain sizes. Although the nanostructured steels are strong, they tend to exhibit unstable plasticity after yielding (Fig. 2.10). The plastic instability occurs in both tension and in compression testing, with shear bands causing failure in the latter case. It is as if the capacity of the material to work harden following yielding diminishes. The consequence is an unacceptable reduction in ductility as the grain size is reduced in the nanometre range. At very fine grain sizes, the conventional mechanisms of dislocation multiplication fail because of the proximity of the closely spaced boundaries. It then becomes impossible to accumulate dislocations during deformation. Grain boundaries are also good sinks for defects. This would explain the observed inability of nanostructured materials to work harden. One way of overcoming this difficulty is described in Chapter 14.

The difficulty that nanocrystalline grains have in deforming by a dislocation mechanism is highlighted in recent experiments [24] where nanocrystals of ferrite were forced to deform in shear. The crystals underwent a shear transformation into austenite.

2.6 DISPERSION STRENGTHENING

In all steels there is normally more than one phase present, and indeed it is often the case that several phases can be recognised in the microstructure. The matrix, which is usually ferrite (bcc structure) or austenite (fcc structure) strengthened by grain size refinement and by solid solution additions, is further strengthened by controlling the dispersions of the other phases in the microstructure. The commonest other phases are carbides formed as a result of the low solubility of carbon in α -iron (Fig. 2.12). In plain carbon steels this carbide is normally Fe_3C (cementite) which can occur in a wide range of morphologies from a coarse apparently-lamellar form in pearlite, to fine platelet or spheroidal precipitates in tempered martensite. In alloy steels, the same range of structures is encountered, except that in many cases, the iron-rich carbide is replaced by alloy carbides such as Mo_2C that are thermodynamically more stable. Other dispersed phases which are encountered include nitrides, intermetallic compounds and, in cast irons, graphite.

Most dispersions lead to strengthening, but they often can have adverse effects on ductility and toughness. In fine dispersions, ideally small spheres randomly dispersed in a matrix, there are well-defined relationships between the yield stress, or initial flow stress, and the parameters of the dispersion. The simplest is that due to Orowan and Ashby, relating the change in the shear yield stress due to a dispersion of non-deforming, spherical particles to be:

$$\Delta\tau \approx \frac{0.81\mu b}{(1-\nu)^{1/2}(L_p - 2r_p)} \ln \left\{ \frac{2r_p}{b} \right\}, \quad (2.12)$$

where L_p is the average centre-to-centre spacing of near-neighbour particles intersected by a random plane, and r_p is similarly the average particle radius intersected by the plane. The factor of 0.81 is a stereological term accounting for the assumed random dispersion of particles [27]. The yield stress increment due to particles therefore varies inversely as the spacing between the particles at constant r_p . It follows that if the dispersion is coarsened by further heat treatment, the strength of the alloy decreases.

We have seen in Fig. 2.12 that the dispersoids are not always spherical and may not be randomly dispersed. They may also prefer to be on certain crystallographic planes where the fit between the precipitate lattice and matrix is optimised. In such cases, the parameters L_p and r_p can be modified to account for specific geometries and arrangements prior to substitution into Equation (2.12), [28].

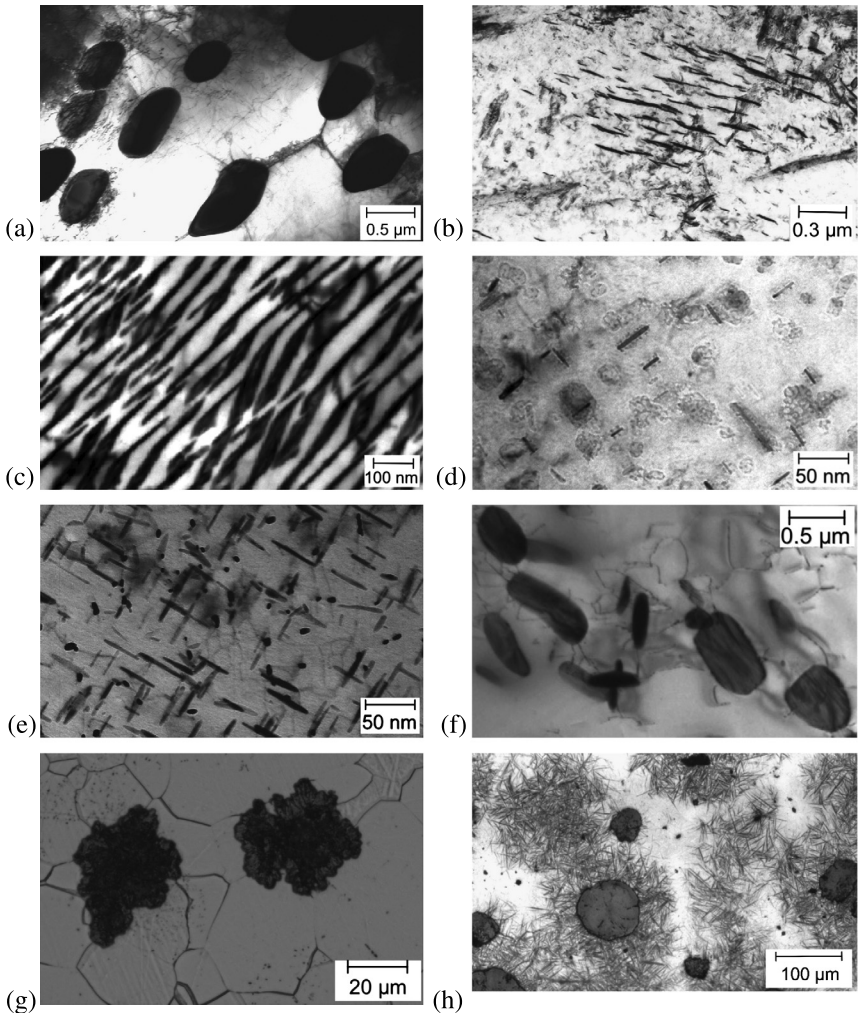


Figure 2.12 A few of the rich variety of dispersoids that help achieve the myriad of properties possible in steels. (a) Spheroidised cementite in a severely tempered high-carbon steel. (b) Fine platelets of cementite in lightly tempered martensite. (c) Lamellae of cementite in fine pearlite (Jaramillo et al. [25], reproduced with the permission of Elsevier). (d) Three orientations of V_4C_3 in secondary hardened steel, one set, the discs, lying in the plane of the image. (e) Needles of molybdenum carbide in secondary hardened steel – the dot-like precipitates are sections of needles normal to the image plane (d, e, courtesy of S. Yamasaki). (f) Fe_2Nb intermetallic precipitates in austenitic stainless steel (Yamamoto et al. [26], with permission from Elsevier). (g) Graphite in annealed steel (courtesy C. Hulme-Smith). (h) Graphite in austempered ductile cast iron (courtesy M.A. Yescas-Gonzalez).

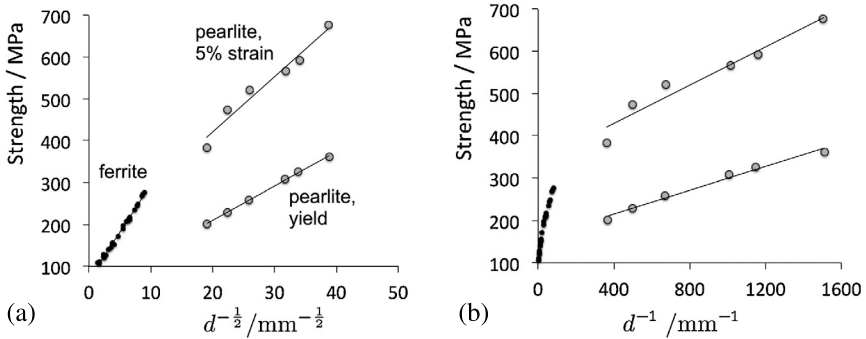


Figure 2.13 (a) Dependence of the flow stress at several strains on the mean free path within the ferrite that is a constituent of pearlite (data from [29]). For comparison, data for ferrite grains from Fig. 2.9 are also plotted. The term d therefore represents the ferrite grain size in the latter case but the mean free path within the ferritic component of pearlite for the remaining data. (b) The same data plotted versus the inverse of d . The data for pearlite continue to show a linear relationship whereas those for ferrite become distinctly non-linear.

Perhaps the most familiar structure in steels is that of the eutectoid pearlite, usually approximated as a lamellar mixture of ferrite and cementite. This can be considered as an extreme form of dispersion of one phase in another, and undoubtedly provides a useful contribution to strengthening. The lamellar spacing can be varied over wide limits, and again the strength is sensitive to such changes (Chapter 3). When the coarseness of the pearlite is represented by a mean uninterrupted free ferrite path in the pearlitic ferrite, it has been shown that the flow stress is related to the mean free path by a Hall-Petch type relationship. However, as seen in Fig. 2.13a, the slope k_y is much smaller in the case of pearlite and the interpretation of the Hall-Petch behaviour in terms of the passage of slip between adjacent grains becomes doubtful. This is because a pearlite colony is strictly a bi-crystal with the ferrite percolating through the microstructure of the colony. In other words, the observation of a Hall-Petch relation does not imply grain size strengthening in the ordinary sense, because the ferrite regions separated by cementite all belong to the same crystal. The strength strictly depends on the cementite acting as partial barriers to dislocation motion in the softer ferrite. It may not therefore be reasonable to assume a Hall-Petch relationship for pearlite – as shown in Fig. 2.13b, the data for pearlite (though not for ferrite) can be interpreted to show a d^{-1} relationship as might be expected from Equation (2.12).

Note also that the dispersion model of strengthening would fail if the cementite within the pearlite also started deforming, as it does during wire drawing to produce very strong ropes for applications in suspension bridges etc.

2.7 OVERALL STRENGTH

Strength in steels arises from several phenomena, which usually contribute collectively to the observed mechanical properties. The heat treatment of steels is aimed at adjusting these contributions so that the required balance of mechanical properties is achieved. Fortunately the γ/α change allows a great variation in microstructure to be produced, so that a wide range of mechanical properties can be obtained even in plain carbon steels. The additional use of metallic alloying elements, primarily as a result of their influence on the transformation, provides an even greater control over microstructure, with consequent benefits in the mechanical properties.

We have not discussed thus far the strengthening and deformation behaviour of mixed microstructures, such as the dual-phase steels which consist of ferrite and harder martensite. This can radically alter the stress *versus* strain behaviour with the deformation being heterogeneous on a microscopic scale with complex constraint and compatibility issues governing plasticity. Some of these aspects of mixed microstructures are described in Chapter 15 as one of the two case studies. However, there are some general and useful approximations that often capture the essence of the problem without introducing excessive complexity [30]. The first requirement is the knowledge of the constitutive equations of each of the phases, i.e., the stress-strain behaviour of the single phase in isolation. Fig. 2.14 shows such curves for phases α and β with volume fractions V_V^α and V_V^β respectively. In the equal work method, the strain experienced by each phase is different, determined by the areas $a + b = b + c$ (Fig. 2.14), so that the softer phase is deformed to a greater extent. The process must be implemented incrementally so that the work hardening characteristics of each phase are properly accounted for. At any stage of deformation, the strength σ_c of the composite microstructure is given by

$$\sigma_c = V_V^\alpha \sigma_\alpha \{\epsilon_\alpha\} + V_V^\beta \sigma_\beta \{\epsilon_\beta\} \quad (2.13)$$

where $\sigma_\alpha \{\epsilon_\alpha\}$ is the stress in α at a plastic strain ϵ_α etc., and V_V represents volume fraction. In contrast, the equal strain model has the composite strain ϵ_c in all phases and Equation (2.13) applies in the calculation of the overall

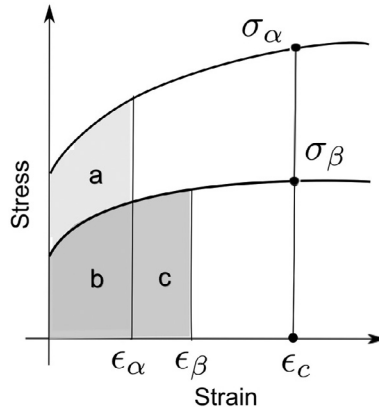


Figure 2.14 An illustration of the equal work, and equal plastic strain methods of estimating the deformation behaviour of mixtures of phases.

stress. The models are clearly approximate and their applicability depends on many factors, for example the extent of the difference in the strengths of the component phases and whether the properties of the pure phases vary with volume fraction within the composite. This is particularly so when solute partitions between the phases during transformation, or when the properties of a phase change due to deformation-induced phase transformation.

Similar difficulties arise when combining the contributions of different strengthening mechanisms to generate the overall strength of a single phase. The extent of dislocation strengthening may depend on the segregation of carbon to dislocations, so that the solution hardening term for carbon becomes uncertain. Assuming that the individual strength components (σ_i) can simply be summed linearly can lead to a large overestimation of strength [31]. A non-linear summation may then be justified, $\sigma^k = \sum \sigma_i^k$, where the exponent k has some fundamental meaning but usually is applied as a fitting constant [32,33, e.g.].

2.8 SOME PRACTICAL ASPECTS

The presence of a sharp yield point in a steel can be detrimental to its behaviour, e.g., when used for pressings, where complex patterns of Lüders bands can produce rough surfaces and lead to poor workability. The severity of the yield point is related directly to the amount of carbon and nitrogen in solution in the ferrite, so that steps taken to reduce these concentrations

are helpful. Unfortunately, yield points can be obtained with very low concentrations of carbon and nitrogen, making it impracticable in industrial conditions to obtain steels below these limits. However, any heat treatment which reduces the concentration of the interstitial solute that is in solid solution, is beneficial, e.g. slow cooling from annealing treatments. The yield point can be more reliably eliminated prior to working by a small amount of cold rolling (0.5–2%), referred to as *temper rolling*. As both nitrogen and carbon diffuse appreciably in ferrite at ambient temperatures, it is desirable to fabricate steels soon after the temper rolling.

While carbon and nitrogen can both cause strain ageing and consequently a yield point, the higher solubility of nitrogen in ferrite means that it provides the greater problem in steels used for deep drawing and pressing. Steps are taken during steelmaking to keep the nitrogen level down, but to minimise its effects, the easiest solution is to add small concentrations of strong nitride formers such as aluminium, titanium or vanadium, which reduce the nitrogen in solution to very low concentrations.

The occurrence of strain ageing can, by increasing both the yield stress and ultimate tensile stress, benefit mild steels which are used for constructional purposes. Furthermore, the fatigue properties are improved, both at room temperature and in the range up to 350°C. The existence of a well-defined fatigue limit in steels, i.e. a fatigue stress limit below which failure does not occur, has been linked to the occurrence of strain ageing during the test, but very pure iron also shows this behaviour. It should be emphasised that even in a relatively simple low carbon steel, the strength arises not only from these effects of carbon and nitrogen, but also from the solid solution hardening of elements such as silicon and manganese, and potentially from the refinement of the ferrite grain size by various means.

Bake-hardening steels [34,35] take advantage of the migration of carbon atoms to dislocations. They have an essentially ferritic microstructure with less than 25 ppm of carbon in solid solution. The steels are used in the manufacture of automobile bodies which after forming into shape are painted. When the paint is baked in the temperature range 150–200°C, the dissolved carbon migrates to pin any free dislocations introduced during the forming operation. The increase in strength illustrated in Fig. 2.15 is significant given that the tensile strength of the steel is only about 300 MPa. It is not surprising that the strengthening is greatest at the temperatures where carbon migration is possible.

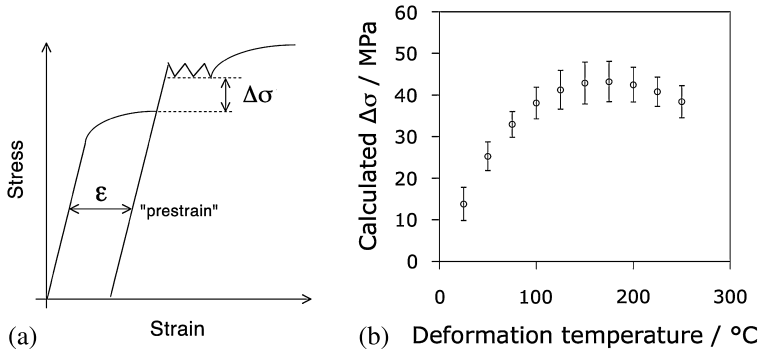


Figure 2.15 (a) Schematic illustration of the increase in strength, $\Delta\sigma$, following plastic deformation and bake-hardening. (b) Dependence of $\Delta\sigma$ on the deformation temperature [35].

2.9 LIMITS TO STRENGTH

Strength is not always the most useful entity. It may not in fact be safe to load an engineering structure to the full capability of the material. To illustrate this and some other limits of scale, a comparison is presented here of the potential strength of steel and that of carbon nanotubes and graphene, which are the subject of much contemporary discussion.

2.9.1 Theoretical strength

The strength of crystals increases sharply as they are made smaller. This is because the chances of avoiding defects become greater as the volume of the sample decreases. In the case of metals, imperfections in the form of dislocations are able to facilitate shear at much lower stresses than would be the case if whole planes of atoms had to collectively slide across each other. Defects are very difficult or impossible to avoid, but supposing that perfection can somehow be achieved, then the strength in the absence of defects is said to be that of an *ideal* crystal.³

In an ideal crystal, the tensile strength $\sigma_t \simeq 0.1E$ where E is the Young's modulus. The corresponding ideal shear-strength is $\sigma_s \simeq b\mu/2\pi a$, where μ is the shear modulus, b is a repeat period along the displacement direction and a is the spacing of the slip planes. For ferritic iron, $\mu = 80.65$ GPa and $E \simeq 208.2$ GPa. It follows that the ideal values of tensile and shear strength should be about 21 and 11 GPa, respectively. In fact, tensile strengths approaching the theoretical values were achieved by Brenner as long ago as 1956 (Fig. 2.16a) during the testing of whiskers of iron with diameters

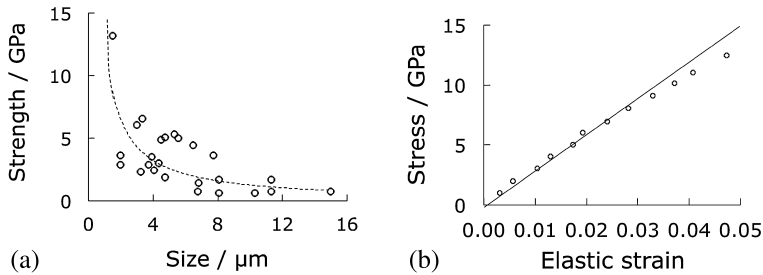


Figure 2.16 (a) The tensile strength of whiskers of iron. (b) Non-linear elasticity at large stresses. Data from Brenner [37,38].

less than $2\mu\text{m}$. It is interesting that these stress levels fall out of the regime where Hooke's law applies (Fig. 2.16b).⁴

The whisker experiments showed that the strength decreased sharply as the dimensions of the test-sample were increased (Fig. 2.16a), because the chances of finding defects increase as the sample gets bigger. It was therefore recognised some six decades ago that it is not wise to rely on perfection as a method of designing strong materials, although it remains the case that incredible strength can be achieved by reducing dimensions, in the case of iron, to a micrometre scale.

It is in this context that we now proceed to examine the notion that large-scale engineering structures can be designed using very long carbon nanotubes [39] and to address claims regarding the strength of graphene.

2.9.2 Hundreds of times stronger than steel

Steel is one of many materials available to create new technologies and concepts. It is, in the scientific and popular literature, treated as the “gold standard” against which new developments are compared. The comparisons are, however, either incorrect, misleading or based on flawed science.

Spider's thread has a tensile strength of about 700 MPa but a density of only 1.3 g cm^{-3} giving it a specific strength that is six times greater than steel of identical tensile strength [40]. Spider's thread is typically $10\mu\text{m}$ in diameter. It is in fact possible to obtain commercially, steel wire of similar diameter that has a strength of 5.5 GPa, i.e., $\approx 8 \times 700\text{ MPa}$ and a greater specific strength than the thread [41]. It is claimed that the spider's thread is tougher than steel on the basis of the area under the stress versus strain curve. So with a strength of 700 MPa and elongation of 30%, the elastic energy per unit volume is 105 MJ m^{-3} . The 5.5 GPa wire when stretched

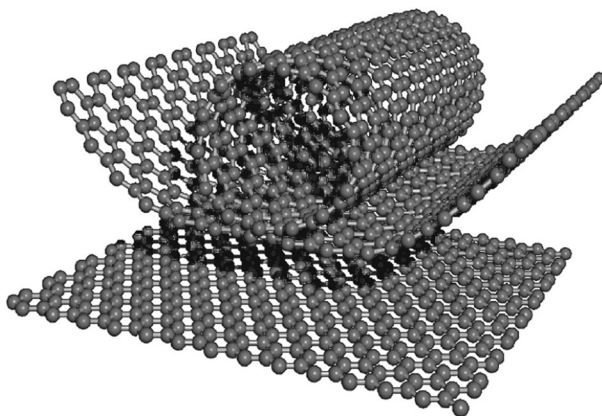


Figure 2.17 Schematic diagram showing how a sheet of graphene might be rolled to form a tube (courtesy of M. Endo).

elastically to a strain of 0.026 would absorb at least 145 MJ m^{-3} before fracture.

Carbon nanotubes can be imagined to be constructed from sheets of graphene consisting of sp^2 carbon arranged in a two-dimensional hexagonal lattice (Fig. 2.17). The sheets, when rolled up and with the butting edges appropriately bonded, are the nanotubes, which may or may not be capped by fullerene hemispheres. The actual form can be complex, e.g. with occasional pentagonal rings of carbon atoms instead of hexagonal to accommodate changes in shape.

The breaking strength of such a tube has been estimated to be an extraordinary 130 GPa; this number is astonishing and has led to many exaggerated comparisons against steel. However, this is the strength of an invisibly small nanotube. Larger tubes will contain defects which lead to a gross deterioration of strength, rather like the behaviour of whiskers of iron. Some of these defects will be there at equilibrium and hence are unavoidable. For example, it is known that metals contain an *equilibrium* concentration of vacancies. The enthalpy change associated with the formation of a vacancy opposes its existence, whereas the change in configurational entropy due to the formation of a vacancy favours its formation.

The total change in free energy on forming n vacancies in a crystal is given by [42]:

$$\Delta G = n\Delta g - kT[(N + n) \ln\{N + n\} - N \ln\{N\} - n \ln\{n\}],$$

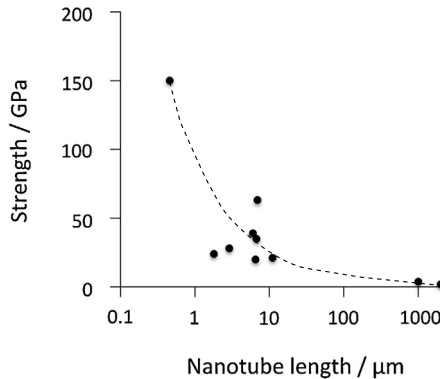


Figure 2.18 Variation in the strength of carbon nanotubes as a function of length. Data collated from [43–45].

where k is the Boltzmann constant, T is the absolute temperature, N is the number of atoms, $\Delta g = \Delta h - T\Delta s$, Δh is the enthalpy of formation of one vacancy and Δs is the entropy of formation of a vacancy excluding any contribution from configurational entropy, which is the second term in the equation. The equilibrium mole fraction of vacancies (x) is obtained by writing $\partial \Delta G / \partial n = 0$ giving:

$$x = n/N \simeq \exp\{-\Delta g/kT\}.$$

On this basis, taking the energy of a vacancy in a nanotube as 7 eV, and setting T to be the manufacturing temperature of the tubes (2000–4000 K), it is possible to show that a carbon nanotube strand appropriate for a space elevator, weighing 5000 kg, would contain approximately 10^{10} – 10^{20} defects. It is not therefore possible to scale the dimensions of a nanotube by some 18 orders of magnitude and assume that the strength will be retained. The particular structure referred to here is the speculated space elevator to replace rocket launches, which would require carbon tube ropes that are some 120,000 km in length. Fig. 2.18 shows how the strength of a carbon nanotube collapses as a function of its size.

This emphasises again that systems which rely on perfection in order to achieve strength necessarily fail on scaling to engineering dimensions. Indeed, there is no carbon tube which can match the strength of iron beyond a scale of 2 mm. These considerations apply also to graphene sheets.

Graphene has been claimed to be between 100–300 times stronger than steel. Lee and co-workers determined the strength of a monolayer of graphene about 1 μm in diameter by a nanoindentation method. They

Table 2.1 Comparison of a fully loaded carbon nanotube and dynamite [47]

	Stored energy J g^{-1}	Detonation velocity m s^{-1}
Dynamite	4650	6000
Carbon nanotube	5420	21,500

measured the intrinsic breaking strength of the perfect layer as 42 N m^{-1} and converted this into a strength of 130 GPa, the same value as reported for carbon nanotubes [46], which may not be surprising given that the data are in both cases for carbon-carbon bonds in perfect samples. Suppose that 130 GPa represents the true strength of two-dimensional graphene. Brenner [37] has measured the tensile strength of a $1.6 \mu\text{m}$ whisker to be 13.4 GPa so the intrinsic tensile strength of iron, along its weakest crystallographic direction is likely to be 14.2 GPa [36]. It follows that pristine graphene is at best about 9 times stronger than steel. When scaled to sizes greater than the micrometre dimensions, it is likely to suffer the same fate as carbon nanotubes, i.e. lose its integrity.

Fracture

Suppose that gigatubes of carbon could be made capable of supporting a stress of 130 GPa. Would this allow for safe engineering design? One aspect of safe design is that fast fracture should be avoided; most metals absorb energy in the form of plastic deformation before ultimate fracture. Energy absorption in an accident is a key aspect of automobile safety. Carbon nanotubes are not in this sense defect tolerant; their deformation prior to fracture is elastic. The stored energy density in a tube stressed to 130 GPa, given an elastic modulus along its length of $E = 1.2 \text{ TPa}$ is in excess of that associated with dynamite (Table 2.1). Dynamite is explosive because of its high energy density and because this energy is released rapidly, the detonation front propagating at some 6000 m s^{-1} . The speed of an elastic wave in the carbon is given by $\sqrt{E/\rho}$ where ρ is the density. In the event of fracture, the rate at which the stored energy would be released is much greater than that of dynamite (Table 2.1), meaning that fracture is unlikely to occur in a safe manner.

It follows that structures in tension, which reversibly store energy far in excess of their ability to do work during fracture must be regarded as unsafe. Strength can only be exploited in a safe manner if the material is capable of absorbing sufficient energy during fracture.

2.10 SUMMARY

The strengthening mechanisms described in this Chapter apply to all metals and alloys. But the yield point effect is less widespread; aluminium containing magnesium shows yielding and serrated flow in appropriate circumstances because magnesium, even though it is a substitutional solute, is quite mobile when dissolved in Al. Crystallography also matters – the yield point effect is much weaker in austenite than in ferrite because of the lower symmetry of the preferred interstice in ferrite.

Although strengthening mechanisms are well understood, it is not simple to combine their contributions to derive an overall strength. There is further complexity in dealing with multiphase alloys because the strains may not then be uniformly distributed.

When looking at combinations of strength and elongation, it simply has not been possible to develop viable steels that are stronger than ≈ 3 GPa and yet have ductility exceeding about 5%. This should not be surprising because strength is achieved by hindering deformation whereas sustained elongation requires a work-hardening capacity that delays plastic instabilities. It may not ever be possible to create steels that are very strong and very ductile. Nevertheless, steels stronger than 3 GPa with an elongation less than 2% are in commercial use in the form of ropes. How is it possible to tolerate such a small ductility? By twining thin strands into ropes; the failure of individual strands does not then lead to catastrophes. Such ropes are in effect steel-air composites and this principle could be exploited in developing laminated steels for the mass market. The utility of a material depends not just on its intrinsic properties but also on how it is deployed. No one, for example, seems to have thought of using wire ropes for the crash-resistant infrastructure of automobiles.

There are advantages in creating polycrystalline steels where individual crystals are fine because this raises both the strength and the toughness. But nanostructured metals where the crystal size is much less than 100 nm can behave quite differently, for example by exhibiting an inverse Hall-Petch relationship. There are other issues that are reserved for Chapter 14. But it is pertinent here to note that claims about the phenomenal strength of various forms of carbon relative to steel are essentially an attempt to mislead.

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BACKNOTES

1. The negative sign in Equation (2.1) indicates that τ is opposed by τ_o and τ^* .
2. The coefficients given should not be taken too seriously because they depend on a variety of factors other than the interstitial content. However, they serve to show that interstitial strengthening is far more potent in ferrite than in austenite.
3. In the case of graphene, this is referred to as the intrinsic strength.
4. In fact, the ideal tensile strength of iron may be about 14.2 GPa along its weakest crystallographic direction of ferrite, because by stretching elastically, the bcc cell of ferrite at that stress transforms into austenite [36]. However, the strength of iron in its fcc form may approach the ideal estimate of 21 GPa.

CHAPTER 3

Iron-Carbon Equilibrium and Plain Carbon Steels

Abstract

The binary Fe-C system at ambient pressure offers at least three crystalline forms, i.e. ferrite, austenite and cementite. Simple permutation would suggest that there are seven possible phase equilibria (six binaries and a ternary) but if δ and α are distinguished then the total is nine. This assumes also that the magnetic transitions that occur in all of these phases are neglected. But the richness of the system increases further when precise atomic mechanisms are invoked dependant on whether the large and small atoms can move during the evolution of microstructure. We have the allotriomorphic and idiomorphic ferrite, where local equilibrium is maintained at the transformation front, and the pearlite which cleverly avoids the accumulation of carbon in the residual austenite. As the deviation from equilibrium increases, Widmanstätten ferrite sets in as a hybrid reaction where the change in crystal structure is achieved by a homogeneous deformation of the austenite, but at a rate controlled by the diffusion of carbon. A few remarkable engineering applications of these incredible microstructures are discussed.

3.1 IRON-CARBON EQUILIBRIUM PHASE DIAGRAM

A study of the constitution and structure of all steels and irons must first start with the iron-carbon equilibrium diagram. Many of the basic features of this system (Fig. 3.2) influence the behaviour of even the most complex of alloy steels. For example, the phases found in the simple binary Fe-C system persist in complex steels, but it is necessary to examine the effects alloying elements have on the formation and properties of these phases. The iron-carbon diagram provides a valuable foundation on which to build knowledge of both plain carbon and alloy steels in their immense variety.

It should first be pointed out that the normal equilibrium diagram really represents the metastable equilibrium between iron and iron carbide (Fe_3C , cementite). Cementite is metastable relative to the equilibrium between iron and graphite. Although graphite occurs extensively in cast irons (2–4 wt% C, Fig. 2.12g), it usually is difficult though not impossible to achieve this equilibrium in steels (0.03–1.5 wt% C) without annealing for a long time. Therefore, the metastable equilibrium between iron and iron carbide should be considered, because it is relevant to the behaviour of

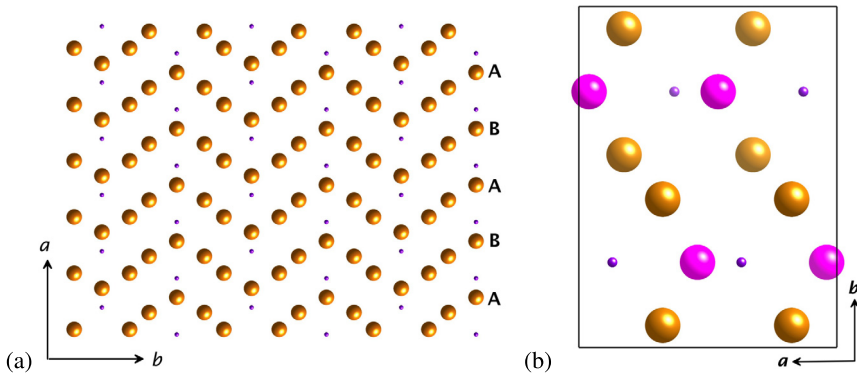


Figure 3.1 (a) A projection of the crystal structure of cementite with the z -axis normal to the plane of the diagram. The larger atoms are iron although the relative sizes are not to scale and the z -coordinates have been omitted for clarity. The puckered layers are stacked in ...ABAB... sequence, noting that the atoms in the 'B' layer have different z -coordinate to those in the 'A' layer. (b) The unit cell of cementite. Eight of the iron atoms are in symmetry related positions ($x = 0.175$, $y = 0.065$, $z = 0.333$) and another four (coloured crimson, $x = 0.04$, $y = 0.25$, $z = -0.167$) in different symmetry related locations. There are four carbon atoms ($x = -0.13$, $y = 0.25$, $z = 0.43$).

most steels in practice. The crystallography of cementite is interesting – the unit cell is primitive orthorhombic, space group $Pnma$, with lattice parameters $a = 0.50837$ nm, $b = 0.67475$ nm, and $c = 0.45165$ nm; the cell includes twelve iron atoms and four carbon atoms. It can be visualised as in Fig. 3.1 where pleated layers of iron atoms are stacked in ...ABAB... formation, rather as in the hcp crystal structure, with carbon atoms in the interstices between the layers [1].

The larger phase field of γ -iron (austenite) compared with that of α -iron (ferrite) reflects the much greater solubility of carbon in γ -iron, with a maximum value of just over 2 wt% at 1147°C when it is in equilibrium with liquid and cementite (E, Fig. 3.2). This relatively high solubility of carbon in γ -iron is of extreme importance in heat treatment, when solution treatment in the γ -region followed by rapid quenching to room temperature allows a supersaturated solid solution of carbon in iron to be formed. The α -iron phase field is severely restricted, with a maximum carbon solubility of 0.02 wt% at 727°C when the ferrite is in equilibrium with austenite or cementite ('P', Fig. 3.2), so over the carbon range encountered in steels from 0.05 to 1.5 wt%, α -iron is normally associated with iron carbide in one form or another. Similarly, the δ -phase field is very restricted

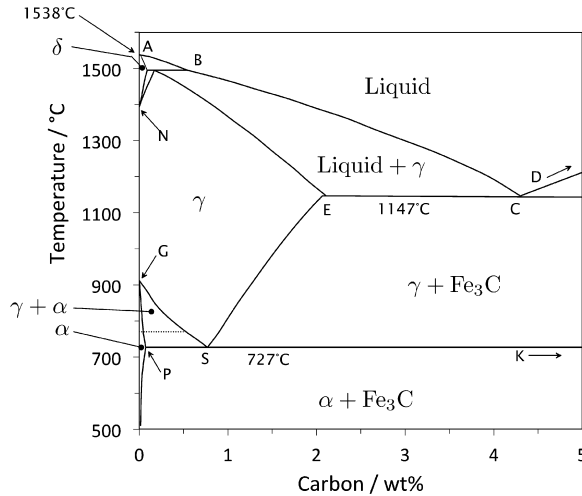


Figure 3.2 The iron-carbon diagram showing the equilibrium between the liquid, ferrite, austenite and cementite phases, adapted from [2]; the dotted line marks the Curie temperature of ferrite. The eutectoid composition is 0.76 wt%. Cementite has the composition ≈ 6.67 wt% carbon corresponding to 25 at%. However, the composition of cementite becomes iron-rich at high temperatures. As a consequence, ferrite precipitates within the cementite produced by the high-temperature eutectic reaction, on cooling to lower temperatures [3].

between 1390 and 1538°C and disappears completely when the carbon content reaches 0.5 wt% (B).

There are several temperatures or critical points in Fig. 3.2 which are important, both from the basic and from the practical point of view. Firstly, there is the Ae_1 temperature at which the eutectoid reaction occurs (P-S-K), which is 727°C in the binary diagram. Secondly, there is the Ae_3 temperature when α -iron transforms to γ -iron. For pure iron this occurs at 912°C, but the transformation temperature is progressively lowered along the line GS by the addition of carbon.¹ The third point is Ae_4 at which γ -iron transforms to δ -iron, 1390°C in pure iron, but this is raised as carbon is added. The Ae_2 point is the Curie temperature when ferritic iron changes from the ferro- to the paramagnetic condition or vice-versa. This temperature is 769°C for pure iron, but there is only a very slight change in crystal structure involved because ferromagnetic ferrite is body-centred tetragonal with the difference between the c and a lattice parameters being small enough to be neglected in most circumstances. The Ae_1 , Ae_3 and Ae_4 points are easily detected by thermal analysis or dilatometry during cooling

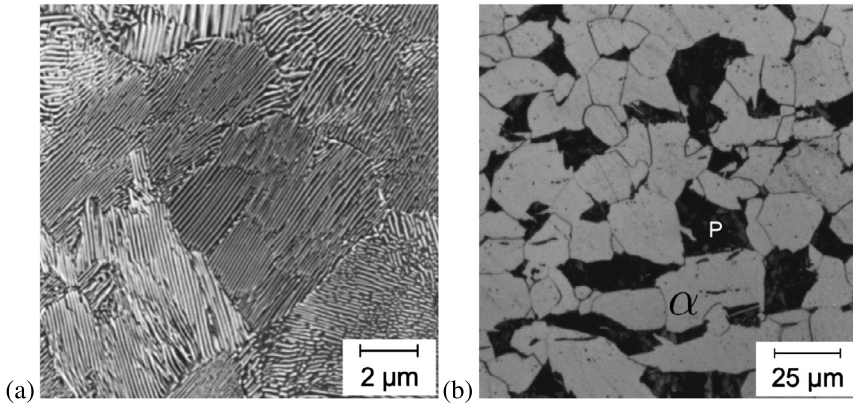


Figure 3.3 (a) Fully pearlitic 0.76 wt% C steel (courtesy S.S. Babu). The structure is often interpreted to consist of alternating lamellae of cementite and ferrite, but each colony is in fact a bi-crystal of the two interpenetrating phases in three dimensions [4]. (b) 0.2 wt% C steel containing a mixture of ferrite and pearlite (courtesy R.C. Cochrane). The pearlite (P) in this case is not resolved but etches relatively dark because of the high density of α/θ interfaces within each colony.

or heating experiments conducted at rates slow enough to achieve equilibrium. When equilibrium experiments are not conducted, two further values are associated with each equilibrium temperature, i.e., A_c for heating (chauffage) and A_r for cooling (refroidissement). It is emphasised that the A_c and A_r values will be sensitive to the rates of heating and cooling, as well as to the presence of alloying elements.

The great difference in carbon solubility between γ - and α -iron leads normally to the rejection of carbon as iron carbide at the boundaries of the γ -phase field. The transformation of $\gamma \rightarrow \alpha$ -iron occurs via a eutectoid reaction which plays a dominant role in heat treatment. The eutectoid temperature is 727°C while the eutectoid composition is about 0.76 wt% C(S) (Fig. 3.2). On cooling alloys containing less than 0.76 wt% C slowly, hypoeutectoid ferrite is formed from austenite in the range 912–727°C with enrichment of the residual austenite in carbon, until at 727°C the remaining austenite, now containing 0.76 wt% carbon transforms to pearlite, an apparently lamellar mixture of ferrite and iron carbide (cementite), Fig. 3.3a. In austenite with 0.76–2.06 wt% carbon, on cooling slowly in the temperature interval from 1147 to 727°C, cementite first forms progressively depleting the austenite in carbon, until at 727°C, the austenite contains 0.76 wt% carbon and transforms to pearlite.

Steels with less than 0.76 wt% carbon are thus hypo-eutectoid alloys with ferrite and pearlite as the prime constituents (Fig. 3.3b), the relative volume fractions being determined by the lever rule which states that as the carbon content is increased, the volume percentage of pearlite increases, until it is 100% at the eutectoid composition.

The three phases, ferrite, cementite and pearlite are thus the principal constituents of the microstructure of plain carbon steels, provided they have been subjected to relatively slow cooling rates to avoid the formation of transient phases. Consequently, it is important to examine the nucleation and growth of these phases, and to determine the factors which control their morphology.

3.2 AUSTENITE-FERRITE TRANSFORMATION

Under equilibrium conditions, pro-eutectoid ferrite will form in iron-carbon alloys containing up to 0.76 wt% carbon. The reaction occurs at 912°C in pure iron, but takes place between 912°C and 727°C in iron-carbon alloys. However, by supercooling the austenitic state to temperatures below the eutectoid temperature, ferrite can be formed in reasonable time periods down to temperatures as low as 600°C.² There are pronounced morphological changes as the transformation temperature is lowered, of a type that applies to both hypo- and hyper-eutectoid phases, although in each case there will be variations due to the precise crystallography of the phases involved. For example, the same principles apply to the formation of cementite from austenite, but it is not difficult to distinguish ferrite from cementite morphologically.

As a result of a survey of the behaviour of plain carbon steels, Dubé proposed an elegant classification of morphologies of ferrite which occur as the γ/α transformation temperature is lowered. Dubé recognised four well-defined morphologies based on optical microscopy, later extended by Aaronson³:

1. *Grain boundary allotriomorphs*: An allotriomorph has a shape which does not reflect its internal crystalline symmetry. This is because it tends to nucleate at the austenite grain surfaces, forming layers which follow the grain boundary contours (Fig. 3.4a, b). Furthermore, allotriomorphic ferrite is able to grow into all the austenite grains with which it has contact; its growth is not hindered by austenite grain boundaries. The layers may be constituted of several different crystals, the morphology arises because the austenite grain surfaces are good nucleation sites and

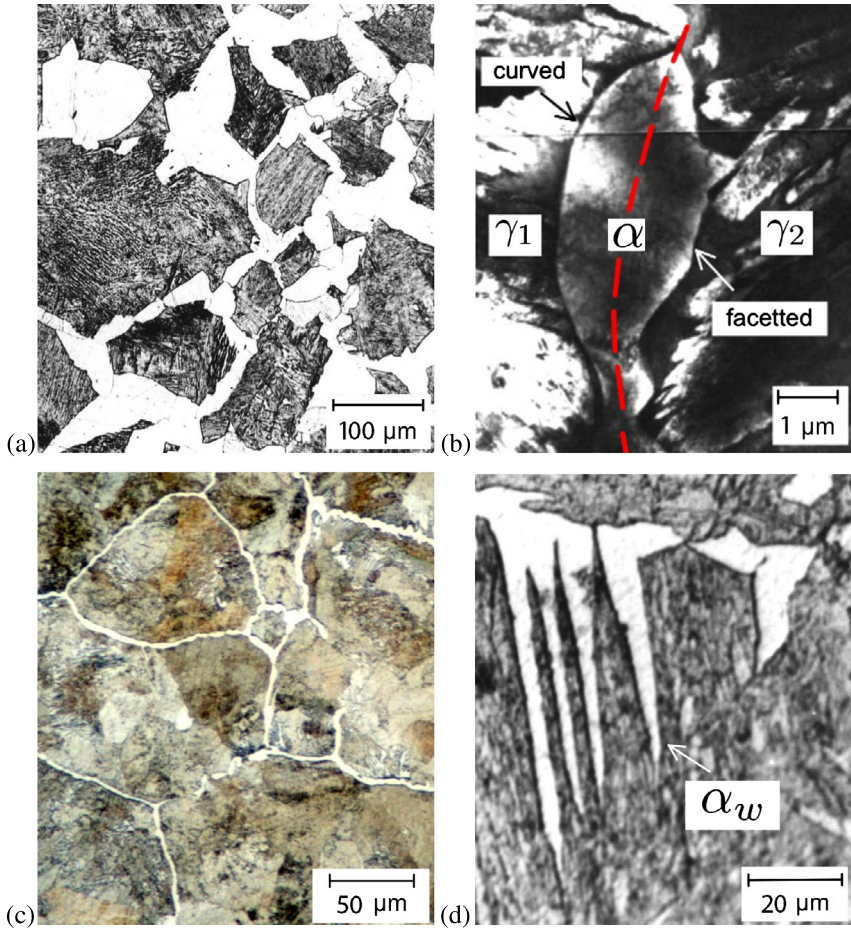


Figure 3.4 (a) Allotriomorphs of ferrite decorating prior austenite grain boundaries. (b) Transmission electron micrograph of ferrite allotriomorph at an austenite grain boundary between γ_1 and γ_2 . There is a crystallographically good match between α and γ_2 . The red line marks the prior austenite grain boundary, emphasising the fact that the ferrite grows into both of the γ -grains with which it has contact. (c) Allotriomorphs of cementite in a hypereutectoid steel (courtesy R.C. Cochrane). (d) Widmanstätten ferrite plates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this chapter.)

since diffusion along these boundaries is more rapid than within the volume of the grains. An allotriomorph is in contact with at least two of the austenite grains and will have a random orientation with one of them, but an orientation which is more coherent with the other. It may,

therefore, be crystallographically faceted on one side but with a curved boundary on the other side. If austenite grains are crystallographically textured, then the probability of ferrite developing a good-fit orientation relationship with all the austenite grains with which it is in contact at the nucleation stage increases. It also is possible to obtain cementite allotriomorphs in hyper-eutectoid steels as shown in Fig. 3.4c.

2. *Widmanstätten ferrite plates or laths*: These plates develop along well-defined planes of the austenite and are unable to grow across the austenite grain boundaries. Primary Widmanstätten ferrite grows directly from the austenite grain surfaces, whereas secondary Widmanstätten ferrite develops from allotriomorphs of ferrite already present in the microstructure (Fig. 3.4d).
3. *Intragranular idiomorphs*: These are equiaxed crystals which nucleate inside the austenite grains (Fig. 3.5), usually on non-metallic inclusions present in the steel. An idiomorph forms without contact with the austenite grain surfaces and has a shape which sometimes shows crystallographic facets.
4. *Intragranular plates*: These plates are similar to those growing from the grain boundaries, but they nucleate entirely within the austenite grains (Fig. 3.5).

Grain boundary allotriomorphs are the first morphology to appear over the whole range of composition and temperature. However, at the highest temperatures (above 800°C), they predominate by growing along the boundaries, and also into the grains to give a well-defined grain structure, generally referred to as equiaxed ferrite. The allotriomorphs nucleate having a reproducible orientation relationship such as the Kurdjumov-Sachs orientation with one austenite grain (γ_2 , Fig. 3.4b):

$$\begin{aligned}\{111\}_{\gamma_2} &\parallel \{110\}_{\alpha}, \\ \langle \bar{1}\bar{1}0 \rangle_{\gamma_2} &\parallel \langle \bar{1}\bar{1}1 \rangle_{\alpha}.\end{aligned}$$

But they also grow into the adjacent austenite grain (γ_1 , Fig. 3.4b) with which they normally should have a random orientation relationship. The disordered boundary responsible for this growth should migrate more readily at high temperatures because such interfaces contain a greater free volume relative to more coherent boundaries.

At lower transformation temperatures, the mobility of curved or random γ/α boundaries decreases, while the coherent interfaces become more dominant for two reasons, first that displacive transformations become kinetically favoured at low temperatures and secondly that such transforma-

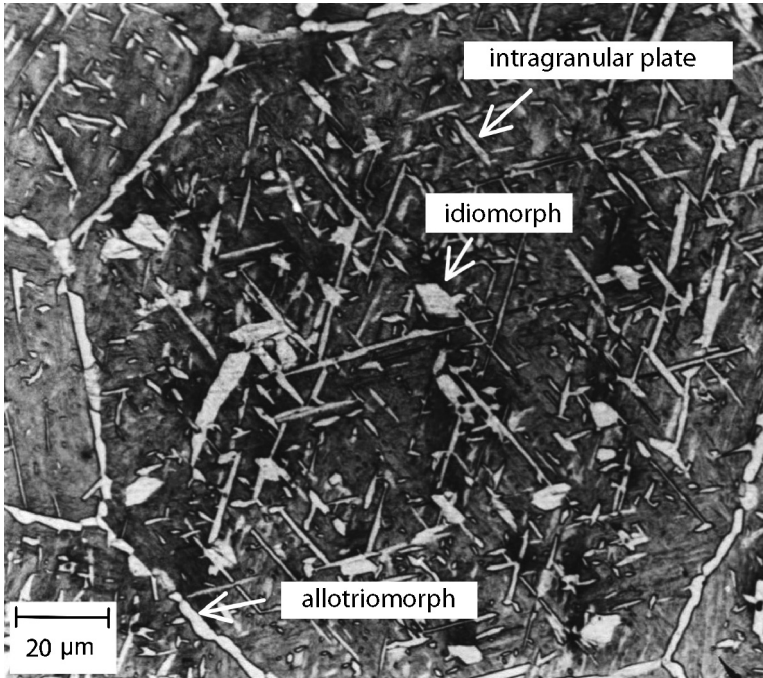


Figure 3.5 Intragranularly nucleated idiomorphic ferrite and Widmanstätten ferrite plates. Allotriomorphic ferrite layers decorate the austenite grain surfaces. Notice the very large austenite grains, which are necessary to permit intragranular nucleation to occur unhindered by transformation products originating at the austenite grain surfaces. Courtesy of Ashraf Ali.

tions require the interfaces to be relatively coherent so that they can move without diffusion (Chapter 5). For example, laths (narrow plates) of ferrite grow from protuberances on the grain boundary ferrite on the side of the coherent boundary, so the laths develop into austenite with which they have the Kurdjumov-Sachs type relationship. The laths can also grow from clean austenite grain boundaries, the net result being a structure which is normally referred to as primary Widmanstätten ferrite. This structure is encouraged by large austenite grain sizes which prevent the impingement of grain boundary ferrite by growth across grains, thus allowing Widmanstätten ferrite room to grow. If the carbon content is too high (>0.4 wt%), the pearlitic regions are sufficiently large to prevent ferrite laths growing. However, if the carbon content is below ≈ 0.2 wt%, impingement of allotriomorphs across γ -grains again minimises the growth of Widmanstätten

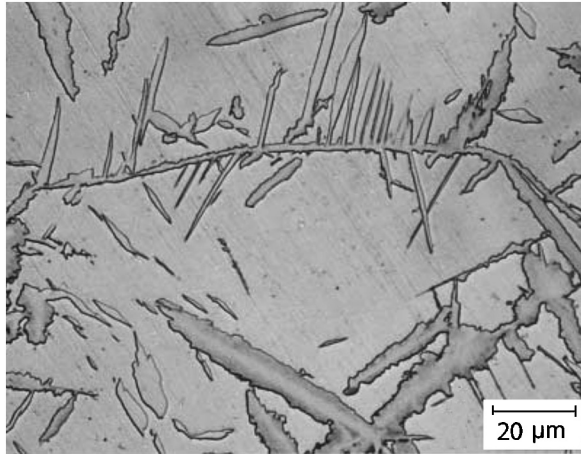


Figure 3.6 Cementite allotriomorphs and Widmanstätten cementite plates in austenite. After Zhang and Kelly [6], reproduced with the permission of Elsevier.

ferrite. But the most important factor is the temperature of growth of the ferrite, which is determined by the overall rate of cooling of the steel, or the temperature of isothermal transformation. An important structural feature found in Widmanstätten ferrite is that the formation of laths is accompanied by surface relief effects in the form of invariant-plane strains with a large shear component, reflecting a disciplined motion of atoms during transformation.

3.3 AUSTENITE-CEMENTITE TRANSFORMATION

The Dubé classification applies equally well to the various morphologies of cementite formed at progressively lower transformation temperatures. The initial development of grain boundary allotriomorphs is very similar to that of ferrite, and the growth of side plates or Widmanstätten cementite follows the same pattern (Figs 3.4, 3.6). Unlike ferrite, the austenite does not have a unique orientation relationship with the proeutectoid cementite even when experimental errors or scatter are taken into account. The orientation relationship with austenite tends to be one in which the close-packed planes in austenite, $\{111\}_\gamma$, are parallel to the most densely packed planes in the cementite, $\{103\}_\theta$ or $\{022\}_\theta$, and with directions in the latter which fit well with the close-packed direction in austenite being parallel,

as follows [6]:

$$\begin{array}{lll} \text{Pitsch} & [010]_{\theta} \parallel [10\bar{1}]_{\gamma} & (\bar{1}03)_{\theta} \parallel (\bar{1}\bar{1}\bar{1})_{\gamma} \\ \text{Zhang and Kelly} & [100]_{\theta} \parallel [121]_{\gamma} & (022)_{\theta} \parallel (\bar{1}\bar{1}\bar{1})_{\gamma} \end{array}$$

As in the case of ferrite, most of the Widmanstätten cementite plates originate from grain boundary allotriomorphs, but in the cementite reaction more side plates tend to nucleate also at twin boundaries in austenite.

3.4 KINETICS OF THE $\gamma \rightarrow \alpha$ TRANSFORMATION

The transformation of austenite in steels can be studied during continuous cooling using various physical measurements, e.g. dilatometry, thermal analysis, electrical resistivity, hot-stage microscopy etc., however, the results obtained are very sensitive to the cooling rate used. Davenport and Bain first introduced the isothermal transformation approach in combination with good microscopy to show that by studying the reaction isothermally at a series of temperatures, a characteristic time-temperature-transformation or TTT curve can be obtained for each particular steel. In their simplest form, these transformation curves have a well-defined ‘C’ shape (Fig. 3.7), where there is a temperature at which the reaction proceeds most rapidly, slowing down both at higher and at lower temperatures. That temperature, at which the reaction rate is fastest, is often referred to as the *nose* of the C-curve. This can be explained in general terms as follows. For a eutectoid steel transformed close to the eutectoid temperature, the degree of undercooling, ΔT , is low so the driving force for the transformation is small. However, as ΔT increases, so does the driving force making the reaction faster, until the maximum rate at the nose of the curve. Below this temperature, the driving force for the reaction continues to increase, but the reaction is now impeded by the slow diffusivity of the rate-controlling element, which in plain carbon steels may be carbon or iron, depending on the transformation conditions.

One of the simplest examples of a TTT curve is that for a steel that has a composition approximating the eutectoid carbon content. In Fig. 3.7 the beginning and end of transformation over a wide temperature range is plotted to produce two curves making up the diagram. When the carbon content of the steel is lowered, the ferrite reaction will also take place and this is represented by another curve which is frequently imposed on the

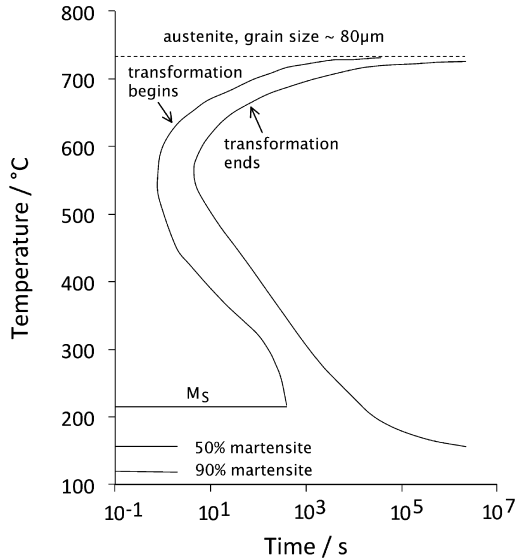


Figure 3.7 TTT diagram for a Fe-0.89C-0.29Mn wt% steel. The curves here represent overlapping information from the separate C-curves of reconstructive and displacive transformations because of the rapid transformation rate and the technique used (adapted from US Steel Co., *Atlas of Isothermal Diagrams*). The carbon concentration exceeds 0.76 wt% so some proeutectoid cementite is possible but not illustrated here.

same diagram, and which normally precedes the pearlite reaction. Similarly, the cementite reaction can be recorded in hyper-eutectoid steels. The TTT curve strictly applies to the nucleation and growth of one phase in austenite, but at the lower temperatures other constituents can appear, e.g. the displacive transformation products Widmanstätten ferrite, bainite, martensite. These have quite different characteristics to ferrite and pearlite that form by a reconstructive mechanism that entails the diffusion of all atoms. Martensite and bainite will be dealt with separately (Chapters 5 and 6).

3.4.1 Growth kinetics of ferrite

Both the lengthening and thickening of grain boundary allotriomorphs has been studied. The latter process is considered first, represented as the one-dimensional thickening of allotriomorphs into the austenite grains in a direction normal to the austenite grain boundaries, controlled by the diffusion of carbon in the austenite ahead of the interface.

Ferrite has a lower solubility ($c^{\alpha\gamma}$) for carbon when in equilibrium with austenite ($c^{\gamma\alpha}$), so carbon is partitioned into the latter phase during trans-

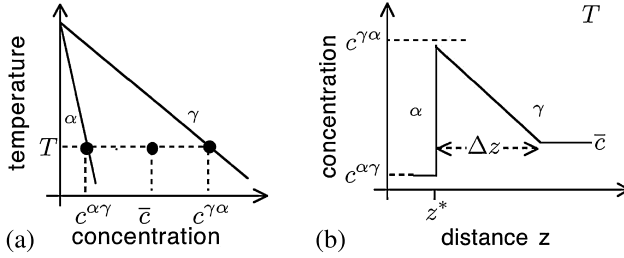


Figure 3.8 Phase diagram and its relationship to the concentration profile at the α/γ interface during diffusion-controlled growth.

formation. As the ferrite grows, so does the extent of its diffusion field in the austenite. This retards growth because the solute then has to diffuse over ever larger distances. As will be proven, the thickness of the ferrite increases with the square root of time, i.e. the growth rate slows down as time increases. Following Zener, it is assumed in the derivation that the concentration gradient in the matrix is constant, and that the far-field concentration $\bar{c}$ never changes (i.e. the matrix is semi-infinite normal to the advancing interface). This is to simplify the mathematics without losing any of the insight into the problem.

For isothermal transformation in a plain carbon steel, the concentrations at the interface are given by a tie-line of the phase diagram as shown in Fig. 3.8. The diffusion flux of solute from the interface must equal the rate at which solute is incorporated in the precipitate so that:

$$\underbrace{(c^{\gamma\alpha} - c^{\alpha\gamma}) \frac{\partial z^*}{\partial t}}_{\text{Rate solute partitioned}} = \underbrace{-D_C^\gamma \frac{\partial c}{\partial z}}_{\text{Diffusion flux from interface}} \simeq D_C^\gamma \frac{c^{\gamma\alpha} - \bar{c}}{\Delta z}, \quad (3.1)$$

where z is a coordinate normal to the interface with a value z^* at the position of the interface. Note that the concentration gradient is evaluated at the position of the interface ($z = z^*$).

A second equation can be derived by considering the overall conservation of mass:

$$(\bar{c} - c^{\alpha\gamma}) z^* = \frac{1}{2} (c^{\gamma\alpha} - \bar{c}) \Delta z.$$

On combining these expressions to eliminate Δz we get:

$$\frac{\partial z^*}{\partial t} = \frac{D_C^\gamma (c^{\gamma\alpha} - \bar{c})^2}{2 z^* (c^{\gamma\alpha} - c^{\alpha\gamma}) (\bar{c} - c^{\alpha\gamma})}. \quad (3.2)$$

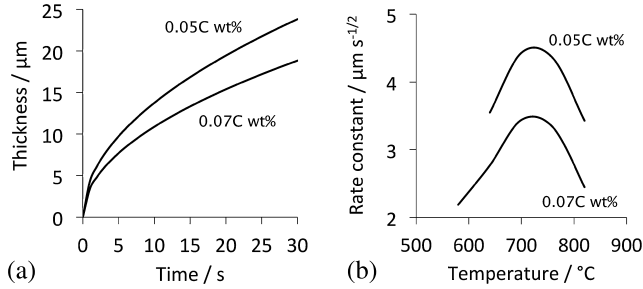


Figure 3.9 Kinetics of allotriomorphic ferrite growth in Fe-C alloys. (a) The allotriomorphic ferrite thickness increases parabolically with time. (b) Parabolic rate constant as a function of transformation temperature.

It follows that:

$$z^* = \sqrt{D_C^\gamma} \underbrace{\frac{(c^{\gamma\alpha} - \bar{c})}{[2(c^{\gamma\alpha} - c^{\alpha\gamma})(\bar{c} - c^{\alpha\gamma})]^{1/2}}}_{\text{parabolic rate constant}} \times \sqrt{t}. \quad (3.3)$$

Since the thickness of an allotriomorph increases parabolically with time (Fig. 3.9a), the growth rate decreases as the ferrite thickens. This is because increasing quantities of carbon are rejected into the austenite as the ferrite thickens, thus reducing the flux of carbon away from the transformation front because Δz increases. Equation (3.3) contains the term $c^{\gamma\alpha} - \bar{c}$ that in effect represents the driving force for transformation since growth ceases when the composition of the austenite is uniformly $c^{\gamma\alpha}$. Therefore, the growth rate in the Fe-0.07C wt% is slower than in the Fe-0.05C wt% steel. Fig. 3.9b illustrates the fact that the growth rate is maximum at an intermediate temperature because the driving force increases with undercooling whereas the diffusivity decreases as the temperature is reduced.

The approximations involved in this simple analysis designed to illustrate the essence of the problem are as follows:

- It is assumed that the far-field concentration $\bar{c}$ is unaffected by the growth of ferrite. This may well be true during the early stages of transformation, but eventually, the accumulation of solute in the austenite will lead to an increase in $\bar{c}$ towards $c^{\gamma\alpha}$. The rate of growth will then be less than predicted by Equation (3.2). Growth ceases when $\bar{c} = c^{\gamma\alpha}$.
- The concentration gradient in the austenite is not constant but decreases with distance ahead of the transformation front, mathematically according to an error function [7].

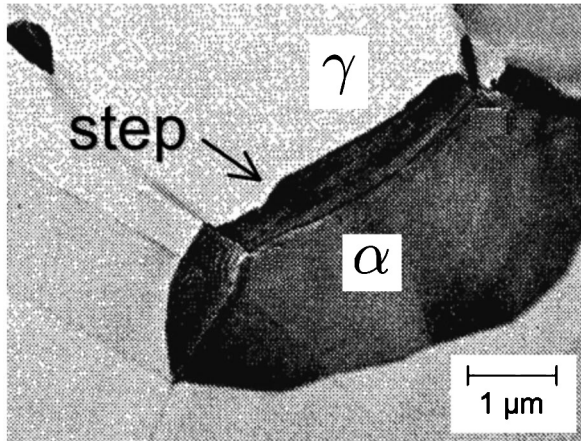


Figure 3.10 Allotriomorphic ferrite forming in austenite with planar and stepped interfaces in a low carbon alloy steel (Edmonds and Honeycombe). Photoemission electron micrograph.

- The diffusion coefficient of carbon in austenite is not constant, but increases dramatically with concentration [8,9].
- The shape of the ferrite may not strictly be in the form of a layer, in which case growth might involve diffusion in two or three dimensions [10].
- There is an implicit assumption that the growth of ferrite is diffusion controlled. Other factors can be rate limiting, for example, the transfer of atoms across the α/γ interface, which becomes of overwhelming importance at low transformation temperatures, typically below about 600°C.
- Fig. 3.10 shows that when the allotriomorphic ferrite has a good-fit orientation relationship with the parent austenite, the transformation proceeds by the translation of steps on an otherwise stationary interface. The parabolic growth rate model described here does not then apply. Although there is considerable theory for the diffusion-controlled motion of individual steps or trains of steps in binary systems [10], there is no method that predicts the height or frequency of steps. In other words, it is impossible at the moment to predict the kinetics of allotriomorphic ferrite growth by a ledge mechanism.

With the exception of the consequences of the step mechanism of growth, there are ways of dealing with all of the approximations listed above [7,10].

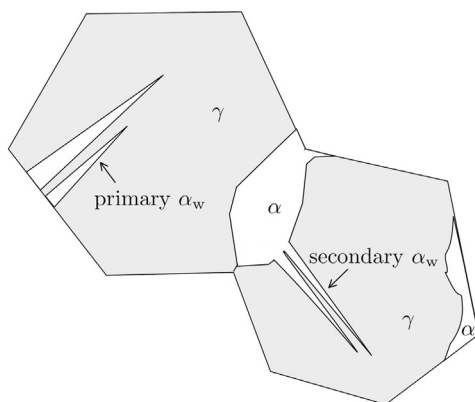


Figure 3.11 Morphology of primary and secondary Widmanstätten ferrite. See also Fig. 3.4d.

The theory described thus far deals with the thickening of allotriomorphs, with thickness varying with $t^{\frac{1}{2}}$ because of the progressive accumulation of solute ahead of the transformation front necessitating ever larger diffusion distances (Δz). The lengthening of an allotriomorph along an austenite grain boundary was initially thought to vary linearly with time because the carbon that is partitioned is left behind the advancing tip of the ferrite. However, measurements [11] show that the lengthening also occurs parabolically with time because the solute is in fact partitioned in two dimensions, both in the thickening and lengthening direction, leading to its accumulation on all transformation fronts. The aspect ratio, i.e. the thickness to length of an allotriomorph is about a third.

3.5 WIDMANSTÄTTEN FERRITE

3.5.1 Morphology

Primary Widmanstätten ferrite either grows directly from the austenite grain surfaces, whereas the secondary form develops from any allotriomorphic ferrite that may be present in the microstructure (Fig. 3.11). Widmanstätten ferrite can form at temperatures close to the A_{e3} temperature and hence can occur at very low driving forces; the undercooling needed amounts to a free energy change of only $\approx 50 \text{ J mol}^{-1}$. This is much less than required to sustain diffusionless transformation.

3.5.2 Shape change

The growth of a single plate of martensite is accompanied by an invariant-plane strain of the type illustrated in Fig. 3.12a. However, at the high temperatures (low undercoolings) at which Widmanstätten ferrite grows, the driving force is not sufficient to support the strain energy associated with a single plate. Widmanstätten ferrite formation therefore involves the simultaneous and adjacent cooperative-growth of two plates, which are crystallographic variants such that their shape deformations mutually accommodate (Fig. 3.12b). This has the effect of cancelling much of the strain energy [12].

It follows that what is seen as a single plate in an optical microscope is actually a combination of two variants, usually separated by a low-misorientation boundary (Fig. 3.12d, e). Widmanstätten ferrite has a habit plane which is close to $\{5\ 5\ 8\}_\gamma$ [13]. Hence, the two plates α_{w1} and α_{w2} which have different variants of this habit with the austenite, together form the thin-wedge shaped plate which is characteristic of Widmanstätten ferrite. A self-consistent set [14] describing the crystallography [13] of a plate of Widmanstätten ferrite has the habit plane normal:

$$\mathbf{p} = (0.5057\ 0.4523\ 0.7346)_\gamma$$

the orientation relationship being irrational but close to Kurdjumov-Sachs:

$$\begin{array}{ll} (1\ 0\ 1)_\alpha & \parallel (0.5916\ 0.5772\ 0.5628)_\gamma \\ [1\ 1\ \bar{1}]_\alpha & \parallel [0.6984\ \overline{0.7157}\ 0.0001]_\gamma \end{array}$$

and the average magnitude of the shape deformation and direction:

$$\begin{array}{l} m = 0.36 \\ \mathbf{d} = [0.8670\ 0.4143\ 0.2770]_\gamma. \end{array}$$

The displacement vector $\mathbf{d}$ does not lie precisely within the habit plane $\mathbf{p}$ because it describes both the shear and dilatational strains, the latter being directed normal to the habit plane (see Fig. 5.3).

Because Widmanstätten ferrite forms at low undercoolings, it is required thermodynamically that the carbon is redistributed during growth. α_w therefore always has a paraequilibrium carbon content and grows at a rate which is controlled by the diffusion of carbon in the austenite ahead of the plate-tip.⁴ For plates, diffusion-controlled growth can occur at a constant rate because solute is partitioned to the sides of the plate, whereas the

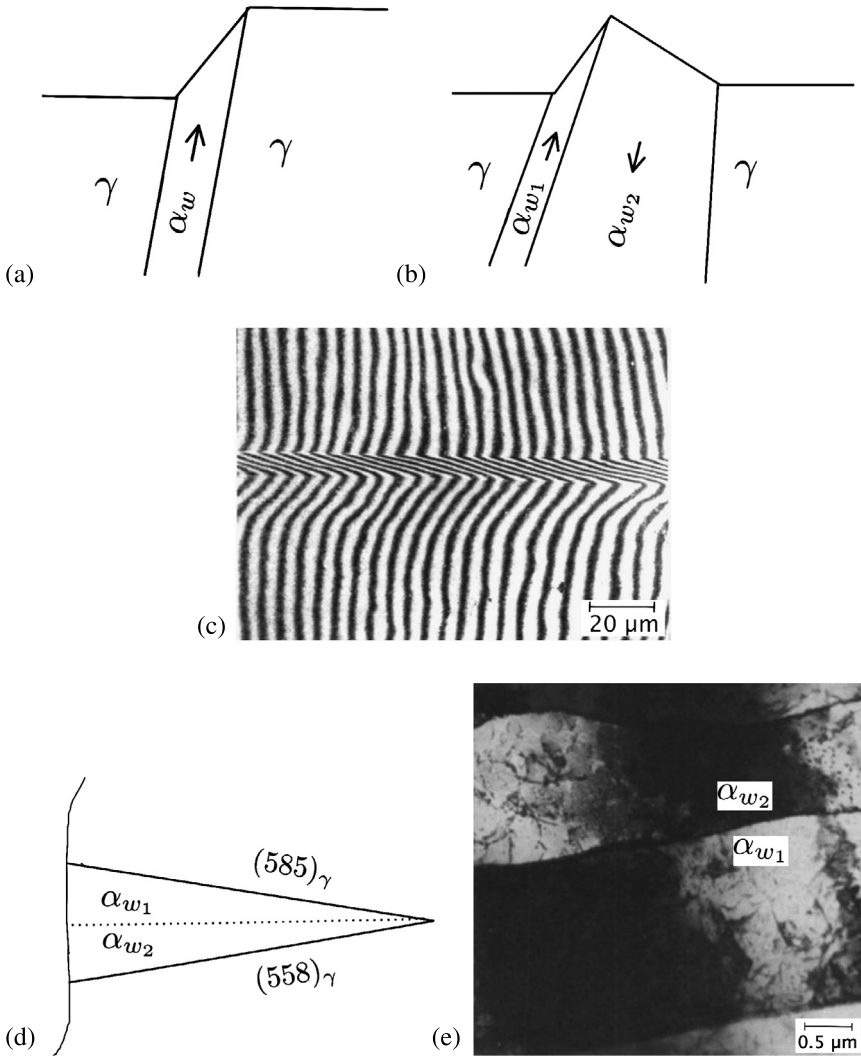


Figure 3.12 (a) A single invariant-plane strain shape deformation. (b) The combined effect of two mutually accommodating, back-to-back IPS deformations. (c) Tolansky interference micrograph showing the surface relief as illustrated schematically in (b). After Watson and McDougall [13], reproduced with permission of Elsevier. (d) The morphology of two plates, with different habit plane variants, growing together in a mutually accommodating manner. (e) Transmission electron micrograph showing two plates that appear in an optical microscope to be just one wedge-shaped plate. After Bhadeshia [12].

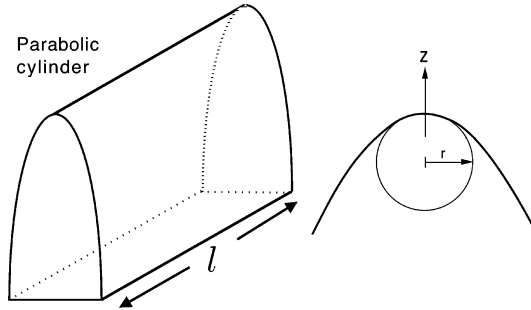


Figure 3.13 Widmanstätten ferrite plate represented as a parabolic cylinder, with tip radius r .

growing tip can advance into fresh austenite. Since the transformation is nevertheless, displacive, substitutional atoms do not partition and an atomic correspondence is maintained between the parent and product lattices.

3.5.3 Growth kinetics of Widmanstätten ferrite

For isothermal transformation during growth in which there is no partitioning of substitutional solutes, the growth rate is governed by the rate at which carbon diffuses ahead of the Widmanstätten ferrite plate tip. In the first approximation, the concentrations at the interface are given by a tie-line of the phase diagram after allowing for the strain energy due to the shape change, as in Equation (3.1).

The plate can be described as a parabolic cylinder in three dimensions (Fig. 3.13), a shape which is preserved as the plate lengthens. If it is assumed that the diffusion distance Δz is equal to the plate tip radius r (Fig. 3.13), then from Equation (3.1) it follows that the lengthening rate $v_l = \partial z^*/\partial t$ is given by

$$v_l \approx \frac{D_C^\gamma}{r} \frac{c^{\gamma\alpha} - \bar{c}}{c^{\gamma\alpha} - c^{\alpha\gamma}}. \quad (3.4)$$

This leads to the obvious difficulty that $v_l \rightarrow \infty$ as $r \rightarrow 0$, caused by the fact that the creation of additional interfacial area as the plate grows is neglected in the derivation. Given that the change in surface area per atom added to the plate is v_a/r , the corresponding increase in the free energy per atom due to the creation of additional interface is $\sigma v_a/r$ where σ is the interfacial energy per unit area and v_a is the volume per atom.⁵ Therefore, the net free

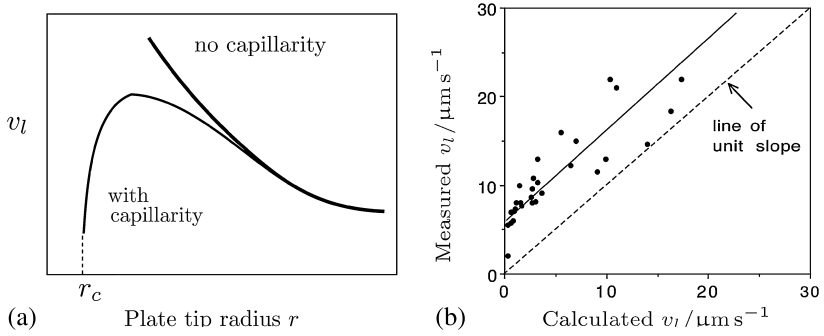


Figure 3.14 (a) Influence of interface curvature on plate lengthening rate. (b) Comparison of measured versus calculated lengthening rates.

energy change per atom, Δg_r , as the plate grows is

$$\Delta g_r = \Delta g_\infty - \frac{\sigma v_a}{r} \quad (3.5)$$

where Δg_∞ represents the free energy change per atom, driving the transformation in the absence of interface creation. At a critical radius r_c , $\Delta g_r = 0$ so that $\Delta g_\infty = \sigma v_a / r_c$ and $v_l = 0$. Equation (3.5) can therefore be written as

$$\Delta g_r = \frac{\sigma v_a}{r_c} - \frac{\sigma v_a}{r} \quad \text{or} \quad \frac{\Delta g_r}{\Delta g_\infty} = 1 - \frac{r_c}{r}. \quad (3.6)$$

The velocity scales with the driving force when the latter is small, so Equation (3.4) can be rewritten to account for the interface creation as follows:

$$v_l \approx \frac{D_C^\gamma}{r} \left(\frac{c^{\gamma\alpha} - \bar{c}}{c^{\gamma\alpha} - c^{\alpha\gamma}} \right) \times \left(1 - \frac{r_c}{r} \right). \quad (3.7)$$

The accounting for interfacial energy in this manner is known as the *capillarity effect* [15] which governs the equilibrium between a curved particle and the matrix. Fig. 3.14 shows how the lengthening rate now goes through a maximum, and it is often assumed that the plate picks a radius consistent with the maximum growth rate. This is approximately consistent with experimental measurements as shown in Fig. 3.14b [16].

3.5.4 Summary

The essential features of Widmansäthen ferrite all relate to the fact that it is a displacive transformation but controlled by the rate at which carbon diffuses, because while the substitutional lattice is deformed into the final structure, the interstitial carbon must partition in order for there to be

a sufficient free energy change to permit the ferrite to grow. An atomic correspondence is therefore maintained for substitutional atoms during the growth of Widmanstätten ferrite but it is a true example of paraequilibrium transformation.

To cope with the limited free energy available to drive the transformation at low undercoolings, the growth occurs by the simultaneous and cooperative formation of a pair of adjacent, self-accommodating plates of Widmanstätten ferrite. This is how the strain energy due to the shape change is mitigated, but the drawback is that two appropriate crystallographic variants must nucleate simultaneously, thus reducing the nucleation rate and leading to a relatively coarse microstructure that is not conducive to good toughness.

3.6 AUSTENITE-PEARLITE REACTION

Pearlite is probably the most familiar microstructural feature in the whole science of metallography (Fig. 3.15). It was discovered by Sorby some 130 years ago, who correctly assumed it to be a lamellar mixture of iron and iron carbide [17]. Pearlite is an extremely common constituent of a wide variety of steels, where it provides a substantial contribution to strength, so it is not surprising that this phase has received intensive study. Lamellar eutectoid structures of this type are widespread in metallurgy, and frequently, pearlite is used as a generic term to describe them. These structures have much in common with the cellular precipitation reactions. Both types of reaction occur by nucleation and growth (Fig. 3.15), and rely on the cooperative growth of phases during diffusional growth. Pearlite nuclei occur on austenite grain boundaries, but it is clear that they can also be associated with both pro-eutectoid ferrite and cementite. In commercial steels, pearlite nodules can nucleate on inclusions.

3.6.1 The morphology of pearlite

The idealised view of pearlite is a hemispherical nodule nucleated at an austenite grain boundary, and growing gradually into the austenite (Fig. 3.16). Apart from examining possible sites for nucleation, the following information is needed to understand the development of pearlite:

- (a) how the lamellae increase in number,
- (b) the crystallographic relationships between the phases,
- (c) the nature of the pearlite/austenite interface,
- (d) the rate-controlling process.

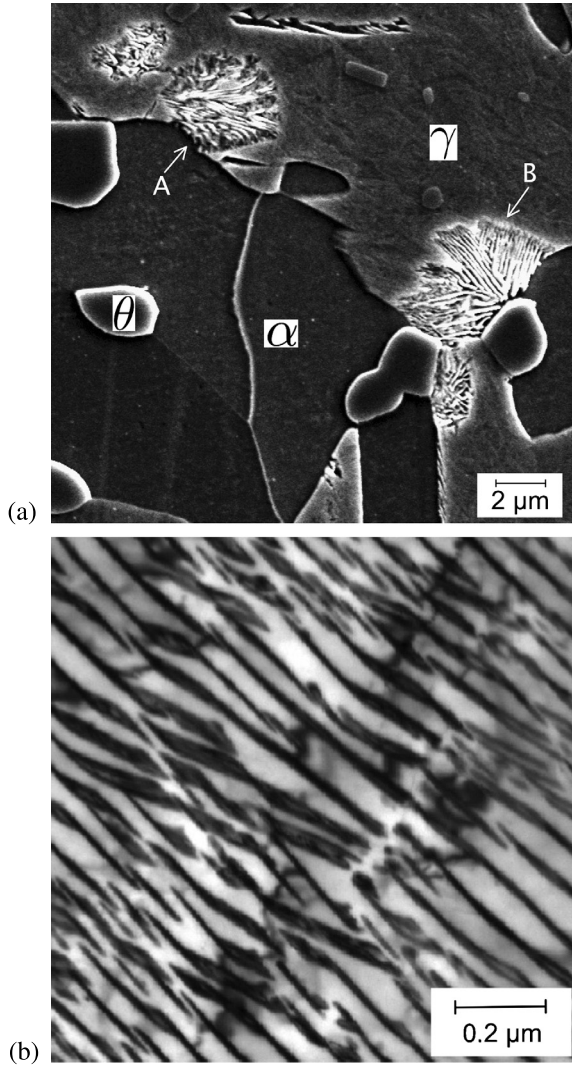


Figure 3.15 (a) The initiation of pearlite colonies during isothermal transformation from a mixture of austenite, ferrite and proeutectoid cementite (θ) (courtesy H.S. Hasan). The colony marked 'A' nucleates on ferrite whereas that marked 'B' on cementite. (b) Transmission electron micrograph of a colony of pearlite showing the intimate mixture of cementite and ferrite (courtesy S.S. Babu).

Not all these questions can yet be fully answered, but the essentials are established. Following the classical work of Mehl and colleagues, Hillert

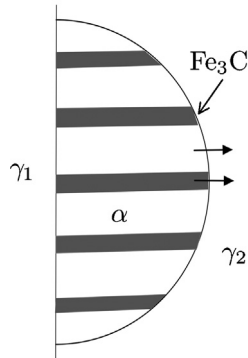


Figure 3.16 Idealised pearlite nodule at austenite grain boundary. In this scenario by Mehl and co-workers, the pearlite grows by sideways nucleation and edge-ways growth. Each layer has to nucleate separately in this model.

and co-workers were able to show that pearlite could be nucleated either by ferrite, or by cementite, depending on whether the steel was hypo- or hyper-eutectoid in composition. They came to this conclusion after observing lattice continuity between the ferrite in pearlite and pro-eutectoid ferrite, as well as between cementite in pearlite and hyper-eutectoid cementite.

Mehl and co-workers took the view that pearlite nodules formed by sideways nucleation and edge-ways growth (Fig. 3.16).⁶ In this way, the rapid increase in the number of lamellae in a nodule which occurred during growth could be explained, but Modin indicated that this could equally well result from the branching of lamellae during growth. Thin-foil electron microscopy work by Dippenaar and Honeycombe on Fe-13Mn-0.8C wt% steel allowed the examination of very small nodules at an early stage of growth in an austenitic matrix rendered stable by addition of manganese. This steel is hyper-eutectoid, so grain boundary cementite forms prior to nucleation of pearlite which frequently takes place on the cementite. This work showed conclusively the continuity of grain boundary and pearlitic cementite (Fig. 3.17), and also indicated that both the cementite and ferrite possessed unique orientations within a particular nodule. Fig. 3.17 also shows the beginning of branching of the Fe_3C lamella. However, in other nodules, sideways nucleation of laths of cementite and ferrite was observed. Nucleation of pearlite also took place on clean austenite boundaries. Hillert has shown that nucleation also occurs on ferrite, so all three types of site are effective, and the predominant sites will be deter-

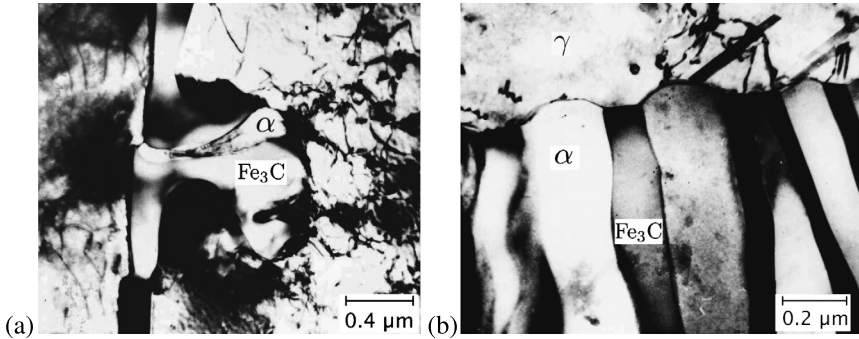


Figure 3.17 Fe-13Mn-0.8C wt% partly transformed at 600°C. Austenite is retained in conjunction with ferrite and cementite: (a) nucleation of a pearlite nodule on grain boundary cementite, (b) interface of nodule with austenite. Thin-foil electron micrographs (courtesy of Dippenaar).

mined primarily by the composition. Alternatively, as illustrated [Fig. 3.15a](#), when the reaction begins from a mixed microstructure containing ferrite, austenite and proeutectoid cementite, the pearlite can begin in contact with just ferrite (region ‘A’) or cementite (region ‘B’).

C.S. Smith first pointed out that the moving pearlite interface in contact with austenite was an incoherent high-energy interface growing into a grain with which the pearlitic ferrite and cementite had no orientation relationship. Therefore, the nodules which nucleated on pre-existing grain boundary cementite and ferrite would choose the higher energy interfaces across which the boundary phase had no orientation relationship with the adjacent austenite. Hillert and co-workers were able to show by suitable heat treatments that pearlite did nucleate in this way, while on the low-energy interfaces Widmanstätten growth of ferrite (or cementite) was usually observed. Electron microscopy observations have confirmed that the pearlite interface with austenite is an incoherent one. The level of incoherency depends also on the orientation of the normal to the interface plane; if there is significant orientation dependence of interfacial energy then the transformation front will translate by the movement of ledges (step mechanism) even if the motion periodically traverses different phases (i.e. α and θ) [19]. [Fig. 3.17b](#) shows a typical interface on a 13Mn-0.8C wt% steel, where the untransformed austenite has been retained at room temperature.

3.6.2 The crystallography of pearlite

In a typical pearlite nodule there are two interpenetrating single crystals of ferrite and of cementite, neither of which may be orientation related to the austenite grain in which they are growing. However, there is always a well-defined crystallographic orientation between the cementite and ferrite lamellae within a pearlite nodule. At least two different relationships have been identified between the cementite and ferrite that form a part of a pearlite colony, the most important being:

Pitsch/Petch relationship

$$\begin{aligned}(001)_\theta &\parallel \{\bar{5}2\bar{1}\}_\alpha, \\ (010)_\theta &2-3^\circ \text{ from } \langle 11\bar{3} \rangle_\alpha, \\ (100)_\theta &2-3^\circ \text{ from } \langle 131 \rangle_\alpha.\end{aligned}$$

Bagaryatski relationship

$$\begin{aligned}(001)_\theta &\parallel \{211\}_\alpha, \\ (010)_\theta &\parallel \langle \bar{1}\bar{1}\bar{1} \rangle_\alpha, \\ (100)_\theta &\parallel \langle 0\bar{1}1 \rangle_\alpha.\end{aligned}$$

The two relationships are found side by side in the same steel, and the frequency of each varies rather unpredictably. Thin-foil electron microscopy has shown that the pearlite nodules nucleating on clean austenite boundaries exhibit the Pitsch/Petch relationship. The pearlitic ferrite is related to the austenite grain γ_1 (Fig. 3.16) into which it is not growing. The relationship is always close to the Kurdjumov-Sachs relationship. Also the pearlitic cementite is related to austenite grain γ_1 , by a relationship found by Pitsch for Widmanstätten cementite in austenite. Both the pearlitic cementite and ferrite are unrelated to austenite grain γ_2 .

In contrast, the Bagaryatski relationship is found to hold for pearlite nodules nucleated on hyper-eutectoid cementite, usually formed at the austenite grain boundaries. In this case, the pearlitic cementite is related to austenite grain γ_1 by the Pitsch relationship for Widmanstätten cementite, while the pearlitic ferrite is not related to grain γ_1 . Clearly the grain boundary cementite shields the newly formed ferrite from any contact with γ_1 . It also follows that the grain boundary cementite and the pearlitic cementite are continuous, i.e. of the same orientation. Again, neither the pearlitic ferrite or cementite are related to austenite grain γ_2 .

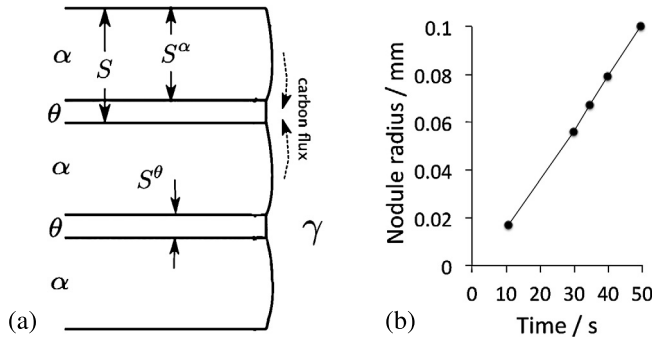


Figure 3.18 (a) Diffusion flux in the austenite parallel to the advancing interface. S is the interlamellar spacing. The thickness S^θ of the cementite relative to that of the ferrite (S^α) is determined by the mean carbon concentration of the steel. (b) The flux illustrated in (a) carries carbon that is partitioned into the austenite as the ferrite grows, to be absorbed by the cementite that grows simultaneously. There is therefore no change in the average composition of the austenite during pearlite growth in binary Fe-C alloys. As a consequence, the pearlite grows at a constant rate. The data are for a steel of approximately eutectoid composition transformed isothermally at 680°C in order to measure the maximum pearlite nodule size (adapted from Mehl and Hagel [22]).

It is, therefore, predicted that Pitsch/Petch-type colonies predominate as the true eutectoid composition is approached, whereas Bagaryatski-type colonies should prevail at higher carbon levels. It is likely that the Bagaryatski relationship will become more dominant in hypo-eutectoid steels as the carbon level is reduced, but this has not yet been conclusively proved.

3.6.3 Kinetics of pearlite growth

A colony of pearlite when viewed in three dimensions consists of an interpenetrating bicrystal of ferrite and cementite [4]. In planar sections the phases appear as lamellae which grow at a common front with the austenite. Cementite is rich in carbon whereas ferrite accommodates very little when it is in equilibrium with either cementite or austenite. It therefore is necessary for carbon to be redistributed at the transformation front. This can happen by diffusion in the austenite in a direction parallel to the transformation front (Fig. 3.18a). The growth must occur at a constant rate because in plain carbon steel, the average chemical composition of the pearlite is identical to that of the parent austenite. Some measurements are illustrated in Fig. 3.18b. The rate of growth is often measured by reacting a series of samples for increasing times at a particular temperature. As a result of measurements on polished and etched sections, the radius of the largest pearlite

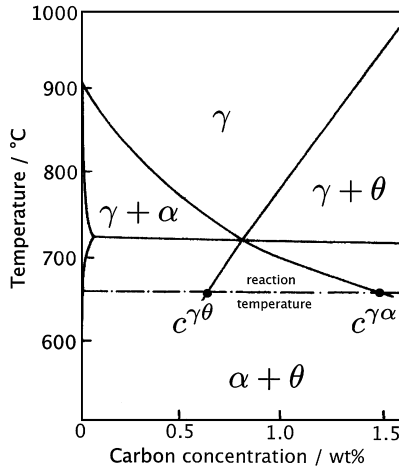


Figure 3.19 Phase diagram with extrapolated phase boundaries to identify the concentrations in the austenite which is in equilibrium with cementite or ferrite. The construction below the eutectoid temperature is known as the *Hultgren extrapolation* [20], the region where supercooled austenite can be transformed into a fully pearlitic structure with the ferrite and cementite maintaining a common transformation front with the austenite.

area, assumed to be a projection of the first nodule to nucleate, can be plotted against time. Normally a straight line is obtained, the slope of which is the growth rate ν_p (Fig. 3.18b).

It has been found that ν_p is structure insensitive, i.e. structural changes such as grain size, presence or absence of carbide particles have little effect. However, the rate is markedly dependent on temperature, specifically the degree of cooling ΔT below the eutectoid temperature T_E , and increases with increasing degree of undercooling until the nose of the TTT curve is reached. The growth rate is also strongly influenced by the concentration of alloying elements present although the detailed role of substitutional solutes will be discussed in the next Chapter 4.

Fig. 3.19 illustrates the Hultgren extrapolation [20]; if the average carbon content, $\bar{c}$, of the steel lies between $c^{\gamma\theta}$ and $c^{\gamma\alpha}$ then the steel is able to transform into a fully pearlitic microstructure even though $\bar{c}$ is not equal to the eutectoid concentration (0.76 wt% in Fe-C). The fraction of cementite within the pearlite will be less than normal if $\bar{c} < 0.76$ wt%, and vice versa. Within the Hultgren extrapolation, the austenite is supersaturated with respect to both cementite and ferrite; this is an essential condition for the development of cooperative growth with a common transformation

front with the austenite. When $\bar{\tau}$ does not fall into the region defined by the Hultgren extrapolation, the pearlite obtained is degenerate, i.e., the cementite lamellae are not continuous [21]. Such a degenerate structure does not strictly represent pearlite since cooperative growth does not occur. Indeed, the mechanical properties of “degenerate pearlite” reflect the lack of continuity of the cementite.

We shall assume that growth is controlled by the diffusion of carbon in the austenite ahead of the interface. The diffusion distance parallel to the interface can be approximated as aS where a is a constant and S is the interlamellar spacing. By analogy with Equation (3.1), it follows that the rate at which solute is absorbed by the cementite must equal the amount arriving there by diffusion, so that

$$v_P(c^\theta - c^{\gamma\theta}) = D_C^\gamma \frac{(c^{\gamma\alpha} - c^{\gamma\theta})}{aS} \quad (3.8)$$

where v_P is the speed of the growth front, D_C^γ is the diffusivity of carbon in austenite and the concentration terms are self-explanatory.

However, there is an additional process which consumes energy, the creation of cementite/ferrite interfaces within the pearlite colony. The minimum value of interlamellar spacing possible is a critical spacing $S_C = 2\sigma^{\alpha\theta}/\Delta G$ where $\sigma^{\alpha\theta}$ is the interfacial energy per unit area and ΔG is the magnitude of the driving force for transformation in Joules per unit volume.⁷ Growth ceases when $S = S_C$. To allow for the energy consumed in the process of interface creation, and following the procedure outlined in section 3.5.3, Equation (3.8) is modified by a term $(1 - [S_C/S])$ as follows:

$$v_P = \frac{D_C^\gamma}{aS} \frac{(c^{\gamma\alpha} - c^{\gamma\theta})}{(c^\theta - c^{\gamma\theta})} \left(1 - \frac{S_C}{S}\right). \quad (3.9)$$

With this modification, the velocity reaches a maximum as a function of the interlamellar spacing, Fig. 3.20. We now need to specify the value that S will adopt during growth, and one assumption is that the spacing will correspond to that consistent with the maximum growth rate, i.e. when $S = 2S_C$.

The kinetic theory predicts that the interlamellar spacing within pearlite should decrease with the transformation temperature, i.e. as the driving force for transformation increases, and this indeed is the case, Fig. 3.21.⁸

Suppose now that the diffusion of carbon during the growth of pearlite occurs by a combination of flux through the volume of the austenite, and through the interface itself, as illustrated in Fig. 3.22a. To account for both

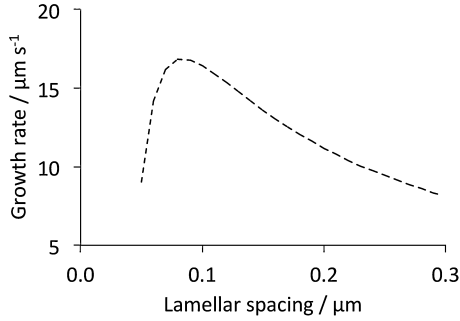


Figure 3.20 The growth rate of pearlite as a function of the interlamellar spacing. The calculations assume that $D_C^\gamma = 3.44 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, the concentration term in Equation (3.8) is 0.00824, $S_C = 0.042 \mu\text{m}$, $a = 1$.

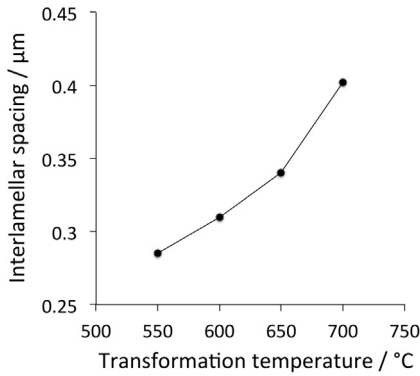


Figure 3.21 Interlamellar spacing in pearlite as a function of the undercooling below the eutectoid temperature. The steel composition is Fe-0.85C-0.67Mn-0.18Si wt%. Data from Ray and Mondal [23].

of these fluxes, Equation (3.8) is modified as follows [24]:

$$\nu_P(c^\theta - c^{\gamma\theta}) = D_{C,V}^\gamma \frac{(c^{\gamma\alpha} - c^{\gamma\theta})}{aS} + D_B\delta \frac{(c^{\gamma\alpha} - c^{\gamma\theta})}{a'S} \quad (3.10)$$

where $D_{C,V}^\gamma$ and D_B are the volume and boundary diffusion coefficients for carbon, δ is the thickness of the boundary (Fig. 3.22a), and a' is a constant. With certain assumptions about the constants, a solution of this then leads to the velocity equation [24,25]:

$$\nu_P = \left(\frac{c_e^{\gamma\alpha} - c_e^{\gamma\theta}}{c^\theta - c^\alpha} \right) \left(2D_{C,V}^\gamma + \frac{12D_B\delta}{S_i} \right) \frac{S_i}{S^\alpha S^\theta} \left(1 - \frac{S_c}{S_i} \right). \quad (3.11)$$

Fig. 3.22b illustrates how the flux through the interface dominates that through the volume of the austenite as the transformation temperature is

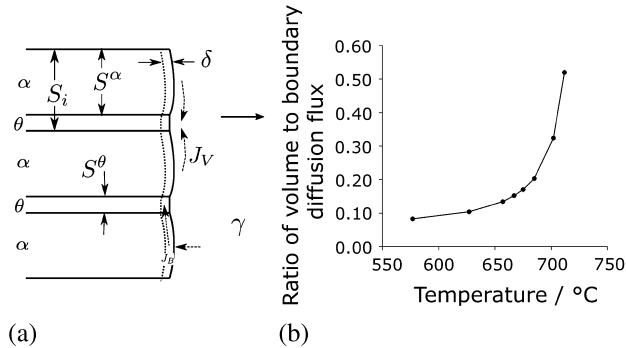


Figure 3.22 (a) Geometry of pearlite colony. The dashed arrows indicate the volume and interface diffusion processes. The thickness of the boundary is written δ and there is an additional flux through it, labelled J_B . (b) Relative contributions of volume and boundary diffusion fluxes during the formation of pearlite in Fe-0.8C wt% steel. Adapted from Pandit and Bhadeshia, [25].

reduced, because although the area through which the boundary flux occurs is much smaller than the volume of austenite available, $D_B \gg D_{C,V}^{\gamma}$ at low temperatures.

3.6.4 Divorced pearlite

The formation of lamellar pearlite, in which the α and θ grow cooperatively at a common front, can be suppressed entirely by ensuring that there is an appropriate distribution of proeutectoid cementite particles present in the austenite before it reaches the eutectoid temperature. During the cooling of such a mixture, a divorced eutectoid occurs in which the proeutectoid cementite particles absorb the carbon that is partitioned by ferrite at the advancing γ/α interface [26–28]. The cementite particles coarsen in the process of absorbing the partitioned carbon, as illustrated in Fig. 3.23a. The conditions necessary to achieve a divorced eutectoid are shown in Fig. 3.23b, with respect to the spacing between the proeutectoid cementite particles and the undercooling below the eutectoid temperature of the steel.

This kind of a heat treatment is particularly useful when strong steels need to be soft during the manufacturing process; a divorced eutectoid is the simplest way of achieving a soft steel that after shaping into the appropriate form, is hardened to a level consistent with its application. The process is routine in the manufacture of bearings that are extremely hard when they enter service but are required to be softer than about 250 HV during the fabrication stage [29].

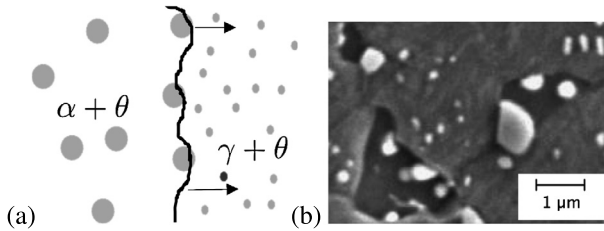


Figure 3.23 (a) The mechanism of the divorced eutectoid transformation of a mixture of austenite and fine cementite [26]. (b) The dark regions are ferrite containing coarse cementite (i.e. the divorced pearlite), surrounded by the austenite and fine proeutectoid cementite particles. The steel has a carbon concentration of about 1 wt% and yet does not transform into hard lamellar pearlite on cooling through the eutectoid temperature. Image courtesy of Danyi Luo.

3.6.5 Overall kinetics of pearlite formation

The formation of pearlite is a good example of a nucleation and growth process. The pearlite nucleates at preferred sites in the austenite and the nuclei then grow until they impinge on each other. The process is both time and temperature dependent, as it is controlled by the diffusivity of the relevant atoms. Johnson and Mehl first applied a detailed analysis of nucleation and growth to the pearlite reaction, which assumed that the fraction of austenite transformed (X) could be expressed in terms of a rate of nucleation $\dot{N}$ defined as the number of nuclei per unit volume of untransformed austenite formed per second, and a rate of growth of these nuclei ν_p , expressed as radial growth in cm s^{-1} . They made certain simplifying assumptions of which the most significant were:

1. Nucleation was regarded as a random event.
2. The rate of nucleation per unit volume, I_V , was assumed to be constant with time.
3. The rate of growth ν_p was, as is the case for pearlite (Fig. 3.18b), assumed to be constant with time.
4. The nuclei were regarded as spherical and in due course impinged on neighbouring spheres.

To model the development of volume fraction, as opposed to individual growth rates or nucleation rates, requires *impingement* between particles to be taken into account.

This is done using the extended volume concept of Kolmogorov, Johnson, Mehl and Avrami [30–34]. Referring to Fig. 3.24, suppose that two particles exist at time t ; a small interval Δt later, new regions marked blue

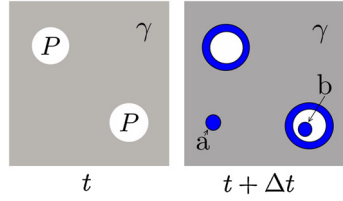


Figure 3.24 An illustration of the concept of extended volume. Two precipitate particles have nucleated together and grown to a finite size in the time t . New regions (blue) are formed as the original particles grow, but a & b are new particles, of which b has formed in a region which is already transformed. 'P' represents a pearlite nodule. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this chapter.)

in colour are formed assuming that they are able to grow unrestricted in extended space whether or not the region into which they grow is already transformed. However, only those components which lie in previously untransformed matrix can contribute to a change in the real volume of the product phase (P). Particles such as b cannot in fact nucleate in regions that already have transformed. To correct for this, the change in real volume is related to an *extended* volume change as follows:

$$dV^P = \left(1 - \frac{V^P}{V}\right) dV_e^P \quad (3.12)$$

where it is assumed that the microstructure develops at random. The subscript e refers to extended volume, V^P is the volume of pearlite and V is the total volume. Multiplying the change in extended volume by the probability of finding untransformed regions has the effect of excluding regions such as b , which clearly cannot contribute to the real change in volume of the product. For a random distribution of precipitated particles, this equation can easily be integrated to obtain the real volume fraction,

$$\frac{V^P}{V} = 1 - \exp\left\{-\frac{V_e^P}{V}\right\}. \quad (3.13)$$

The extended volume V_e^P is straightforward to calculate using nucleation and growth models and neglecting completely any impingement effects. Assuming that pearlite grows isotropically at a constant rate v_p with a nucleation rate per unit volume, I_V , the volume of a nodule nucleated at time $t = \tau$ (Fig. 3.25) is given by

$$v_\tau = \frac{4}{3}\pi v_p^3 (t - \tau)^3. \quad (3.14)$$

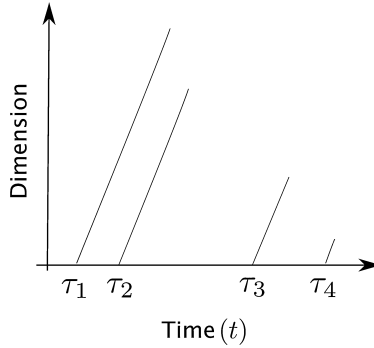


Figure 3.25 An illustration of the incubation time τ for each particle. For example, particle 1 does not exist before $t = \tau_1$.

The change in extended volume over the interval τ and $\tau + d\tau$ is

$$dV_e^P = \frac{4}{3}\pi v_p^3(t - \tau)^3 \times I_V \times V \times d\tau. \quad (3.15)$$

On substituting into Equation (3.13) and writing $\xi = V^P/V$, we get

$$\begin{aligned} dV^P &= \left(1 - \frac{V^P}{V}\right) \frac{4}{3}\pi v_p^3(t - \tau)^3 I_V V d\tau \\ \text{so that} \quad -\ln\{1 - \xi\} &= \frac{4}{3}\pi v_p^3 I_V \int_0^t (t - \tau)^3 d\tau \\ \text{and} \quad \xi &= 1 - \exp\{-\pi v_p^3 I_V t^4/3\} \end{aligned} \quad (3.16)$$

which is the equation derived by Johnson and Mehl for the evolution of the volume fraction of pearlite during isothermal transformation. Here ξ is the volume fraction of the growing phase can consume all of the austenite, but in general the volume fraction normalised by the equilibrium volume fraction.

This relationship gives a sigmoidal type of curve, when ξ is plotted against t for chosen values of I_V and v_p . A typical curve is shown in Fig. 3.26a for particular values of I_V and v_p . If X is plotted against $\sqrt[4]{(I_V v_p^3)t}$, a sigmoidal master curve is obtained which expresses the basic kinetic behaviour expected of a nucleation and growth process in a given alloy (Fig. 3.26b).

The assumptions made in reaching Equation (3.16) are not in fact necessary, for example that the nucleation sites are randomly distributed. Rate laws have been derived for grain surface, edge and corner nucleation, while

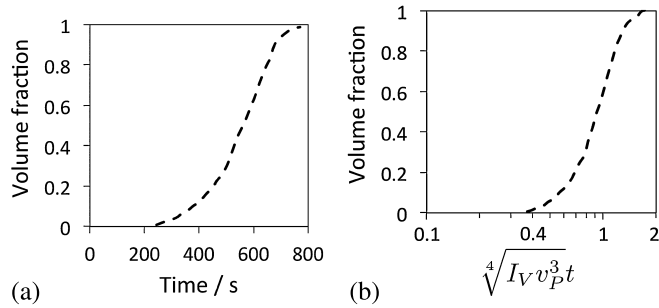


Figure 3.26 Kinetics of pearlite reaction: (a) calculated curve for specific $I_V = 1000 \text{ cm}^{-3} \text{ s}^{-1}$ and $v_P = 0.003 \text{ cm s}^{-1}$, (b) master reaction curve for general nucleation (after [22]).

accounting for *site saturation*, i.e. the complete exhaustion of particular kinds of initiation sites [35]. A thorough review of overall transformation theory is available in [7]. There are further complications if the steel contains substitutional solutes, which will be dealt with in Chapter 4.

3.6.6 The strength of pearlite

Pearlite on its own can be incredibly strong with commercial wires available routinely with strength in the range 3–4 GPa. The longest single-span suspension bridge in the world, the Akashi-Kaikyo Bridge, utilises exceptionally strong pearlitic ropes to suspend the deck. The bridge connects Kobe with Awaji Island and has a span of 1.9 km between the towers. There is enough steel wire used in the bridge to circle the earth seven times, with the bridge being designed to withstand an earthquake of Richter 8.5 magnitude. The bridge represents a magnificent triumph of engineering and steel in the form of pearlite (Fig. 3.27a). The strong wires do not use pearlite in its as-transformed condition, but in a cold-deformed state so that dislocation cell structures are created that reduce the spacing between structural barriers even more. The deformation is carried out by wire drawing in which case the cementite also experiences substantial plastic deformation.

The strength of pearlite would be expected to increase as the interlamellar spacing S is reduced. This is indeed the case as illustrated in Fig. 3.27b where the yield stress is plotted as a function of $S^{-\frac{1}{2}}$ consistent with the Hall-Petch relationship described in section 2.5. This would imply that macroscopic yielding propagates by the stimulation of dislocation sources in adjacent ferrite lamellae in the first instance, with the cementite beginning to deform as the material work hardens and strength incompatibilities

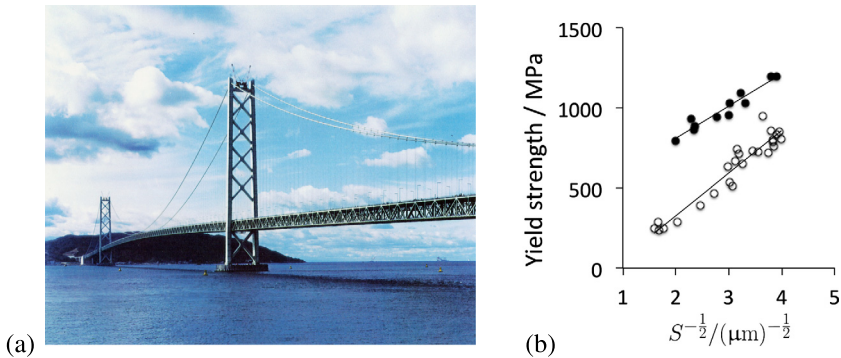


Figure 3.27 (a) The Akashi-Kaikyo Bridge in Japan, the longest single-span suspension bridge, which relies on huge cables made from pearlitic steel. Photograph courtesy of Professor Nobutaka Yurioka. (b) Strength of fully pearlitic eutectoid and hypereutectoid pearlite (filled circles) as a function of the interlamellar spacing. Adapted from [36].

between the different phases diminish. However, it is known that the data can also be represented equivalently using a S^{-1} relation [36] which might be consistent with a mechanism in which dislocation sources are required to be stimulated in the interfaces [37,38].

The situation is rather different for lower carbon steels, i.e. below 0.3 wt%, where pearlite occupies a substantially smaller volume of the microstructure. In these steels the yield stress is not markedly affected as the proportion of pearlite is increased, provided other factors, e.g. ferrite grain size, are kept constant. However, the tensile strength is quite sensitive to the pearlite content which is explained by the fact that there is a linear relationship between work hardening and the pearlite content (Fig. 3.28a), which arises because pearlite has a larger work hardening coefficient than the ferrite – it is generally the case in two-phase deformation theory that the composite work hardening coefficient is somewhere between that of the individual phases because of strain partitioning.

Pearlite has, however, an adverse effect on ductility and toughness of plain carbon steels. For example, the impact transition temperature (Chapter 11) is raised substantially as the carbon content is increased (Fig. 3.28b), and quantitative studies have shown that 1 wt% by volume of pearlite raises the transition temperature by about 2°C. The presence of pearlite in the microstructure provides sites of easy nucleation of cracks, particularly at the ferrite-cementite interfaces. However, as a crack can only propagate in ferrite a short distance before encountering another cementite lamella, energy is absorbed during propagation. The result is that there is a wide

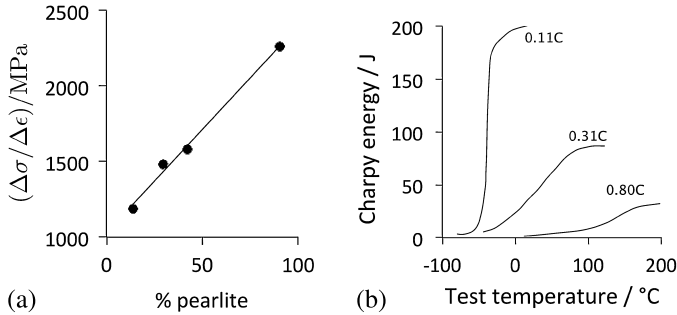


Figure 3.28 (a) Effect of pearlite content on work hardening rate expressed as the increase in strength for a unit increase in true strain. After [39]. (b) Effect of pearlite on toughness measured by Charpy impact transition temperature. After [39].

transition temperature range (Fig. 3.28b). In contrast, the low energy absorbed overall in impact tests on pearlitic structures arises from the fact that many crack nuclei can occur at the pearlitic interfaces which, together with the high work hardening rate, restricts plastic deformation in the vicinity of the crack. These naturally are mechanistic explanations, but a simple interpretation is that the strength increases with the volume fraction of pearlite, so the toughness is expected to decrease unless another mechanism is invoked whereby the entire structure is refined – how this can be achieved will be discussed in Chapter 10, suffice it to note here the ferrite-pearlite steels are incredibly successful.

3.7 FERRITE-PEARLITE STEELS

A very high proportion of the steels used in industry has a ferrite-pearlite structure. These include a wide range of plain carbon steels where alloying additions are primarily made for steel-making purposes, although they do have a strengthening role as well. For example, manganese is added to combine with sulphur, but it is also a strengthener, while manganese and silicon are deoxidisers and aluminium is used as a deoxidiser and as a grain refiner, and therefore a strengthener. Many low and medium alloy steels, e.g. those with nickel, give ferrite-pearlite structures, but here only essentially plain carbon steels will be dealt with.

Most plain carbon steels are not subject to heat treatment in the sense of quenching followed by tempering, but they are cooled at different rates to obtain a range of structures. Two important treatments are *normalising* and

annealing which have special, but not very precise, meanings when applied to steels.

Normalising

In the process of normalising the steel is reheated about 100°C above the A_{c3} temperature to form austenite, followed by air cooling through the phase transformation. This has as its object the refinement of the austenite and ferrite grain sizes, and the achievement of a relatively fine pearlite. It is often used after hot rolling, where a high finishing temperature can lead to a coarse microstructure.

The rate of cooling during normalising is dependent on the dimensions of the steel, but some control can be exerted by using forced air cooling.

Annealing

An annealed steel usually means one which has been austenitised at a fairly high temperature, followed by slow cooling, e.g. in a furnace. This results in transformation at the higher temperatures in the pearlite range, giving a coarse pearlite which provides good machinability.

There are other types of annealing which are commonly practiced, e.g. *isothermal annealing*, in which the steel is cooled to a high subcritical transformation temperature, where it is allowed to transform isothermally to ferrite and coarse pearlite. *Spheroidising annealing* is applied to higher carbon pearlitic steels to improve their machinability. The steel is held at a temperature just below A_{e1} for sufficient time for the cementite lamellae of the pearlite to spheroidise. This happens because it leads to a reduction in surface energy of the cementite–ferrite interfaces.

Ferrite–pearlite steels are essentially those which depend for their properties on the presence of carbon and manganese. The carbon content can be varied from 0.05–1.0 wt% while the manganese content is from 0.25 wt% up to about 1.7 wt%. Fig. 3.29 shows the effect on the tensile strength of varying the concentration of these two elements. It has also been possible by regression analysis to determine the relative contributions to the strength of the three important mechanisms: solid solution hardening; grain size and dispersion strengthening from lamellar pearlite. The results plotted are from steels in the normalised condition which ensures that the austenite grain sizes are roughly comparable. Variation of the carbon at constant manganese level causes a substantial increase in strength, which is almost entirely due to an increasing proportion of pearlite in the structure. The situation is rather more complex when manganese is varied at constant carbon content, as all

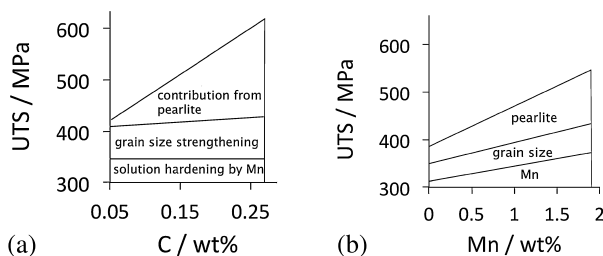


Figure 3.29 Factors contributing to the strength of C-Mn steels. Data from Irvine [40].

three strengthening mechanisms are influenced. Manganese causes the eutectoid composition to occur at lower carbon contents, and so increases the proportion of pearlite in the microstructure. Manganese is also an effective solid solution strengthener, and has a grain refining influence.

It is clear that carbon provides a very cheap way of strengthening normalised steels, but the extent to which this approach can be used depends on whether the steel is to be welded or not. Welding of higher carbon steels leads to the easier formation of cracks within the weld zone, so it usually is necessary to limit the carbon content to not greater than 0.2 wt%. In these circumstances, additional strength can then be obtained by solid solution hardening by raising the manganese content to between 1 and 1.5 wt%.

Alternatively, refinement of the grain size can be achieved by minor alloying additions such as aluminium, vanadium, titanium and niobium, in concentrations not normally exceeding 0.1 wt% (Chapter 9). Aluminium forms a stable dispersion of AlN particles, some of which remain in the austenite grain boundaries at high temperatures, and by pinning these boundaries prevent excessive grain growth. On transformation to ferrite and pearlite, grain sizes around 5–6 μm can be achieved with as little as 0.03 wt% AlN in the steel. Vanadium, titanium and niobium form very stable carbides, which also lock austenite grain boundaries, and thus allow much finer ferrite grain sizes to be achieved when the austenite transforms (Chapter 10).

Much plain carbon steel is used in the hot-finished condition, i.e. straight from hot rolling without subsequent cold rolling or heat treatment. This represents the cheapest form of steel, containing less than about 0.25 wt% carbon in order to avoid the formation of martensite in the heat-affected zone during welding. The most important group of hot-finished plain carbon steels contains less than 0.25 wt% carbon and is used in structural shapes such as plates, I-beams, angles, etc., in buildings, bridges, ships,

pressures vessels and storage tanks. Hot-rolled low carbon steel sheet is an important product and used extensively for fabrication where surface finish is not of prime importance. Cold rolling is used for finishing where better finish is required, and the additional strength from cold working is needed. However, for high quality sheet to be used in intricate pressing operations it is necessary to anneal the cold-worked steel to cause the ferrite to recrystallise. This is done below the A_{e1} temperature (subcritical annealing).

Carbon steels are also used extensively for closed die or drop forgings, usually containing 0.2–0.5 wt% carbon, and covering a very wide range of applications, e.g. shafts and gears. The other important field of application of plain carbon steels is as castings. Low carbon cast steels containing up to 0.25 wt% C are widely used for miscellaneous jobbing casting as reasonable strength and ductility levels are readily obtained. Yield strengths of 240 MPa and elongations of 30% are fairly typical for this type of steel.

3.8 SUMMARY

The carbon atom is small and hence it resides in the spaces between the iron atoms. The allotropic forms of iron are sufficiently different in their crystal structures to have vastly different capacities to dissolve carbon. This has major consequences when transformations occur, because carbon must then be partitioned into the phase where it is more soluble. The transformation front can then only move at a rate consistent with the diffusion of the excess carbon into the far-field, such that equilibrium is maintained at the boundary between the parent and product crystals. This basic principle leads to the kinetic theory for diffusion-controlled growth, in which the shape of the transformation product also matters. Thus, allotriomorphic ferrite grows at a diminishing rate, Widmanstätten ferrite at a constant rate because of its plate shape, and pearlite at a constant rate because there is no net partitioning of carbon. When nucleation and growth theory can be combined with a model for the impingement of particles that originated from different sites, it becomes possible to calculate time-temperature-transformation diagrams that depict the isothermal evolution of structure as a function of time.

There are many approximations involved in all of the theory presented in this Chapter, but the essence of the principles involved are clear and more elaborate theory is available [7,41].

Returning now to the iron-carbon equilibrium diagram, it is intriguing that the concentration scale does not extend beyond cementite which

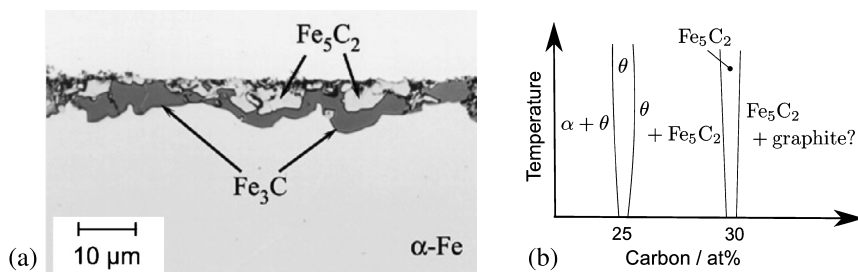


Figure 3.30 (a) Micrograph of carburised iron showing an initial layer of cementite followed by Hägg carbide. After Schneider and Inden [42], reproduced with the permission of Elsevier. (b) Schematic of the Fe-C equilibrium phase diagram for carbon concentrations beyond cementite.

contains 25 at.% or 6.67 wt% carbon. Fig. 3.30a shows that a carbide with even greater carbide concentration, known as Hägg carbide which has the formula Fe_5C_2 (≈ 30 at.% carbon) forms when the steel is exposed to a sufficient carbon activity during carburisation [42]. The Hägg carbide forms after cementite grows on the iron surface. Given the micrograph in Fig. 3.30a where all three phases (α , θ and Hägg) are present, it is possible suggest that the Fe-C equilibrium diagram beyond the concentration corresponding to 100% cementite, might appear as in Fig. 3.30b. There may in such a phase diagram be other carbides that have a concentration greater than cementite, for example, ϵ -carbide which has a hexagonal crystal structure so that the actual diagram might be more complex.

Hägg carbide in isolation is known to decompose into a mixture of cementite and carbon during appropriate high-temperature heat treatment [43]. It is assumed here that any pure carbon that is precipitated would be in the form of graphite.

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BACKNOTES

1. The A_{e1} temperature has the more generic meaning that it is the lowest temperature at which the α -ferrite and austenite can exist in equilibrium. Similarly, the A_{e3} temperature can be identified with the temperature at which a hypereutectoid steel becomes fully austenitic.
2. In fact, such ferrite can grow at even lower temperatures but at incredibly slow rates. In a Fe-0.3C-4.08Cr wt% steel it took 43 days at 478°C for the ferrite to grow by 0.1 μm [5].
3. Some of the micrographs presented in this chapter are not necessarily from plain carbon steels because without other austenite stabilising solutes, they transform so rapidly that it

become difficult to preserve the morphologies of individual precipitates in the partially transformed state.

4. The concept of a T_0 temperature, above which transformation without a composition change is not possible, will be introduced in Chapter 5.
5. Zener treated the tip of a plate to be a cylinder of radius r and length l . Since the change in area $dA = 2\pi l dr$ and the corresponding change in volume is $dV = 2\pi l r dr$, $dA/dV = 1/r$.
6. An excellent review of the evolution of pearlite theory is available [18].
7. If a cube with sides of length $2S$ contains three parallel lamellae (two of them forming the opposite faces of the cube) then the amount of α/θ interface is $4 \times 4S^2$ in a volume $8S^3$. Therefore, the interfacial area per unit volume is $S_V = 2/S$ so the energy due to interfaces is $2\sigma^{\alpha\theta}/S$. This equals ΔG when $S = S_C$ so that $S_C = 2\sigma^{\alpha\theta}/\Delta G$.
8. At the eutectoid temperature T_E , $\Delta G = 0$ so that ΔH , the enthalpy change is equal to $T_E \Delta S$ where ΔS is the entropy of transformation, assumed to be constant. Therefore, as an approximation, $\Delta G = T_E \Delta S - T \Delta S$, i.e., ΔG is proportion to the undercooling $T_E - T$.

CHAPTER 4

Solutes that Substitute for Iron

Abstract

If the wealth of structures available in the binary Fe-C is impressive, the addition of substitutional solutes creates a breathtaking variety of phases and structures, a seemingly endless palette that makes it feasible to custom design alloys of iron. The substitutional solutes influence the thermodynamics of all transformations, but have the most profound effect when they are required to diffuse. While all this is terribly useful, the complexity of the theory necessary to deal with multicomponent steels also increases, ameliorated by the availability of modern computer programs and databases. The understanding necessary to deal with such complexity is introduced so that the reader can make an intelligent use of the mathematical models that are implemented in the software.

4.1 GENERAL PRINCIPLES

The term *alloying elements* in the context of steels is often used to denote substitutional solutes, which can and do dramatically influence the structure and properties of steels. Indeed, they are responsible for the incredible versatility and utility of steels. The general effects of substitutional solutes are summarised in Fig. 4.1 and will be discussed in context throughout this Chapter. The solutes affect the relative free energies of the relevant phases, a thermodynamic effect that applies to all of the phase transformations irrespective of the detailed atomic mechanisms of transformation. New phases frequently appear, for example ϵ -iron, intermetallic compounds such as Laves phase, carbides, nitrides and oxides that are rich in substitutional solutes and an array of transition phases such as glassy precipitates. Some of these phases may be confined to the surface of the steel.

The second effect is kinetic and tends to be more complex because it is dependent also on the atomic mechanisms involved in any phase transformation. For example, when the alloying elements partition between the phases, there is a reduction in rate consistent with the need to diffuse substitutional solutes during the course of any phase change. However, this effect naturally is confined to reconstructive transformations because there is no substitutional atom partitioning in the case of any of the displacive reactions where the change in crystal structure is achieved by a homogeneous deformation of the parent austenite, into Widmanstätten ferrite, bainite or martensite. The consequence of atomic mechanisms is vividly

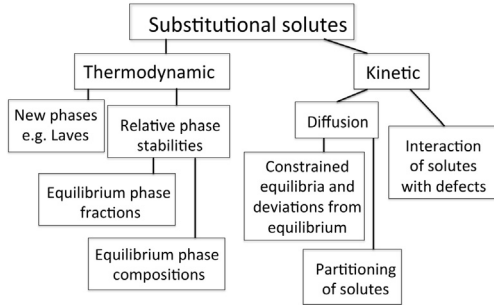


Figure 4.1 The variety of ways in which substitutional solutes can affect phase transformations and phase stabilities in steels.

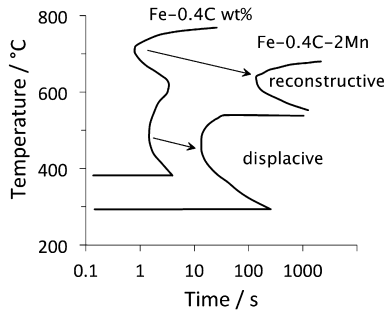


Figure 4.2 TTT diagrams for two steels, one of which contains manganese. Notice that the time scale is logarithmic so the effect of the Mn on the displacive transformation is much smaller than on the reconstructive reactions.

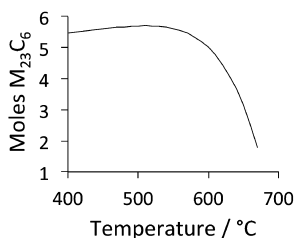
illustrated in TTT diagrams, which consist essentially of two C-curves, the one at higher temperatures representing reconstructive and that at temperatures below about 600°C, the displacive reactions. The change in kinetics on adding an element such as manganese is much larger for reconstructive transformations due to the partitioning of manganese between the parent and product phases, whereas the thermodynamic effect that is common to all transformations has a smaller consequence on displacive transformation, Fig. 4.2.

4.2 ALLOYING ELEMENTS: γ AND α PHASE FIELDS

While it would be impossible to include a comprehensive discussion of the thermodynamic effects of substitutional solutes, it is possible to describe some useful generic concepts that are helpful in classifying their roles,

Table 4.1 Calculated equilibrium phase data for a multicomponent steel at 400°C. 'M' in $M_{23}C_6$ stands for metal atoms

Phase	Moles of phase per 100 kg	Atomic percent					
		C	Si	Mn	Ni	Mo	Cr
α	1517	0.0006	0.59	0.02	0.01	0.00	0.03
Cementite	342	25.00	0.00	1.77	0.04	0.00	7.83
$M_{23}C_6$	5.46	20.69	0.00	0.03	0.52	9.51	0.13

**Figure 4.3** Calculated change in the number of moles in 100 kg of steel, of $M_{23}C_6$ that is in equilibrium with α and cementite, as a function of temperature.

beginning with the consequences on the binary iron–carbon equilibrium diagram.

Commercial alloys of iron are almost never simple binary or ternary mixtures because there are specific additions made in order to achieve the combination of properties required for specific applications; a typical steel will contain ten or more deliberate additions of solutes at concentrations ranging from parts per million to a few weight percent. It is necessary therefore to deal with multicomponent systems and fortunately, it is possible now to calculate with some confidence, multicomponent phase diagrams on a routine basis. Such diagrams may not be as easily visualised as their binary or ternary counterparts, but multicomponent phase diagrams carry the same basic information, i.e., phase fractions and phase compositions as a function of chemical composition, temperature and pressure. Such data can easily be tabulated and selectively plotted instead of struggling with multi-dimensional plots or their projections into three dimensions. Consider, for example, a steel of the following chemical composition:

Fe-1.04C-0.25Si-0.35Mn-0.125Ni-0.05Mo-1.45Cr wt%.

A multicomponent, multiphase diagram calculation yields the data listed in Table 4.1 and Fig. 4.3 is an example of the selective plot where the amount of the carbide $M_{23}C_6$ that is in equilibrium with ferrite and ce-

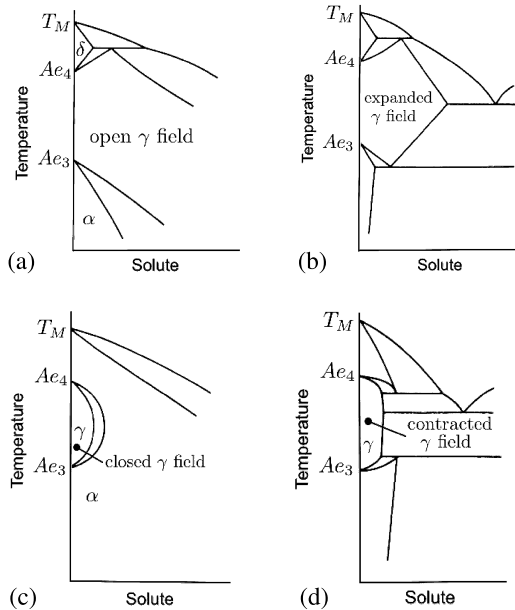


Figure 4.4 Classification of iron alloy phase diagrams: (a) open γ -field; (b) expanded γ -field; (c) closed γ -field; (d) contracted γ -field. After Wever [1].

mentite is plotted as a function of temperature.¹ The plot may need to be supplemented by others that show its chemical composition as a function of temperature, and there may be several other similar plots for the variety of phases present.

Having described the complexity of multicomponent steels, it nevertheless is useful to look at certain simplifications of the role of alloying elements on the relative stabilities of austenite and ferrite, which after all, are the dominant phases in most steels. Wever pointed out that iron/substitutional-solute binary equilibrium systems fall into four main categories (Fig. 4.4): open and closed γ -field systems, and expanded and contracted γ -field systems. This approach indicates that alloying elements can influence the equilibrium diagram in two ways:

- (a) By expanding the γ -field, and encouraging the formation of austenite over wider compositional limits. These elements are called γ -stabilisers.
- (b) By contracting the γ -field, and encouraging the formation of ferrite over wider compositional limits. These elements are called α -stabilisers.

The form of the diagram depends to some degree on the electronic structure of the alloying elements which is reflected in their relative positions in the periodic classification.

Class 1: Open γ -field To this group belongs the important steel alloying elements manganese and nickel, as well as cobalt and the exotic metals ruthenium, rhodium, palladium, osmium, iridium and platinum. Both nickel and manganese, if added in sufficiently high concentration, completely eliminate the bcc α -iron phase and replace it, down to room temperature, with the γ -phase. So nickel and manganese depress the phase transformation from γ to α to lower temperatures (Fig. 4.4a), i.e. both A_{e1} and A_{e3} are lowered. It also is easier to obtain metastable austenite by quenching from the γ -region to room temperature, consequently nickel and manganese are useful elements in the formulation of austenitic steels (Chapter 11). Concentrations of nickel or manganese in austenitic steels can be as large as 20 wt%; commercial manganese rich alloys of this kind have the peculiar characteristic that there is intense mechanical twinning during plastic deformation at ambient temperature, leading to much increased uniform elongation; these particular alloys, known as the TWIP steels, are discussed in Chapter 10. It should be noted, however, that both the manganese and nickel rich alloys have other alloying elements that also play a role in determining the phase stabilities.

Class 2: Expanded γ -field Carbon and nitrogen are the most important elements in this group. The γ -phase field is expanded, but its range of existence is cut short by compound formation (Fig. 4.4b). Copper, zinc and gold have a similar influence. The expansion of the γ -field by carbon, and nitrogen, underlies the whole of the heat treatment of steels, by allowing the formation of a homogeneous solid solution (austenite) containing up to 2.0 wt% of carbon or 2.8 wt% of nitrogen.

Class 3: Closed γ -field Many elements restrict the formation of γ -iron, causing the γ -area of the diagram to contract to a small area referred to as the gamma loop (Fig. 4.4c). This means that the relevant elements are encouraging the formation of bcc iron (ferrite), and one result is that the δ - and α -phase fields become continuous. Alloys in which this has taken place are, therefore, not amenable to the normal heat treatments involving cooling through the γ/α -phase transformation. Silicon, aluminium, beryllium and phosphorus fall into this category, together with the strong carbide-forming elements, titanium, vanadium, molybdenum and chromium. It

sometimes is useful to avoid austenite altogether. A coarse ferrite grain structure is exploited in steels which have to be magnetically soft for applications in electrical transformers. The δ -ferrite grains form at temperatures close to melting and hence are coarse. By adding 4 wt% Si, austenite is avoided enabling the grains to be retained at room temperature.

Class 4: Contracted γ -field Boron is the most significant element of this group, together with the carbide-forming elements tantalum, niobium and zirconium. The γ -loop is strongly contracted, but is accompanied by compound formation (Fig. 4.4d).

The overall behaviour can be approximated in thermodynamic terms along the lines developed by Zener [2].

When α and γ are in equilibrium, the chemical potential μ_i of each element is identical in both phases²:

$$\mu_i^\alpha = \mu_i^\gamma \quad \text{for all } i. \quad (4.1)$$

The chemical potential is expanded as $\mu_i = \mu_i^\circ + RT \ln\{a_i\}$, where i represents a particular element, μ_i° represents the free energy per mole of the pure component i in the structure of the phase concerned and a_i is the activity of i and may be approximated by the concentration c_i for dilute solutions. Therefore,

$$\begin{aligned} \mu_i^{\circ,\alpha} + RT \ln\{c_i^\alpha\} &= \mu_i^{\circ,\gamma} + RT \ln\{c_i^\gamma\}, \\ \frac{c_i^\alpha}{c_i^\gamma} &= \exp\left\{\frac{\mu_i^{\circ,\gamma} - \mu_i^{\circ,\alpha}}{RT}\right\}, \end{aligned}$$

$$\begin{aligned} \text{for ferrite formers,} \quad & \mu_i^{\circ,\alpha} < \mu_i^{\circ,\gamma} & \Delta\mu_i^\circ + ve, \\ \text{for austenite formers,} \quad & \mu_i^{\circ,\alpha} > \mu_i^{\circ,\gamma} & \Delta\mu_i^\circ - ve. \end{aligned}$$

In the simple treatment two fundamentally different types of equilibrium diagrams are obtained where the phase boundaries are represented by similar thermodynamic equations, but, depending on whether ΔH is positive or negative, are mirror images of each other (Fig. 4.5). In the $\Delta\mu_i^\circ$ negative case the γ -field is unlimited, while in the $\Delta\mu_i^\circ$ positive case, the γ -loop is introduced. $\Delta\mu_i^\circ$ will vary widely from element to element. In Fig. 4.6 histograms illustrate the relative strengths of alloying elements in terms of ΔH_i ,³ which at zero Kelvin will relate to $\Delta\mu_i^\circ$. The ferrite formers are listed in (a) and the austenitic formers in (b). Apart from these general considerations, any solute or combination of solutes that increase the free energy of austenite relative to that of ferrite will stabilise the latter phase

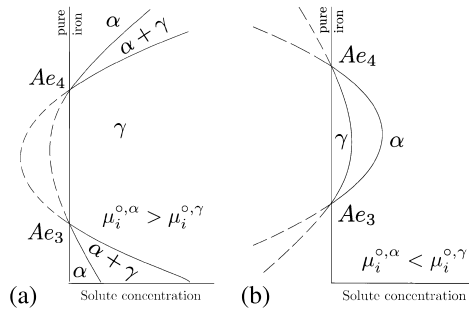


Figure 4.5 Two basic phase diagrams: (a) γ favoured; (b) α favoured (after Zener [2]).

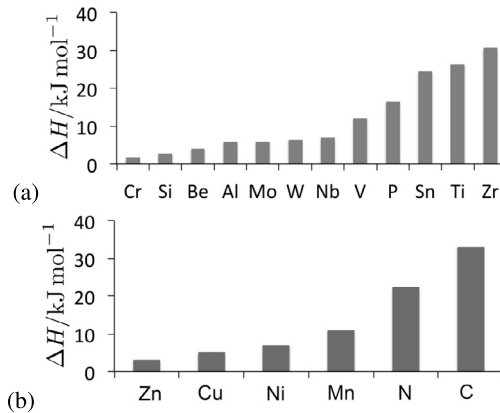


Figure 4.6 Relative potency of alloying elements as: (a) ferrite formers; (b) austenite formers (after Andrews [4]).

and accelerate the $\gamma \rightarrow \alpha$ transformation, as illustrated in Fig. 4.7. Elements such as silicon (Co, Al) therefore accelerate transformation whereas Mn, Ni and Cr are seen to retard transformation.

4.3 DISTRIBUTION OF ALLOYING ELEMENTS IN STEELS

The discussion in section 4.2 focuses on how substitutional alloying influences the relative stabilities of austenite and ferrite, in binary mixtures. The general trends are in many cases similar when carbon is added to form ternary steels. For a fixed carbon content, as the alloying element is added the γ -field is either expanded or contracted depending on the particular solute. With an element such as silicon the γ -field is restricted and there

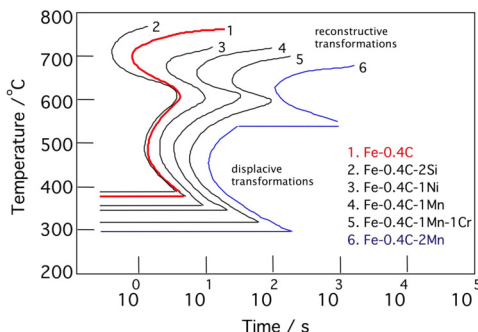


Figure 4.7 Time-temperature-transformation diagrams for the initiation of transformation in a variety of steels [5]. Each diagram consists of two 'C'-curves, the one for high temperatures representing reconstructive and that at lower temperatures, displacive transformations. The curves are experimentally difficult to separate if the reaction rate is rapid.

is a corresponding enlargement of the α -field. If vanadium is added, the γ -field is contracted and there will be vanadium carbide in equilibrium with ferrite over much of the ferrite field. Nickel does not normally form a carbide in steel, its important contribution is to expand the γ -field. Normally elements with opposing tendencies will cancel each other out at the appropriate combinations, but in some cases anomalies occur. For example, chromium added to nickel in a steel in concentrations around 18 wt% helps to stabilise the γ -phase, as shown by 18Cr-8Ni wt% austenitic steels (Chapter 12).

One convenient way of illustrating quantitatively the effect of an alloying element on the γ -phase field of the Fe-C system is to project on to the Fe-C plane of the ternary system the γ -phase field boundaries for increasing concentration of a particular alloying element. This is illustrated in Fig. 4.8 for titanium and chromium, from which it can be seen that just over 1 wt% Ti will eliminate the γ -loop, while 20 wt% Cr is required to reach this point. Other ternary systems can be followed in the same way, e.g. in Fe-V-C, vanadium has an effect intermediate between that of titanium and of chromium.

For more precise and extensive information, it is necessary to consider a series of isothermal sections in true ternary systems Fe-C-X, but even in some of the more familiar systems the full information is not available, partly because the acquisition of accurate data can be a difficult and very time-consuming process. Recently the introduction of computer-based methods has permitted the synthesis of extensive thermochemical and phase

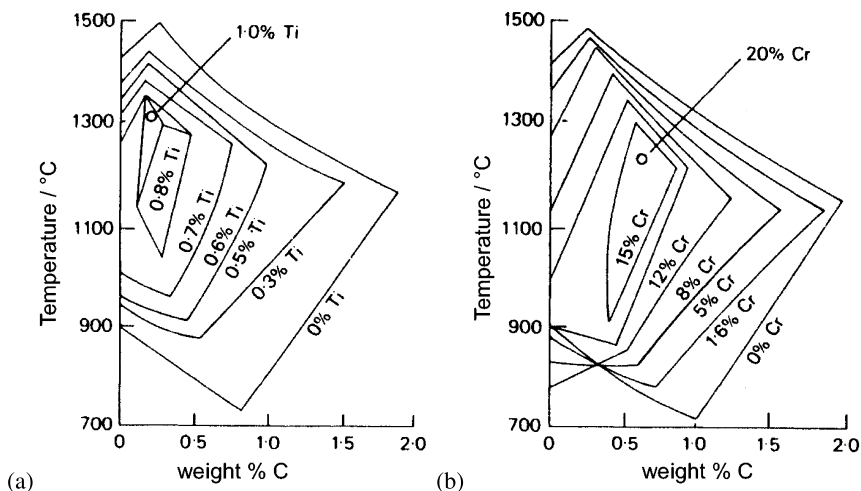


Figure 4.8 Effect of alloying elements (wt%) on the γ -phase field: (a) titanium; (b) chromium (after Tofaute [6]).

equilibria data, and its presentation in the form, e.g., of isothermal sections over a wide range of temperatures (Chapter 15). A journal⁴ now publishes the work of laboratories concerned with such work, including the assessment of thermodynamic data which forms the fundamental basis of the calculations.

If only steels in which the austenite transforms to ferrite and carbide on slow cooling are considered, the alloying elements can be divided into three categories:

- (a) elements which enter only the ferrite phase;
- (b) elements which form stable carbides and also enter the ferrite phase;
- (c) elements which enter only the carbide phase.

In the first category there are elements such as nickel, copper, phosphorus and silicon which, in transformable steels, are normally found in solid solution in the ferrite phase, their solubility in cementite or in alloy carbides being quite low.

The majority of alloying elements used in steels fall into the second category, in so far as they are carbide formers and as such, at low concentrations, go into solid solution in cementite, but will also form solid solutions in ferrite. At higher concentrations most will form alloy carbides, which are thermodynamically more stable than cementite. Typical examples are manganese, chromium, molybdenum, vanadium, titanium, tungsten and

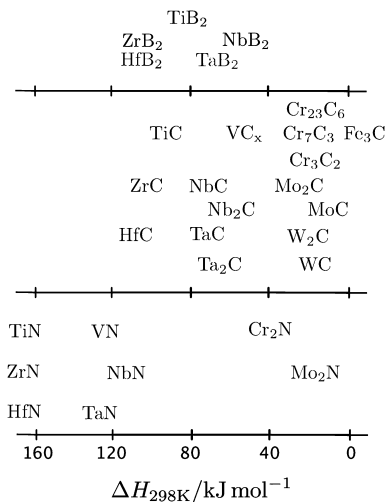


Figure 4.9 Enthalpies of formation of carbides, nitrides and borides (after Schick [7]).

niobium. The stability of the alloy carbides and nitrides frequently found in steels relative to that of cementite is shown in Fig. 4.9, where the enthalpies of formation, ΔH , are plotted. Manganese carbide is not found in steels, but instead manganese enters readily into solid solution in Fe_3C . The carbide-forming elements are usually present greatly in excess of the amounts needed in the carbide phase, which are determined primarily by the carbon content of the steel. The remainder enter into solid solution in the ferrite with the non-carbide-forming elements nickel and silicon. Some of these elements, notably titanium, tungsten and molybdenum, produce substantial solid solution hardening of ferrite.

In the third category there are a few elements which enter predominantly the carbide phase. Nitrogen is the most important element and it forms carbo-nitrides with iron and many alloying elements. However, in the presence of certain strong nitride-forming elements, e.g. titanium and aluminium, separate alloy nitride phases can occur.

While ternary phase diagrams, Fe-C-X , can be particularly helpful in understanding the phases which can exist in simple steels, isothermal sections for a number of temperatures are needed before an adequate picture of the equilibrium phases can be built up. For more complex steels the task is formidable and equilibrium diagrams can only give a rough guide to the structures likely to be encountered. It is, however, possible to construct pseudobinary diagrams for groups of steels, which give an overall

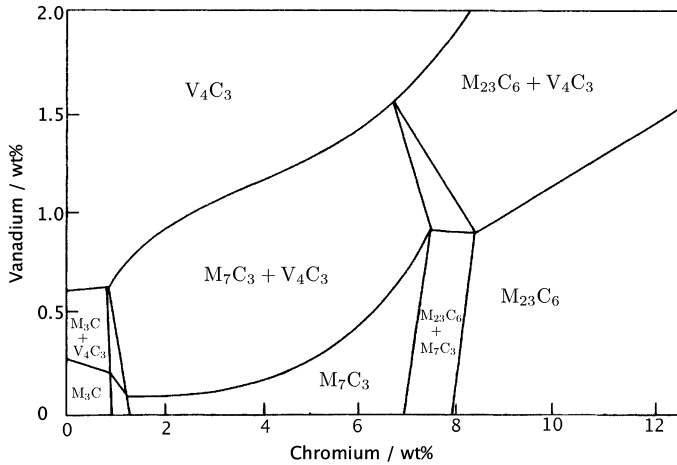


Figure 4.10 Carbide constitution in 0.2 wt% C steels at 700°C as a function of vanadium and chromium content (after Shaw [8]).

view of the equilibrium phases likely to be encountered at a particular temperature. For example, Cr-V steels are widely used in the heat-treated condition, and both chromium and vanadium are carbide formers. If a particular carbon level, e.g. 0.2 wt% and a temperature at which equilibrium can be readily reached, e.g. 700°C, is chosen, it is possible to examine a wide range of different compositions to identify the carbide phases in equilibrium with ferrite at that temperature. The phase fields can then be plotted on a diagram as a function of chromium and vanadium, as shown in Fig. 4.10. It should be noted that cementite is only stable up to about 1.5 wt% chromium or 0.6 wt% vanadium and, for much of the diagram, several alloy carbides replace cementite.

4.4 EFFECT OF ALLOYING ELEMENTS ON THE KINETICS OF THE γ/α TRANSFORMATION

Since alloying elements have different tendencies to exist in the ferrite and carbide phases, it might be expected that the rate at which the decomposition of austenite occurs would be sensitive to the concentration of alloying elements in steel. Both the growth of ferrite or pearlite are affected, so these reactions will be considered separately. Most familiar alloying elements displace the time-temperature-transformation curve for a plain carbon steel to the right, i.e. towards longer transformation times. However, a small group

of elements, e.g. Co and Al, move the curve to shorter transformation times.

4.4.1 The effect of alloying elements on the ferrite reaction

Consider now a ternary steel, say Fe-Mn-C, with the growth of ferrite occurring in a manner that maintains local equilibrium at the α/γ interface. It would be necessary to satisfy two equations of the form of Equation (3.1), simultaneously, for each of the solutes:

$$\left. \begin{aligned} (c_C^{\gamma\alpha} - c_C^{\alpha\gamma})\nu &= -D_C^\gamma \nabla c_C \\ (c_{Mn}^{\gamma\alpha} - c_{Mn}^{\alpha\gamma})\nu &= -D_{Mn}^\gamma \nabla c_{Mn} \end{aligned} \right\}. \quad (4.2)$$

Because $D_C^\gamma \gg D_{Mn}^\gamma$, these equations cannot in general be satisfied simultaneously for the tie-line passing through the alloy composition $\bar{c}_C, \bar{c}_{Mn}$. It is, however, possible to choose other tie lines which satisfy Equation (4.2). If the tie-line is such that $c_C^{\gamma\alpha} = \bar{c}_C$ (e.g. line *cd* for alloy A of Fig. 4.11a), then ∇c_C will become very small, the driving force for carbon diffusion in effect being reduced, so that the flux of carbon atoms is forced to slow down to a rate consistent with the partitioning of manganese. Ferrite forming by this mechanism is said to grow by a ‘Partitioning, Local Equilibrium’ (or PLE) mechanism, in recognition of the fact that $c_{Mn}^{\alpha\gamma}$ can differ significantly from $\bar{c}_{Mn}$, giving considerable partitioning and long-range diffusion of manganese into the austenite.

An alternative choice of tie-line could allow $c_{Mn}^{\alpha\gamma} \rightarrow \bar{c}_{Mn}$ (e.g. line *cd* for alloy B of Fig. 4.11b), so that ∇c_{Mn} is drastically increased since only very small amounts of Mn are partitioned into the austenite. The flux of manganese atoms at the interface correspondingly increases and manganese diffusion can then keep pace with that of carbon, satisfying Equations (4.2). The growth of ferrite in this manner is said to occur by a ‘Negligible Partitioning, Local Equilibrium’ (or NPLe) mechanism, in recognition of the fact that the manganese content of the ferrite approximately equals $\bar{c}_{Mn}$, so that little if any manganese partitions into austenite.

What circumstances determine whether growth follows the PLE or NPLe mode? Fig. 4.12a shows the Fe-Mn-C phase diagram, now divided into domains where either PLE or NPLe is possible but not both. The domains are obtained by drawing right-handed triangles on each tie-line in the $\alpha + \gamma$ phase field and joining up all the vertices.⁵ For example, if an attempt is made to define NPLe conditions in the PLE domain, then the tie-line determining interface compositions will incorrectly show that both

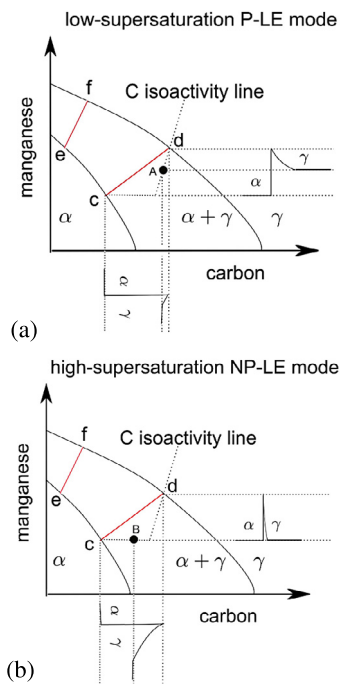


Figure 4.11 Schematic isothermal sections of the Fe-Mn-C system, illustrating ferrite growth occurring with local equilibrium at the α/γ interface. (a) Growth at low supersaturations (PLE) with bulk redistribution of manganese, (b) growth at high supersaturations (NP-LE) with negligible partitioning of manganese during transformation. The bulk alloy compositions ($\bar{c}_{\text{Mn}}$, $\bar{c}_{\text{C}}$) are designated by the symbol $\bullet$ in each case.

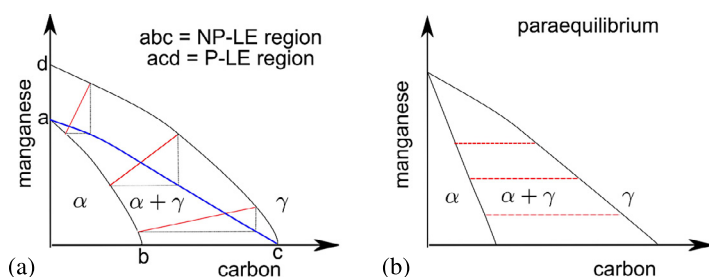


Figure 4.12 (a) Regions of the two-phase field where either PLE or NP-LE modes of transformation are possible. The figure is an isothermal section of a ternary phase diagram and the tie-lines are in red. (b) An isothermal section of a paraequilibrium phase diagram. The Mn/Fe ratio remains identical in α and γ , but carbon redistributes subject to that constraint. Since the carbon concentration is usually small, the tie-lines are almost parallel to the carbon axis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this chapter.)

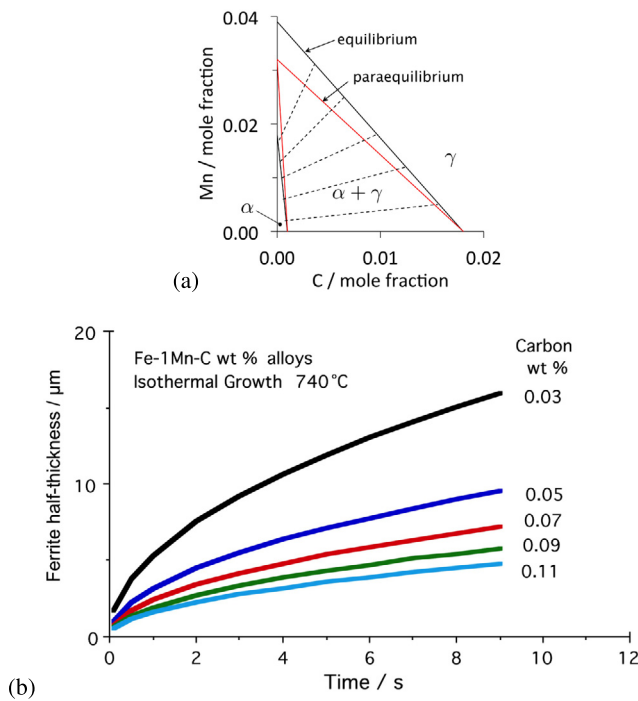


Figure 4.13 (a) Superimposed isothermal sections (1053 K) of the equilibrium and paraequilibrium Fe-Mn-C phase diagrams. The equilibrium tie-lines are marked dashed. (b) An illustration of the thickening of allotriomorphs of ferrite, for steels containing a variety of carbon concentrations. The calculations assume paraequilibrium transformation so that the manganese influences only the thermodynamics of the phase change.

austenite and ferrite contain less carbon than $\bar{c}_C$, a circumstance which is physically impossible.

Paraequilibrium is a constrained equilibrium. It occurs at temperatures where the diffusion of substitutional solutes is not possible within the time scale of the experiment. Nevertheless, interstitials may remain highly mobile. Thus, in a steel, manganese does not partition between the ferrite and austenite, but subject to that constraint, the carbon redistributes until it has the same chemical potential in both phases. Therefore, the tie lines in the phase diagram (Fig. 4.12b) are all virtually parallel to the carbon axis, since Mn to Fe ratio remains the same everywhere during ferrite growth.

In an isothermal section of the ternary phase diagram, the paraequilibrium phase boundaries must lie within the equilibrium phase boundaries as illustrated in Fig. 4.13a. This is because there is no difference between

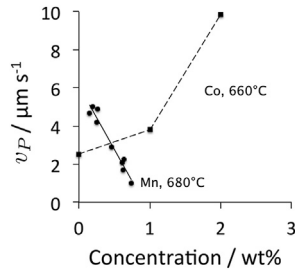


Figure 4.14 The growth rate v_P of pearlite as a function of manganese, which retards the reaction, and cobalt, that accelerates it. Data from Mehl and Hagel [9].

the equilibrium and paraequilibrium cases in the absence of manganese, so the phase boundaries meet on the horizontal axis. For paraequilibrium, α and γ have identical manganese content in the absence of carbon, so the $\alpha/\alpha + \gamma$ and $\gamma/\gamma + \alpha$ phase boundaries meet at a point $\bar{c}_{\text{Mn}}$ on the vertical axis. In contrast, the manganese concentrations of these two phases are different at equilibrium even in the absence of carbon.

Fig. 4.13b shows how the thickness of allotriomorphic ferrite changes parabolically with time during paraequilibrium growth. The carbon concentration changes by a regular 0.02 wt% between the different curves, but the change in the rate of transformation becomes very large when the average concentration approaches the solubility of carbon in ferrite that is in equilibrium with austenite ($\bar{c}_C \rightarrow c_C^{\alpha\gamma}$). The rate of diffusion-controlled growth would be infinite when $\bar{c}_C = c_C^{\alpha\gamma}$ but obviously, other rate limiting factors such as the barrier to the transfer of atoms across the α/γ interface become rate limiting.

4.4.2 The effect of alloying elements on the pearlite reaction

The pearlite reaction is a typical nucleation and growth reaction and, under the appropriate experimental conditions, rates of nucleation I_V and rates of growth v_P can be determined (Equation (3.11)). The work of Mehl and coworkers showed that many alloying elements reduce both I_V and v_P , although in rare cases, e.g. cobalt can accelerate the growth rate (Fig. 4.14). Pearlite is a reconstructive transformation and there are no reported instances where the substitutional solute does not partition between the phases. Therefore, the idea of paraequilibrium pearlite does not apply. The growth rate will therefore be influenced by the requirement to diffuse all solutes (including those that are substitutional), and there naturally must

also be a thermodynamic effect whereby the driving force for the $\gamma \rightarrow \alpha + \theta$ transformation is changed by the addition of the solute.

The situation therefore is more complex for Fe-C-X steels containing a substitutional solute (X) in addition to interstitial carbon. Local equilibrium requires the compositions at the interface to be maintained at levels that are consistent with a tie-line of the Fe-C-X phase diagram. At a constant temperature, this in general is not possible to achieve for the tie line passing through $\bar{c}_{\text{Mn}}, \bar{c}_c$ because the rate at which each solute is partitioned must then equal to that at which it is carried away from the interface by diffusion. By analogy with Equations (4.2), it is necessary therefore that

$$\text{at } \alpha/\gamma \text{ interface: } \begin{cases} v_P(c_C^{\gamma\alpha} - c_C^{\alpha\gamma}) = -D_{C,V}^{\gamma} \nabla c_C \\ v_P(c_{\text{Mn}}^{\gamma\alpha} - c_{\text{Mn}}^{\alpha\gamma}) = -D_{\text{Mn},V}^{\gamma} \nabla c_{\text{Mn}} \end{cases} \quad (4.3)$$

$$\text{at } \theta/\gamma \text{ interface: } \begin{cases} v_P(c_C^{\gamma\theta} - c_C^{\theta\gamma}) = -D_{C,V}^{\gamma} \nabla c_C \\ v_P(c_{\text{Mn}}^{\gamma\theta} - c_{\text{Mn}}^{\theta\gamma}) = -D_{\text{Mn},V}^{\gamma} \nabla c_{\text{Mn}} \end{cases} \quad (4.4)$$

where the subscripts identify the solute. Given that $D_{\text{Mn},V}^{\gamma} \ll D_{C,V}^{\gamma}$, it becomes impossible to simultaneously satisfy either Equation (4.3) or (4.4) if the tie-line passing through $\bar{c}_{\text{Mn}}, \bar{c}_c$ is selected. But given that a ternary alloy can, at a constant temperature offer a myriad of other tie lines that would link the $c^{\gamma\alpha} \leftrightarrow c^{\alpha\gamma}$ and separately link $c^{\gamma\theta} \leftrightarrow c^{\theta\gamma}$, the condition for local equilibrium at the α/γ and γ/α interfaces can be satisfied in principle by selecting a suitable set that does not pass through $\bar{c}_{\text{Mn}}, \bar{c}_c$.

Such a set of tie lines can be found by considering the following equations that are analogous with Equation (3.11), but the number of equations is now two in order to allow for both the Mn and C [10,11]:

$$\begin{aligned} v_P^C &= \left(2D_{C,V}^{\gamma} + \frac{12sD_{C,B}\delta}{S} \right) \frac{S}{S_{\alpha}S_{\theta}} \left(\frac{c_C^{\gamma\alpha} - c_C^{\gamma\theta}}{c_C^{\theta\gamma} - c_C^{\alpha\gamma}} \right) \left(1 - \frac{S_C}{S} \right), \\ v_P^{\text{Mn}} &= \left(2D_{\text{Mn},V}^{\gamma} + \frac{12sD_{\text{Mn},B}\delta}{S} \right) \frac{S}{S_{\alpha}S_{\theta}} \left(\frac{c_{\text{Mn}}^{\gamma\alpha} - c_{\text{Mn}}^{\gamma\theta}}{c_{\text{Mn}}^{\theta\gamma} - c_{\text{Mn}}^{\alpha\gamma}} \right) \left(1 - \frac{S_C}{S} \right), \end{aligned} \quad (4.5)$$

where the velocities v_P^C and v_P^{Mn} are calculated on the basis of the diffusion of only carbon or only manganese, respectively. Clearly, since there is only one transformation front, the equations must be solved such that $v_P^C = v_P^{\text{Mn}}$. Bearing in mind that the interlamellar spacing is also identical in these equations, a further condition arises that:

$$\frac{D_C}{D_{\text{Mn}}} = \frac{R_{\text{Mn}}}{R_C} \quad \text{with} \quad \begin{cases} D_i \equiv D_{i,V} + \frac{6sD_{i,B}\delta}{S}, \\ R_i \equiv \frac{c_i^{\gamma\alpha} - c_i^{\gamma\theta}}{c_i^{\theta\gamma} - c_i^{\alpha\gamma}}. \end{cases} \quad (4.6)$$

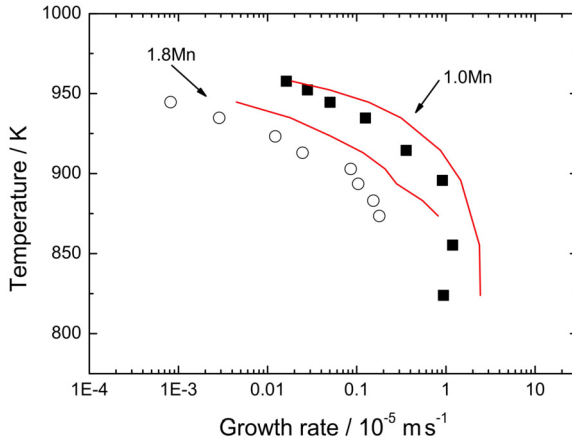


Figure 4.15 Mixed diffusion-controlled model applied to 1.0 and 1.8 wt% Mn eutectoid steels and experimental data for comparison (after Seo et al. [11]).

The R_i condition ensures that the weighted average of the ferrite and cementite yields the mean composition of the steel; s is a length normal to the growth direction. With these two constraints and in addition the local equilibrium condition, it is possible to find unique interface compositions at the growth front by coupling the conditions and the velocity equations. Some comparisons of the calculations with experimental data for ternary steels are shown in Fig. 4.15; there is a reasonable agreement given the uncertainties that exist in the boundary diffusion coefficients that are necessary for the calculations. The method outlined above can in principle be extended to steels containing more than one substitutional solute.

Other effects

Fully pearlitic steel is vital in the manufacture of the strongest ropes available for engineering applications, as discussed in section 3.6.6. Much research has therefore been done to increase the strength of the ropes, one approach being to increase the amount of carbon without inducing the formation of any proeutectoid cementite. Proeutectoid cementite precipitates as allotriomorphs on the austenite grain boundaries and as Widmanstätten plates (Fig. 3.6); both of these cause a deterioration in the ductility of the steel and therefore should be avoided.

Substitutional solutes can affect the eutectoid composition which in a plain carbon steel is just below 0.8 wt%; Fig. 4.16a shows that silicon, which does not dissolve in cementite, reduces the eutectoid concentration.

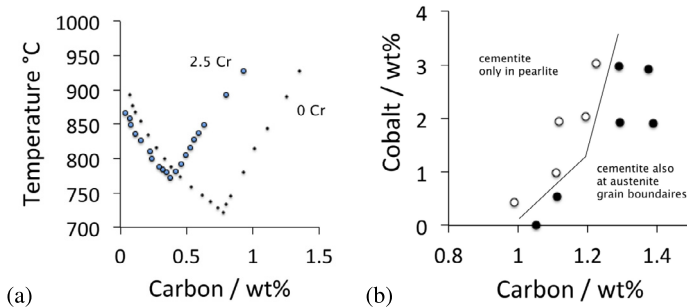


Figure 4.16 (a) Change in the eutectoid composition as the chromium concentration is increased. After [12]. (b) Fully pearlitic state (open circles) obtained in steels containing more than 0.8 wt% carbon, with the addition of cobalt. The filled circles represent cases where allotropic and Widmanstätten cementite were present in addition to pearlite. In all cases, the steels were patented by isothermal transformation at 550°C (after Kanetsuki et al. [13]).

Cobalt, on the other hand, has the opposite effect so that steels with large carbon concentrations can be made fully pearlitic, Fig. 4.16b. The concept of a eutectoid composition is of course different between Fe-C and Fe-C-X because in the latter case the eutectoid reaction has greater degrees of freedom according to the phase rule, and hence can occur over a range of temperatures.

It is possible in a ternary Fe-C-X system for austenite, cementite and ferrite to co-exist in equilibrium. The pearlite that grows does not then have the average composition of the steel so the austenite composition changes as the pearlite grows. This causes the driving force for transformation to decrease as the pearlite grows, to a point where it reaches zero when equilibrium is achieved. The reduction in driving force as the pearlite grows leads to a progressive increase in its interlamellar spacing so that the microstructure is known as *divergent pearlite* [14], Fig. 4.17.

4.4.3 Alloy pearlite

Once the alloying element concentration reaches a critical level, the cementite will be replaced by another carbide phase. For example, in a chromium, tungsten or molybdenum steel, the cubic $M_{23}C_6$ carbide can form, where M can include iron, chromium, molybdenum or tungsten (Figs 4.18 and 4.19). This change in the carbide phase does not necessarily alter the basic pearlitic morphology and consequently ‘alloy pearlites’ are obtained in which an alloy carbide is associated with ferrite (Fig. 4.19).

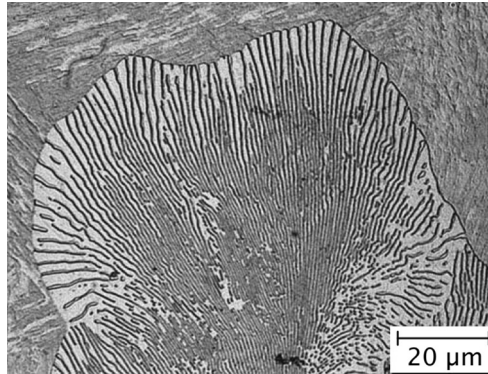


Figure 4.17 Fe-2.5C-5.4Mn at% steel transformed in the $\gamma + \alpha + \theta$ phase field where the three phases can coexist at equilibrium, showing divergent pearlite. The interlamellar spacing increases as the colony grows (after Hutchinson et al. [15], reproduced with the permission of Elsevier).

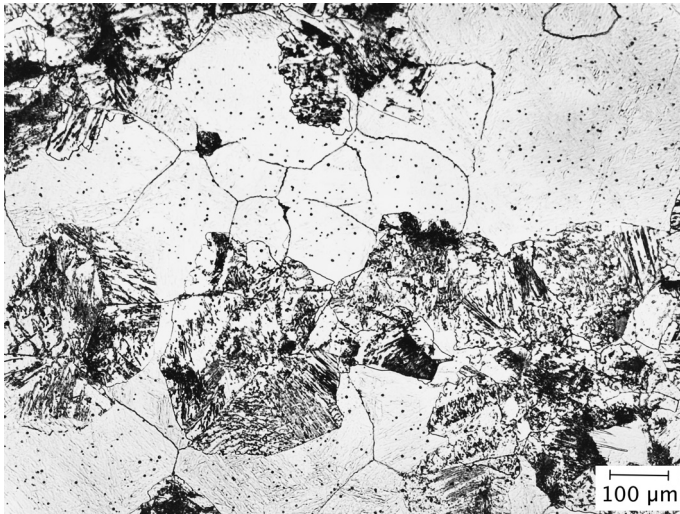


Figure 4.18 Fe-12Cr-0.2C wt% transformed 30 min at 775°C. Pearlite-type reaction involving $M_{23}C_6$ instead of cementite as the carbide phase (courtesy of Campbell).

These pearlites occur only in medium and highly alloyed steels, usually at the highest transformation temperatures. At lower transformation temperatures in the same steel, cementitic pearlite may still form because of the inadequate diffusion of the alloying element.

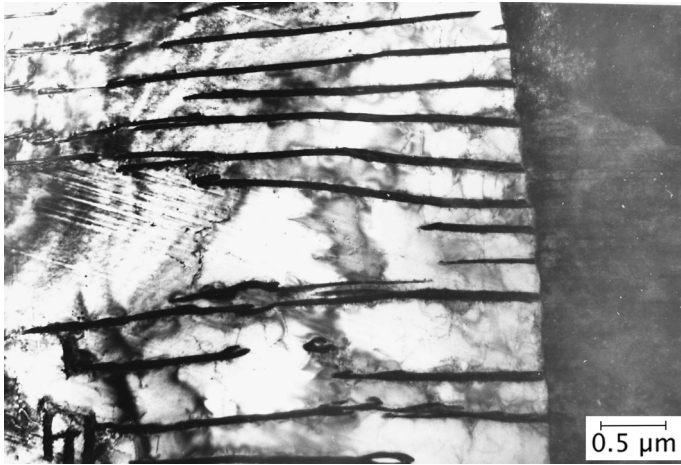


Figure 4.19 Fe-12Cr-0.2C transformed 15 min at 750°C. Alloy pearlite. $M_{23}C_6$ /ferrite (courtesy of Campbell).

4.5 STRUCTURAL CHANGES RESULTING FROM ALLOYING ADDITIONS

The addition to iron-carbon alloys of elements such as nickel, silicon and manganese, which do not form carbides in competition with cementite, does not basically alter the microstructures formed after transformation. However, in the case of strong carbide-forming elements such as molybdenum, chromium and tungsten, cementite will be replaced by the appropriate alloy carbides, often at relatively low alloying element concentrations. Still stronger carbide-forming elements such as niobium, titanium and vanadium are capable of forming alloy carbides preferentially at alloying concentrations less than 0.1 wt%. It would, therefore, be expected that the microstructures of steels containing these elements would be radically altered.

The tendency for forming carbides and nitrides can be expressed in terms of bonding. Cottrell has been able to explain many of the observed trends in the stability, crystal structure and stoichiometry of the carbides of transition metals in terms of chemical bonds [16]. He points out that Ti, Zr and Hf, which in the periodic table are elements near the beginning of the long periods, form very stable MC carbides but the affinity for carbon diminishes further along the rows of the periodic table (Fig. 4.20). A part of the reason for this is that more electrons have to be accommodated for elements further along the rows, so antibonding states are progressively

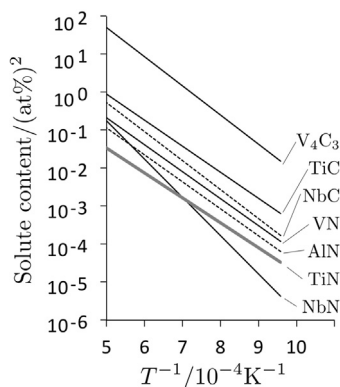


Figure 4.21 Solubility products for carbides and nitrides in austenite as a function of temperature (after Aronsson [18]). Note that for multicomponent steels, the estimation of carbide solubility with respect to another phase is best done using phase diagram calculation methods [19,20].

are much less soluble in austenite than is cementite. In Fig. 4.21 the solubility products in austenite of vanadium, titanium and niobium carbides and nitrides are plotted as a function of $1/T$. Chromium and molybdenum carbides are not included, but they are substantially more soluble in austenite than the other carbides. Detailed consideration of such data, together with practical knowledge of alloy steel behaviour, indicates that, for niobium and titanium, concentrations of greater than about 0.25 wt% will form excess alloy carbides which cannot be dissolved in austenite at the highest solution temperatures. With vanadium the limit is higher at 1–2 wt%, and with molybdenum up to about 5 wt%. Chromium has a much higher limit before complete solution of chromium carbide in austenite becomes difficult. This argument assumes that sufficient carbon is present in the steel to combine with the alloying element. If not, the excess metallic element will go into solid solution both in the austenite and the ferrite.

4.5.1 Ferrite/alloy carbide aggregates

Steels containing strong carbide-forming elements transform from austenite to ferrite in a similar way to, e.g., steels containing nickel or silicon. However, the carbide-forming elements substantially restrict the γ -loop (Fig. 4.4), so that the eutectoid composition is depressed to much lower carbon levels and to higher transformation temperatures. One result is that pearlite can completely disappear from the transformed microstructures,

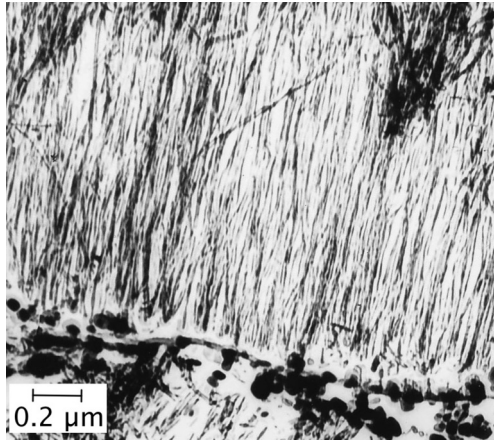


Figure 4.22 Fe-4Mo-0.2C transformed 4 days at 600°C. Fibrous Mo_2C growth from γ boundary (courtesy of Berry). The prior austenite grain boundary is at the bottom of the image where the coarse, spheroidal Mo_2C particles are present.

which now exhibit very different ferrite/carbide aggregates, usually on a much finer scale than pearlite. Apart from the alloy carbide based pearlites, particularly found in high chromium steels, there are three morphologies of alloy carbides which are intimately associated with ferrite in the transformation temperature range in which plain carbon steels form ferrite/pearlite structures.

Continuous growth of fibres/laths

The alloy carbides form as fine fibres or laths which grow normal to the γ - α interface which then moves forward forming fibrous aggregates of carbide and ferrite (Fig. 4.22).

Repeated nucleation of carbides (interphase precipitation)

In this growth mode the carbide particles, usually in the form of small plates or rods, nucleate at the γ - α interface which then moves to a new position where the nucleation cycle again occurs. This process can be repeated many hundreds of times within a particular austenite grain leading to a ferrite matrix with very fine banded dispersions as, e.g., in the 0.75 wt% vanadium steel shown in Fig. 4.23. Chromium steels give coarser dispersions (Fig. 4.25).

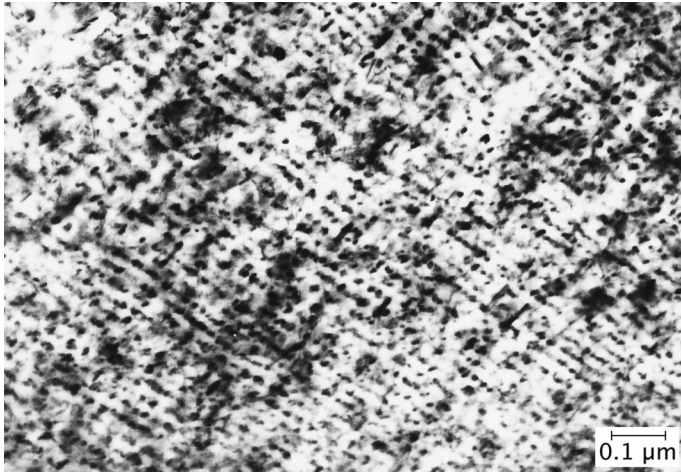


Figure 4.23 Fe-1V-0.2C-0.02Nb wt% alloy transformed 5 min at 775°C. Interphase precipitation of VC in ferrite (courtesy of Batte).

Nucleation in supersaturated ferrite

In microalloyed steels, where strong carbide-forming elements are present in concentrations less than 0.1 wt%, it often is possible to obtain the ferrite in a supersaturated condition with little or no carbide precipitation taking place during the γ/α transformation. Instead, while the steel is held at the transformation temperature, carbide precipitates form within the newly formed ferrite grains, usually on dislocations (Fig. 4.24).

While it is possible by careful choice of alloy and experimental conditions to obtain each of the above microstructures separately, in practice they are often all present in transformed alloy steels, provided the steel contains a strong carbide-forming element. Consequently the microstructures of transformable alloy steels can be very complex, the full extent of these complexities only being revealed when high-resolution electron microscopy is used to study them.

In general, the fibrous morphology represents a closer approach to an equilibrium structure so it is more predominant in steels which have transformed slowly. In contrast, the interphase precipitation and dislocation nucleated structures occur more readily in rapidly transforming steels, where there is a high driving force, e.g., in microalloyed steels (Chapter 10).

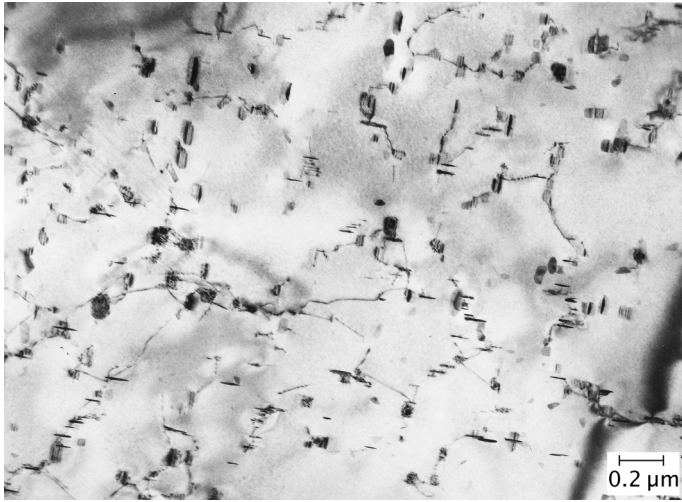


Figure 4.24 Fe-0.25V-0.05C transformed and held at 2.5 h at 740°C. VC precipitation on dislocations (courtesy of Ballinger).

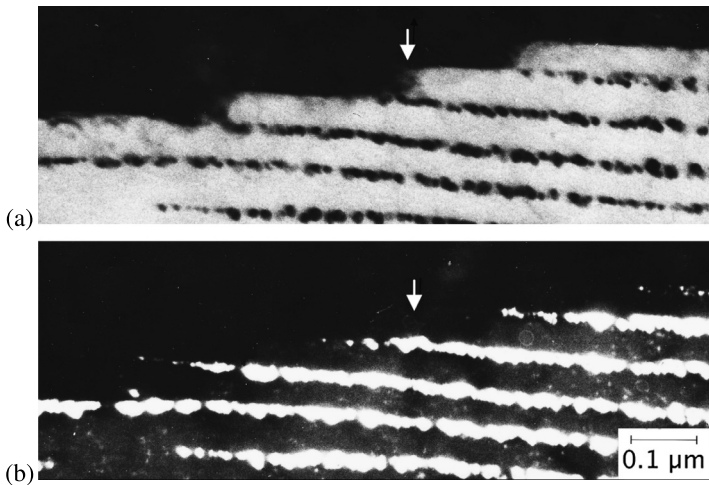


Figure 4.25 Fe-12Cr-0.2C wt% transformed 30 min at 650°C. Precipitation of $M_{23}C_6$ at stepped γ/α interface: (a) bright field; (b) precipitate spot dark field (courtesy of Campbell).

4.5.2 Alloy carbide fibres and laths

The clearest analogy with pearlite is found when the alloy carbide in lath morphology forms nodules in association with ferrite. These pearlitic nod-

ules are often encountered at temperatures just below A_{e1} in steels which transform relatively slowly. For example, these structures are obtained in chromium steels with between 4 and 12 wt% chromium (Fig. 4.18), and the morphology is analogous to that of cementitic pearlite. It is, however, different in detail because of the different crystal structures of the possible carbides, e.g. M_7C_3 is hexagonal and $M_{23}C_6$ is cubic. The structures observed are relatively coarse, but finer than pearlite formed under equivalent conditions, because of the need for the partition of the alloying element, e.g. chromium between the carbide and the ferrite. To achieve this, the interlamellar spacing must be substantially finer than in the equivalent iron-carbon case.

At lower temperatures the lath morphology is largely replaced by much finer fibrous aggregates, e.g. in high Cr steels coarse laths of $M_{23}C_6$ can be replaced by fine fibres of the same carbide usually 500 Å in diameter. Their length, which is determined by the size of the ferrite colony, can be up to 10 µm with little or no branching. Similar morphologies occur, but are much less dominant, in steels containing W, Ti, V and Nb.

Carbide fibres are frequently associated with planar interfaces, as well as with pearlitic-type interfaces. Nevertheless, these are boundaries which can apparently propagate rapidly without the need for step migration. An analysis of similar boundaries in austenitic steels has shown that they possess comparatively high densities of coincident lattice sites [21].

4.5.3 Interphase precipitation

Interphase precipitation is associated with the periodic nucleation of carbides at the γ/α interface during the transformation. The precipitate particles form in bands which are closely parallel to the interface, and which follow the general direction of the interface even when it changes direction sharply. A further characteristic is the frequent development of only one of the possible Widmanstätten variants, e.g. VC platelets in a particular region are all only of one variant of the habit, i.e. that in which the plates are most nearly parallel to the interface. The bands are often associated with planar low-energy interfaces, and the spacing between bands is determined by the height of steps which move along the interface (Fig. 4.25). The nucleation of the carbide particles occurs normally on the low energy planar interfaces, rather than on the rapidly moving high-energy steps.

The need for step movement on the γ/α interface is in contrast to the growth of fibrous carbides behind an interface on which no steps are observed. Indeed if, in these circumstances, a step does move along the

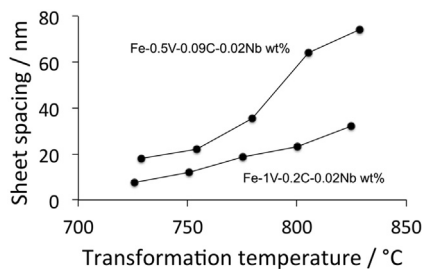


Figure 4.26 Interphase precipitation of VC in vanadium steels. Precipitate sheet spacing as a function of transformation temperature (courtesy of Ballinger). The higher vanadium steel has about twice as much of a volume fraction of vanadium carbide.

interface, the fibrous growth is stopped and replaced by interphase precipitation. The step height and, therefore, the band spacing of the precipitation, is dependent on the temperature of transformation and on the composition. As the temperature of transformation is lowered the band spacing is reduced, e.g. in a 1 wt% V 0.2 wt% carbon steel, the spacing varies from 25 nm at 825°C to 7.5 nm at 725°C (Fig. 4.26), and at lower temperatures has been observed to be less than 5 nm. The extremely fine scale of this phenomenon in vanadium steels, which also occurs in Ti and Nb steels, is due to the rapid rate at which the γ/α transformation takes place. At the higher transformation temperatures, the slower rate of reaction leads to coarser structures. Similarly, if the reaction is slowed down by addition of further alloying elements, e.g. Ni and Mn, the precipitate dispersion coarsens. The scale of the dispersion also varies from steel to steel, being coarsest in chromium, tungsten and molybdenum steels where the reaction is relatively slow, and much finer in steels in which vanadium, niobium and titanium are the dominant alloying elements and the transformation is rapid.

One of the recent successes in the field of high-strength low-alloy steels has the trade name *Nanohiten* [22] of composition Fe-0.043C-0.2Si-1.6Mn-0.0035N wt%, with titanium in the range 0.018–0.186 wt% and molybdenum from 0–0.37 wt%. The steel contains (Ti,Mo)C in the form of interphase precipitates in the ferrite, which adds about 300 MPa to the total of 780 MPa ultimate tensile strength. Furthermore, the alloy microstructure can be obtained in the hot-rolled state and has an excellent formability which makes it suitable for large-scale automotive applications. An example is illustrated in Fig. 4.27. First principles calculations indicate that the dissolution of molybdenum in TiC is not favoured from a thermodynamic

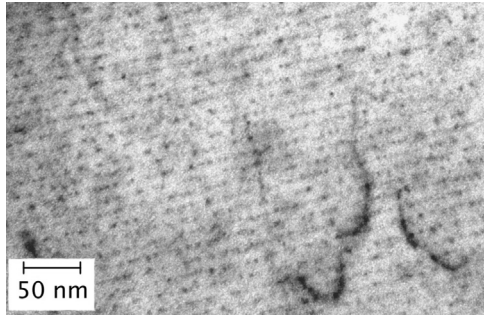


Figure 4.27 Interphase precipitation of (Ti,Mo)C in ferrite within a high-strength low-alloy steel. The chemical composition is Fe-0.06C-1.5Mn-0.1Si-0.1Ti-0.2Mo wt%. The precipitates are about 4.5 nm in length and the precipitate sheet spacing is about 20 nm (after Yen et al. [24], reproduced with the permission of Elsevier).

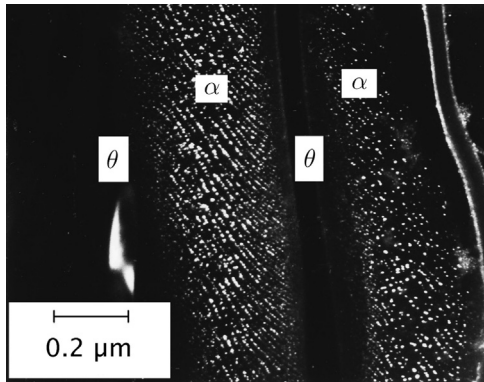


Figure 4.28 A dark field transmission electron micrograph showing rows of vanadium carbide precipitation within the pearlitic ferrite of a steel (0.5C-0.3Si-0.82Mn-0.3V wt%) cooled to produce a mixture of allotriomorphic ferrite and pearlite. Reproduced with the permission of Maney Publishing from [25].

point of view, but that it decreases the misfit between the carbide and the ferrite, thus reducing the activation energy for nucleation [23]. The same influence of molybdenum on the interfacial misfit, which is related to the interfacial energy per unit area, also reduces the coarsening rate of the precipitate. This is important because steels produced on a large scale, by hot rolling, are coiled while the steel is hot so that the slow cooling process to room temperature can induce coarsening of the microstructure.

Surprisingly, interphase precipitation can also be found within the ferritic component of pearlite. Fig. 4.28 [25] shows the precipitation of

vanadium carbides within the pearlitic-ferrite in row formations that are consistent with interphase precipitation, presumably by the movement of steps at the pearlite-austenite interface (section 3.6.1). The precipitation is of technological importance because it offers an additional method of strengthening pearlite.

4.5.4 Nucleation in supersaturated ferrite

It has been shown that ferrite can occur in different morphologies depending on the transformation temperature. At the highest transformation temperatures, equiaxed boundary allotriomorphs form at the austenite grain boundaries, and carbon diffuses to the austenite. In alloy steels, e.g. low V steels, there is evidence that the alloying element can also partition. As a result no alloy carbide forms in this ferrite, which is thus truly pro-eutectoid. At lower temperatures the ferrite formed is still equi-axed, but the alloy carbide forms at the same time either as interphase precipitate or as fibres. This is probably the closest approach to true eutectoid behaviour in an alloy steel containing a strong carbide-forming element.

At still lower transformation temperatures the ferrite adopts a Widmanstätten habit and forms as laths, as in pure iron-carbon alloys. However, this ferrite can be supersaturated when first formed. If held only for a short time at the transformation temperature, precipitation of the alloy carbide occurs within the ferrite on dislocations. Such behaviour would be expected in alloy steels with acicular ferrite provided a strong carbide former such as V, Ti or Nb is present although, in theory, similar structures should be possible in plain carbon steels.

4.6 TRANSFORMATION DIAGRAMS FOR ALLOY STEELS

The transformation of austenite below the eutectoid temperature can best be presented in an isothermal transformation diagram (Chapter 3), in which the beginning and end of transformation is plotted as a function of temperature and time. Such curves are known as time-temperature-transformation, or TTT, curves and form one of the important sources of quantitative information for the heat treatment of steels. In the simple case of an eutectoid plain carbon steel, the curve is roughly 'C'-shaped with the pearlite reaction occurring down to the nose of the curve and a little beyond. At lower-temperatures bainite and martensite form (Chapters 5 and 6). The diagrams become more complex for hypo- and hyper-eutectoid alloys as

the ferrite or cementite reactions have also to be represented by additional lines.

Alloying elements, on the whole, retard both the pro-eutectoid reactions and the pearlite reaction, so that TTT curves for alloy steels are moved increasingly to longer times as the alloy content is increased. Additionally, those elements which expand the γ -field depress the eutectoid temperature, with the result that they also depress the position of the TTT curves relative to the temperature axes. This behaviour is shown by steels containing manganese or nickel. For example, in a 13Mn-0.8C wt% steel, pearlite can form at temperatures as low as 400°C. In contrast, elements which favour the ferrite phase raise the eutectoid temperature and the TTT curves move correspondingly to higher temperatures. The slowing down of the ferrite and pearlite reactions by alloying elements enables these reactions to be more readily avoided during heat treatment, so that the much stronger low-temperature phases such as bainite and martensite can be obtained in the microstructure. The hard martensitic structure is only obtained in plain carbon steels by water quenching from the austenitic condition whereas, by the addition of alloying elements, a lower critical cooling rate is needed to achieve this condition. Consequently, alloy steels allow hardening to occur during oil quenching, or even on air cooling, if the TTT curve has been sufficiently displaced to longer times.

4.7 LIGHT STEELS

The density of iron can be reduced by alloying with light elements such as silicon and aluminium and there may be smaller contribution from an expansion of lattice parameter. Early work on the subject was published in the Soviet Union [26,27] where alloys with a density 13–15% lower than that of iron were obtained by adding aluminium to a steel that is otherwise made austenitic because of its large manganese (≈ 30 wt%) and carbon (≈ 0.9 wt%) concentrations. When aged the alloy precipitates a carbide $(\text{Fe,Mn})_3\text{AlC}_x$ that leads to strengthening. This is important because it is the density normalised strength (often referred to as specific strength) that features in many designs.

Low-density steels are currently the subject of intense research, but there are three essential approaches. The first has already been mentioned, i.e. precipitation hardened austenite (e.g. [28]), multiphase steels containing ferrite, austenite and carbides [29], and finally, steels in which ferrite is the major phase (e.g. [30,31]).

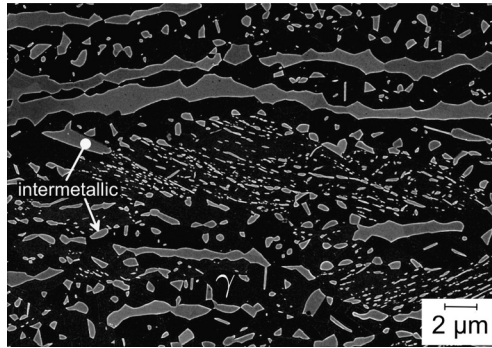


Figure 4.29 The microstructure of a low density steel containing FeAl intermetallic compound precipitate in an austenitic matrix. Image courtesy of Sang-Heon Kim, Hansoo Kim and Nack J. Kim.

Fig. 4.29 shows the microstructure of an Fe-10Al-15Mn-5Ni-0.5C wt% steel which has an austenitic matrix precipitation hardened with an Fe-Al intermetallic compound that has a primitive cubic structure with a motif of one Fe atom at 0, 0, 0, and an Al atom at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ [28]. This intermetallic compound is a formidable barrier to the penetration of dislocations present in the austenite leading to a large work hardening rate that is conducive to ductility and high strength. The density is just 6.82 g cm^{-3} so the steel has a specific strength and ductility combination that is greater than that of Ti-6Al-4V, at a cost that is claimed to be a tenth that of the titanium alloy.

The physical metallurgy and mechanical properties of these lightweight steel concepts have been demonstrated, but there are difficulties in producing large quantities using continuous casting. Alumina formation can cause the casting nozzles to be blocked and manganese has a large vapour pressure. But these are not insurmountable so the future for low-density steels looks promising.

4.8 SUMMARY

Elements that substitute for iron influence the relative stabilities of austenite and ferrite and at large concentrations can secure the stability of either phase at all temperatures in the solid state. More generally, a thermodynamic effect such as this can affect the rate of transformation through free energy terms that feature explicitly or implicitly (in determining equilibrium compositions) in the theories of nucleation and growth. In fact, equilibrium may not be respected if circumstances arise where only carbon is sufficiently mo-

bile; thus, during paraequilibrium, substitutional atoms are trapped at the transformation front because they are unable to move whereas subject to this constraint, the carbon achieves a uniform chemical potential throughout. Although the theory described in this Chapter refers to equilibrium or paraequilibrium, it is quite possible that the conditions at the interface may not respect either condition.

Beyond thermodynamics, there are profound effects of the introduction of substitutional solutes on reconstructive transformations in particular, which occur over temperature and time combinations that permit atoms to move over substantial distances comparable to the scale of the microstructure. Since the mobility of substitutional solutes is far smaller than that of interstitials, the rate of reconstructive transformation is dramatically retarded. But in addition, alloy-rich carbides may form, giving rise to a variety of microstructures including pearlite without cementite, interphase precipitation of sheets of carbides in ferrite, fibrous precipitation, heterogeneous precipitation on defects etc.

It becomes possible in a ternary system to have equilibrium between α , γ and θ , so that the chemical compositions of all three phases change as pearlite forms, leading to an ever diminishing driving force for transformation as equilibrium is achieved. The interlamellar spacing therefore increases with the volume fraction of pearlite, giving rise to the so-called divergent pearlite.

Finally, it is this luxuriance of the microstructures that can occur in alloyed steels that makes it possible to tune steels for specific requirements. There are few readily available elements that do not dissolve in iron; and those that do not, for example lead, still are utilised, for example to make free-machining steels.

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BACKNOTES

1. ‘M’ in $M_{23}C_6$ stands for metal atoms.
2. See [3] for an introduction to equilibria between phases.
3. ΔH_i is the heat of solution of i in γ less that in α .
4. *CALPHAD, Computer Coupling of Phase Diagrams and Thermochemistry*.
5. Strictly not right-handed, but accounting for isoactivity as illustrated in Fig. 4.11.
6. When two hydrogen atoms, each with a single electron, are brought together, they no longer have separate atomic orbitals. Instead they have a pair of communal orbitals (bonding and antibonding) each of which can hold two electrons. It follows that for H_2 both the electrons are in the bonding orbitals giving a bond order of 2 and a strong molecule. For He_2 , on the other hand, the four electrons fill up both the bonding and the antibonding orbitals so the bond order is zero, the molecule is not formed.

CHAPTER 5

Formation of Martensite

Abstract

A spaceship reenters the earth's atmosphere at about 8000 m s^{-1} . Martensitic transformation in steel has been recorded to occur at 1000 m s^{-1} , i.e. an incredible eighth of the reentry speed. How can this happen, and sometimes at temperatures where helium liquifies? Clearly, the atoms must move in a choreographed manner that enables an orderly transfer of atoms because stochastic motion takes time to achieve the same change in structure. The complete theory of martensite is described in this chapter, with consequences on properties explained in context.

5.1 INTRODUCTION

The quenching to room temperature of austenite in a steel can lead to the formation of martensite, a very hard phase in which the carbon, formerly in solid solution in the austenite, remains in solution in the new phase. The velocity of the interface is greater than the ability of carbon to diffuse away into the austenite:

$$\nu_{\alpha'} > \frac{D_{\text{C}}'}{\lambda}, \quad (5.1)$$

where λ is the distance between the interstices in which carbon resides, so the term on the right is the speed with which the carbon can diffuse. The carbon is said to be trapped within the martensite.¹

Unlike ferrite or pearlite, martensite forms by a deformation of the austenite lattice without any diffusion of atoms. The deformation causes a change in the shape of the transformed region, consisting of a large shear and a volume expansion. Martensite is, therefore, often referred to as a diffusionless, shear transformation, which is highly crystallographic in character because it is generated by a specific deformation of the austenite. When the formation of martensite is constrained by its surroundings, it forms as thin plates or laths in order to minimise the strain energy due to the deformation.

5.2 GENERAL CHARACTERISTICS

The martensite reaction in steels normally is said to occur athermally, i.e. the fraction transformed depends on the undercooling below a 'martensite-

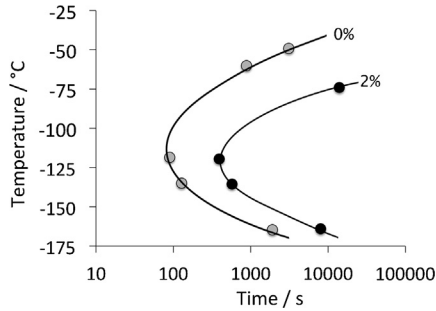


Figure 5.1 A time-temperature-transformation diagram for the isothermal formation of martensite in Fe-0.05C-23.6Ni-3.3Mn-0.2Cu wt%. These are the first experiments to reveal the role of thermal activation in martensitic transformation. Selected data from Kurdjumov and Maximova [3].

start temperature, M_S .² The extent of transformation does not seem to depend on time, as expressed in the Koistinen and Marburger equation [2] which describes the progress of transformation below M_S :

$$1 - V_V^{\alpha'} = \exp\{\beta(M_S - T_Q)\} \quad \text{where } \beta \simeq -0.011. \quad (5.2)$$

$V_V^{\alpha'}$ is the volume fraction of martensite and T_Q the temperature below M_S to which the sample is cooled. This apparent athermal character is a pragmatic description – the absence of time in Equation (5.2) is a consequence of very rapid transformation on time scales much shorter than observable by ordinary perception. In such cases, the reason why the undercooling below M_S must be increased in order to achieve further transformation is because the easy nuclei are triggered at small undercoolings, followed progressively by the remaining less potent nuclei as $M_S - T_Q$ increases. Martensite is, like all other phases that evolve from austenite, a first order transformation involving nucleation and growth. Both of these processes require thermal activation, but the activation energy is small because there is no diffusion required during martensitic transformation, and because the interfacial structure is conducive to easy glide.

Nevertheless, the fact that thermal activation is required to overcome the small barriers means that there is a time dependence of transformation, which can be detected readily if the transformation occurs at cryogenic temperatures. Using a richly alloyed steel, Kurdjumov and Maximova first demonstrated the isothermal formation of martensite, following a classical C-curve behaviour, Fig. 5.1 [3]. On the same reasoning, the transformation to martensite can also be suppressed completely by cooling sufficiently

Table 5.1 The temperature M_S at which martensite first forms on cooling, and the approximate Vickers hardness of the resulting martensite for a number of materials

Composition	M_S / K	Hardness / HV
ZrO ₂	1200	1000
Fe-31Ni-0.23C wt%	83	300
Fe-34Ni-0.22C wt%	<4	250
Fe-3Mn-2Si-0.4C wt%	493	600
Cu-15Al at%	253	200
Ar-40N ₂ at%	30	
In-25Tl at%	125	
In-29Tl at%	193	
Gd-35Ce at%	763	

rapidly to very low temperatures; a Fe-33Ni wt% alloy cooled to 4 K remained fully austenitic but then began to transform into martensite on warming to about 42 K [4].

Nevertheless, for most steels where the M_S temperature is well above ambient, the kinetics of transformation appear independent of time and follow Equation (5.2), from which it is evident that some austenite remains untransformed when T_Q is set to room temperature. This is referred to as *retained austenite*. It is also clear that there is no martensite-finish temperature, M_F , but for convenience the latter is frequently defined at the point where 95% of the martensitic transformation is completed.

Martensite is not restricted to steels although its technological importance in steels is unsurpassed. Table 5.1 lists a variety of materials which exhibit martensitic transformation, together with M_S temperatures and hardness values.

To obtain martensite, it usually is necessary for the steel to be cooled from the austenite phase field at a rate which is sufficiently fast to avoid all other solid-state transformations such as ferrite and pearlite. This cooling rate can be very high for plain carbon steels but quite slow for a heavily alloyed steel containing large concentrations of austenite stabilising solutes.

Martensite can form at very low temperatures, where diffusion, even of interstitial atoms, is not conceivable over the time period of the experiment. Table 5.1 gives typical values of the martensite-start temperature for a variety of materials. Martensite plates can grow at speeds which are a substantial fraction of the speed of sound in the steel, some 1100 m s^{-1} [5].

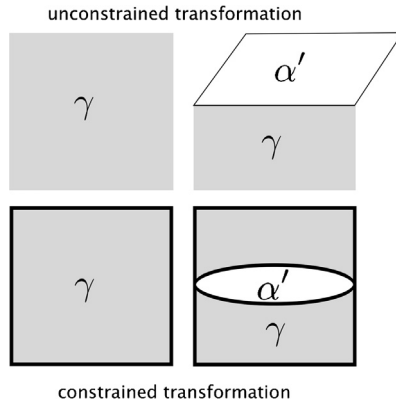


Figure 5.2 Definition of the *habit plane*, the broad interface between the martensite and austenite. The interface is flat during unconstrained transformation but curved when the displacements due to martensitic transformation are constrained by the surrounding material. The average plane of the martensite is then the habit plane, which is parallel to the flat plane of the unconstrained transformation.

Such a high rate of growth is inconsistent with diffusion during transformation. Transformations which involve diffusion are much slower – the fastest recorded solidification rate is about 80 m s^{-1} in pure nickel [6], illustrating the difference between coordinated and uncoordinated atomic motions. The difference is even greater when the random diffusional jumps happen in the solid state; thus the speed of a massive transformation³ has been reported to be only 0.03 m s^{-1} [7].

The chemical composition of martensite can be measured and shown to be identical to that of the parent austenite. These observations also demonstrate convincingly that martensitic transformations are diffusionless.

5.2.1 The habit plane

The habit refers to the interface plane between austenite and martensite as measured on a macroscopic scale (Fig. 5.2). For unconstrained transformations this interface plane is flat, but the need to minimise strains introduces some curvature when the transformation is constrained by its surroundings. Nevertheless, the macroscopic habit plane is identical for both cases, as illustrated in Fig. 5.2.

Steels of vastly different chemical composition can have martensite with the same habit plane (Table 5.2), and indeed, have other identical crystallographic characteristics.

Table 5.2 Habit plane indices for martensite. With the exception of ε -martensite, the quoted indices are approximate because the habit planes in general have irrational indices (e.g. $\sqrt{2}$ is not a rational number)

Composition / wt%	Approximate habit plane indices
Low-alloy steels, Fe-28Ni	$\{1\ 1\ 1\}_\gamma$
Plate martensite in Fe-1.8C	$\{2\ 9\ 5\}_\gamma$
Fe-30Ni-0.3C	$\{3\ 15\ 10\}_\gamma$
Fe-8Cr-1C	$\{2\ 5\ 2\}_\gamma$
ε -martensite in 18/8 stainless steel	$\{1\ 1\ 1\}_\gamma$

5.2.2 Orientation relationships

The formation of martensite involves the coordinated movement of atoms. It follows that the austenite and martensite lattices will be intimately related. All martensitic transformations therefore lead to a reproducible orientation relationship between the parent and product lattices. It frequently is the case that a pair of corresponding close-packed⁴ planes in the ferrite and austenite are parallel or nearly parallel, and it usually is the case that corresponding directions within these planes are roughly parallel:

Kurdjumov-Sachs orientation relationship:

$$\begin{aligned}\{1\ 1\ 1\}_\gamma &\parallel \{0\ 1\ 1\}_\alpha, \\ \langle 1\ 0\ \bar{1} \rangle_\gamma &\parallel \langle 1\ 1\ \bar{1} \rangle_\alpha,\end{aligned}$$

Nishiyama-Wasserman orientation relationship:

$$\begin{aligned}\{1\ 1\ 1\}_\gamma &\parallel \{0\ 1\ 1\}_\alpha, \\ \langle 1\ 0\ \bar{1} \rangle_\gamma &\text{ about } 5.3^\circ \text{ from } \langle 1\ 1\ \bar{1} \rangle_\alpha \text{ towards } \langle \bar{1}\ 1\ \bar{1} \rangle_\alpha,\end{aligned}$$

Greninger-Troiano orientation relationship:

$$\begin{aligned}\{1\ 1\ 1\}_\gamma &\text{ about } 0.2^\circ \text{ from } \{0\ 1\ 1\}_\alpha, \\ \langle 1\ 0\ \bar{1} \rangle_\gamma &\text{ about } 2.7^\circ \text{ from } \langle 1\ 1\ \bar{1} \rangle_\alpha \text{ towards } \langle \bar{1}\ 1\ \bar{1} \rangle_\alpha.\end{aligned}$$

Note that these have been stated approximately: the true relations are irrational, meaning that the indices of the parallel planes and directions cannot be expressed using rational numbers. One consequence is that there will always be 24 crystallographic variants of α' martensite possible in a single grain of austenite.⁵

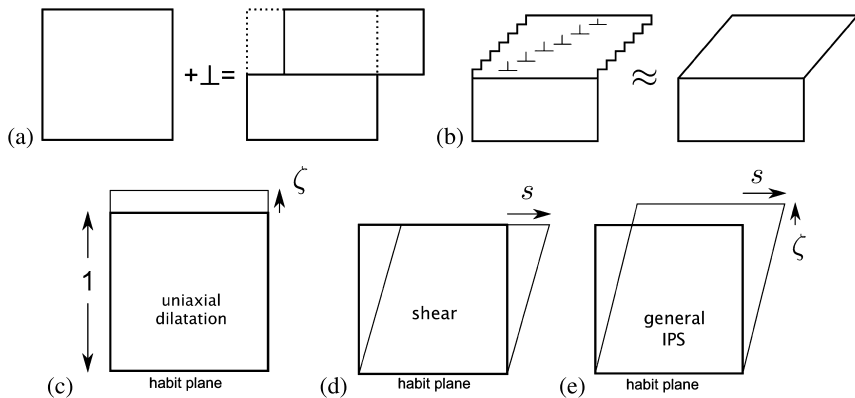


Figure 5.3 (a) Step caused by the passage of a slip dislocation. (b) Many slip dislocations, causing a macroscopic shear. (c) An invariant-plane strain with a uniaxial dilatation. (d) An invariant-plane strain which is a simple shear. (e) An invariant-plane strain which is the combined effect of a uniaxial dilatation and a simple shear.

5.2.3 Structure of the interface

Any process that contributes to the formation of martensite cannot rely on assistance from thermal activation. There must, therefore, exist a high level of continuity across the interface between martensite and austenite. The interface must be coherent or semicoherent; in the latter case, the dislocations in the interface must be able to glide as the martensite grows. It turns out that a stress-free coherent interface cannot be found between austenite and α' -martensite in steel, the best that can be achieved is semicoherency, with one direction within the interface remaining fully coherent. This direction is known as an *invariant-line* since it is unrotated and undistorted.

5.2.4 The shape deformation

The passage of a slip dislocation through a crystal causes the formation of a step where the glide plane intersects the free surface (Fig. 5.3a). The passage of many such dislocations on parallel slip planes causes macroscopic shear (Fig. 5.3b). Slip causes a change in shape but not a change in the crystal structure, because the Burgers vectors of the dislocations are lattice vectors.

During martensitic transformation, the pattern in which the atoms in the parent crystal are arranged is *deformed* into that appropriate for martensite, so there must be a corresponding change in the macroscopic shape of the crystal undergoing transformation. The dislocations responsible for the deformation are in the α'/γ interface, with Burgers vectors such that

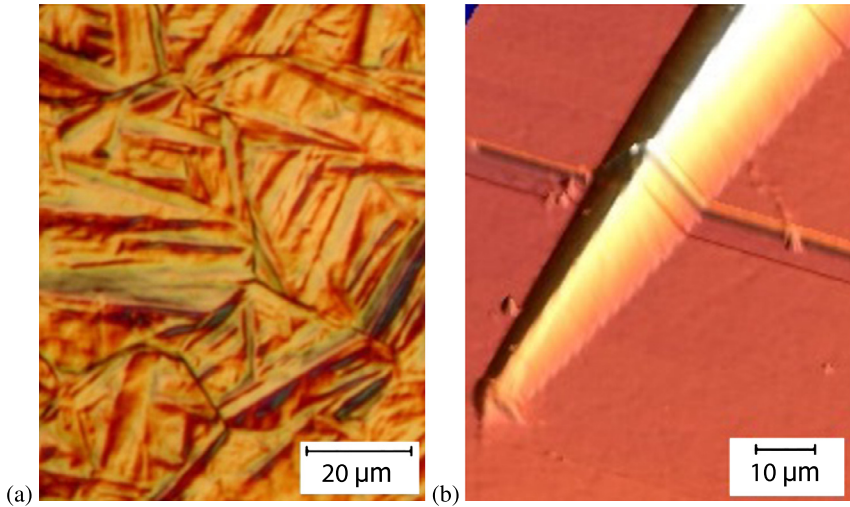


Figure 5.4 Samples of steel polished flat followed by transformation into martensite. (a) Normarsky interference contrast due to a large fraction of martensitic transformation in a low alloy steel. (b) Atomic force microscope image showing the upheavals caused by transformation, together with the shear displacement of scratches. Notice that the scratches are continuous across the habit plane, showing that there is no expansion in that plane. The regions surrounding the martensite is untransformed austenite. Image courtesy of Stefan Forsik.

in addition to deformation they also cause the change in crystal structure. The deformation is such that an initially flat surface, on a macroscopic scale, becomes uniformly tilted about the line formed by the intersection of the interface plane with the free surface. Any scratch traversing the transformed region is similarly deflected though the scratch remains connected at the α'/γ interface. These observations, and others, confirm that the measured shape deformation belongs to a class of deformations known as invariant plane strains (Figs 5.3c–e), with martensite being the most general case in this class with a combined shear (s) and dilatational strain (ζ), the latter being directed normal to the habit plane.

Evidence that the transformation involves large shears can easily be obtained by polishing a surface, or better two surfaces at right angles, prior to transformation. After martensite plates form, the surface reveals relief including large shear displacements and any scratches present prior to transformation are themselves displaced (Fig. 5.4). The characteristic surface relief can also be analysed by using two-beam interferometry or atomic force microscopy, and quantitative data obtained from the displacement of

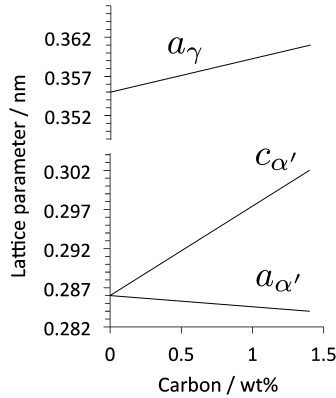


Figure 5.5 Effect of carbon on the lattice parameters of austenite and of martensite. Carbon atoms distributed randomly in the austenite end up on just one sub-lattice of octahedral interstices in the ferrite, causing it to become tetragonal. There are three such interstices per iron atom in ferrite compared with just one per iron atom in austenite.

the fringe patterns or surface contours, respectively. Experiments like these reveal that the shear strain is of the order of $\epsilon \simeq 0.26$ and the dilatational strain normal to the habit plane is typically $\zeta \simeq 0.03$.

5.3 CRYSTAL STRUCTURE OF MARTENSITE

Martensite in steels is a supersaturated solid solution of carbon in ferritic iron. For alloys which have a low martensite-start temperature or a high carbon concentration, the carbon atoms tend to order in such a way that the crystal structure changes from body-centred cubic (bcc) to body-centred tetragonal (bct). The tetragonality of the ordered martensite, measured by the ratio between the axes, $c_{\alpha'}/a_{\alpha'}$, increases with carbon content:

$$\frac{c_{\alpha'}}{a_{\alpha'}} = 1 + 0.045 \text{ wt\% C} \quad (5.3)$$

implying that at zero carbon content the structure would be bcc, free of distortion. The effect of carbon on the lattice parameter of austenite, and on the $c_{\alpha'}$ and $a_{\alpha'}$ parameters of martensite is shown in Fig. 5.5.

It is interesting to note that carbon in interstitial solid solution expands the fcc iron lattice uniformly, but with bcc iron the expansion is non-symmetrical giving rise to tetragonal distortion. To understand this important difference in behaviour, it is necessary to compare the interstitial sites for carbon in the two lattices. In each case, carbon atoms occupy

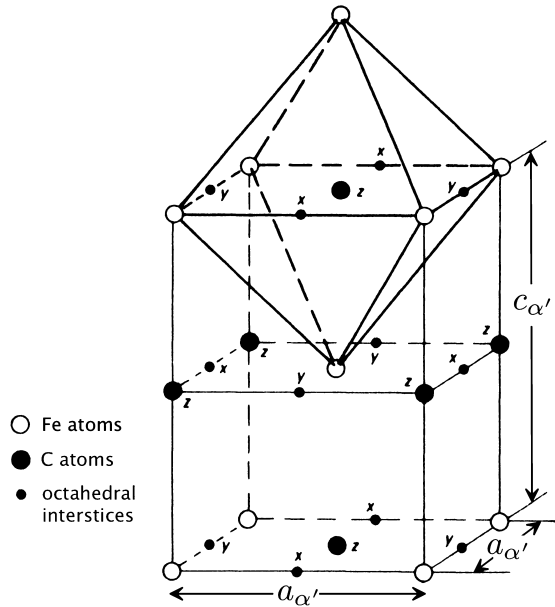


Figure 5.6 Martensite bct lattice illustrating the three sets of octahedral interstices. The z-set is fully occupied by carbon atoms (after Cohen [8]).

octahedral sites, indicated for martensite in black in Fig. 5.6, and have six near-neighbour iron atoms. In the fcc lattice the six iron atoms around each interstitial carbon atoms form a regular octahedron, whereas in the bcc case the corresponding octahedra are not regular, being shortened along the z -axis (Figs 1.4e, f). These compressed octahedra only have four-fold symmetry along the shortened axis in each case, in contrast to the fcc structure in which the regular octahedra have three four-fold axes of symmetry.

Analysis of the distortion produced by carbon atoms in the several types of site available in the fcc and bcc lattices, has shown that in the fcc structure the distortion is completely symmetrical, whereas in the bcc one, interstitial atoms in z positions will give rise to much greater expansion of iron-iron atom distances along z than in the x and y positions.

Assuming that the fcc $\rightarrow$ bcc transformation occurs in a diffusionless way, there is no opportunity for carbon atoms to move. The ferrite contains three octahedral interstices per iron atom whereas the austenite has only one octahedral interstice per iron atom. Each of the three sets of octahedral interstices (the three sublattices) in the ferrite is associated with one of the cube edges of the ferrite unit cell. Upon diffusionless transformation, all

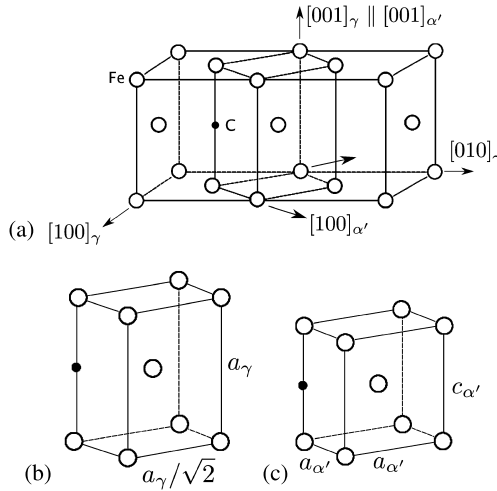


Figure 5.7 The Bain strain. (a) The lattice correspondence for formation of martensite from austenite, showing a single carbon atom in an octahedral interstice on the $[001]_{\gamma}$ axis. (b) Tetragonal unit cell outlined in austenite. (c) Lattice deformation (compression along c -axis) to form martensite with an appropriate c/a ratio.

the carbon atoms in the austenite end up on just one of the octahedral sublattices of ferrite, causing a tetragonal distortion of the bcc lattice into a bct lattice. Thus, in Fig. 5.6, since only the z sites are common to both the fcc and bcc lattices, on transformation the z -axis becomes the c -axis of the tetragonal form.

Therefore, the tetragonality of martensite arises as a direct result of interstitial solution of carbon atoms in the bcc lattice, together with the preference for a particular type of octahedral site imposed by the diffusionless character of the reaction.⁶

5.4 CRYSTALLOGRAPHY OF MARTENSITIC TRANSFORMATIONS

Martensitic transformation is diffusionless so the change in crystal structure is achieved by a homogeneous deformation of austenite. The strain needed to transform the fcc lattice of γ into the bcc or bct lattice of α' was first proposed by Bain in 1924 and hence is known as the 'Bain strain' (Fig. 5.7). There is a compression of about 17% along the $[0\ 0\ 1]_{\gamma}$ corresponding to the c -axis of the martensite cell, and a uniform expansion of about 12% in the $(0\ 0\ 1)_{\gamma}$ plane.

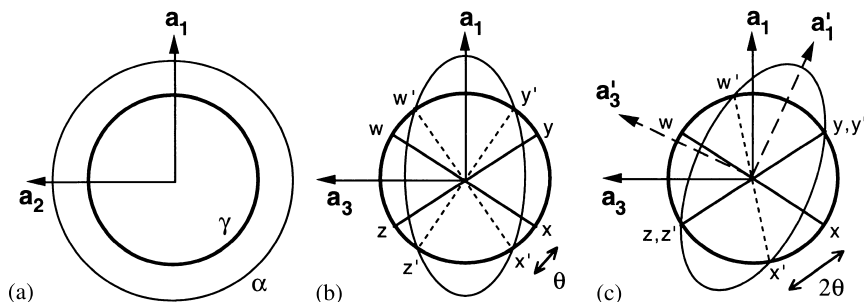


Figure 5.8 (a) and (b) show the effect of the Bain strain on austenite, which when undeformed is represented as a sphere of diameter $wx = yz$ in three-dimensions. The strain transforms it into an ellipsoid of revolution. (c) shows the ILS obtained by combining the Bain strain with a rigid body rotation through an angle θ . $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ refer to $[100]_\gamma$, $[010]_\gamma$ and $[001]_\gamma$ axes respectively.

The Bain strain implies the following orientation relationship between the parent and the product lattices:

$$[0\ 0\ 1]_\gamma \parallel [0\ 0\ 1]_{\alpha'} \quad [1\ \bar{1}\ 0]_\gamma \parallel [1\ 0\ 0]_{\alpha'} \quad [1\ 1\ 0]_\gamma \parallel [0\ 1\ 0]_{\alpha'},$$

but this is inconsistent with the observed orientation relationship which is irrational, and has corresponding closest-packed planes and close-packed directions approximately parallel. The reason is that the Bain strain on its own is not the complete deformation because it is necessary to ensure a high degree of coherency in the interface. It is a requirement that the deformation which changes austenite into martensite must leave one line fully coherent, i.e. it must be unrotated and undistorted, an invariant line. Such a deformation is said to be an invariant-line strain (ILS).

In Figs 5.8a, b, the austenite is represented as a sphere which, as a result of the Bain strain $\mathbf{B}$, is deformed into an ellipsoid of revolution which represents the martensite. There are no lines which are left undistorted or unrotated by $\mathbf{B}$. The lines wx and yz are undistorted but are rotated to the new positions $w'x'$ and $y'z'$. Such rotated lines are not invariant. However, the combined effect of the Bain strain $\mathbf{B}$ and the rigid body rotation $\mathbf{R}$ is indeed an ILS because it brings yz and $y'z'$ into coincidence (Fig. 5.8c). This is the reason why the observed irrational orientation relationship differs from that implied by the Bain strain. Indeed, the rotation required to convert $\mathbf{B}$ into an ILS precisely corrects the Bain orientation into that which is observed experimentally.

There remains a further discrepancy. As can be seen from Fig. 5.8c, there is no rotation which can make $\mathbf{B}$ into an invariant-plane strain since

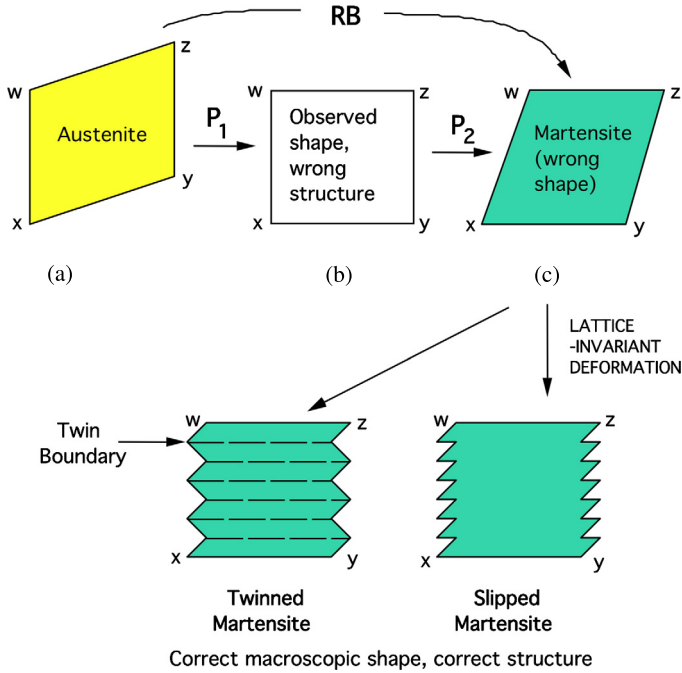


Figure 5.9 The phenomenological theory of martensite crystallography.

this would require two non-parallel invariant lines. It follows that austenite cannot be transformed into martensite by a homogeneous strain which leaves a plane invariant. And yet, the observed shape deformation leaves the habit plane undistorted and unrotated, i.e. it is an invariant-plane strain.

The phenomenological theory of martensite crystallography elegantly solves this remaining problem (Fig. 5.9). The Bain strain converts the structure of the parent phase into that of the product phase. When combined with an appropriate rigid body rotation, the net homogeneous lattice deformation **RB** is an ILS (step *a* to *c* in Fig. 5.9). However, the observed shape deformation is an invariant-plane strain **P₁** (step *a* to *b* in Fig. 5.9), but this gives the wrong crystal structure. If a second homogeneous shear **P₂** is combined with **P₁** (step *b* to *c*), then the correct structure is obtained but the wrong shape since:

$$\mathbf{P}_1 \mathbf{P}_2 = \mathbf{RB}. \quad (5.4)$$

These discrepancies are all resolved if the shape changing effect of **P₂** is cancelled macroscopically by an inhomogeneous lattice-invariant deformation, which may be slip or twinning as illustrated in Fig. 5.9.

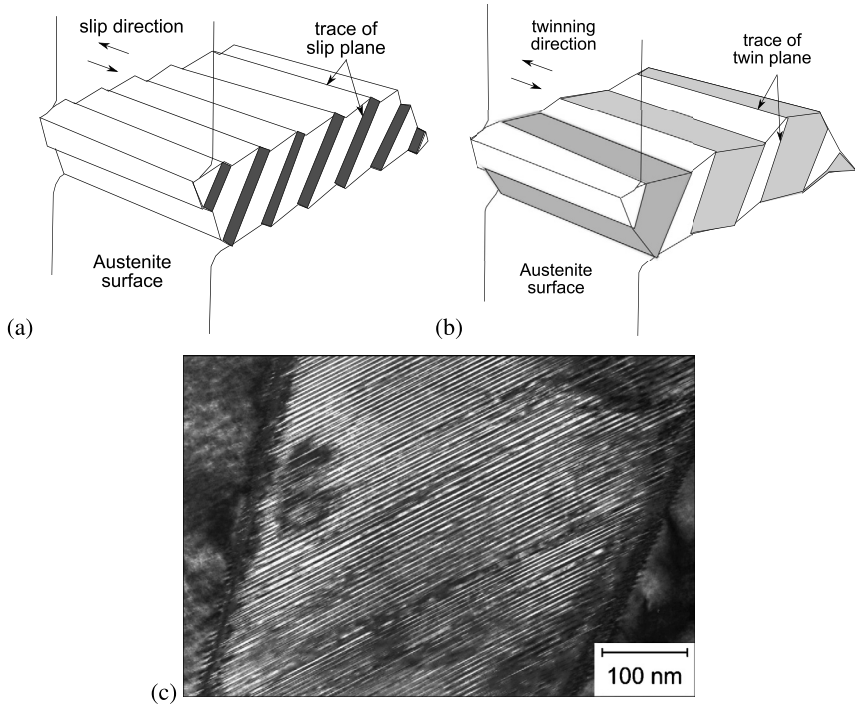


Figure 5.10 Formation of martensite plate, illustrating schematically, two types of lattice deformation. The broad faces in these schematics represent the habit planes: (a) slip and (b) twinning (adapted from Christian [10]). (c) Transmission electron micrograph showing a finely twinned plate of martensite in Fe-22Ni-20Co-0.6C wt% steel. Micrograph courtesy of A. Shibata and T. Maki.

The theory explains all the observed features of the martensite crystallography. The orientation relationship is predicted by deducing the rotation needed to change the Bain strain into an ILS. The habit plane does not have rational indices because the amount of lattice-invariant deformation needed to recover the correct macroscopic shape is not usually rational. The theory predicts a substructure in plates of martensite (either twins or slip steps) as is observed experimentally. The transformation goes to all the trouble of ensuring that the shape deformation is macroscopically an invariant-plane strain because this reduces the strain energy when compared with the case where the shape deformation might be an ILS.

Fig. 5.10 shows schematically the two types of lattice invariant deformation occurring within a martensite plate. It should be noted that the block of martensite formed has produced a surface tilt and that the ob-

served habit is preserved by the accommodation provided by either slip (Fig. 5.10a) or twinning (Fig. 5.10b). The result is a macroscopically planar interface which would clearly have irregularities on a very fine scale.

The above theoretical approach had considerable success in predicting the observed habit planes, the orientation relationships between matrix and the martensite, as well as the shape deformation for a number of martensitic transformations including ferrous martensites. It is, however, necessary to have accurate data, so that the habit planes of individual martensite plates can be directly associated with a specific orientation relationship of the plate with the adjacent matrix. For example, Greninger and Troiano used an iron-22 nickel-0.8 wt% carbon alloy in which austenite was retained in association with martensite to predict successfully the correct habit plane, which in this alloy is an irrational plane near $\{3\ 10\ 15\}_\gamma$, and also the shape change and the orientation relationship between martensite and austenite.

An important point to note from Equation (5.4) is that the shape deformation, habit plane and the orientation relationship are uniquely mathematically connected. In other words, it is not in general possible for two plates to have the same habit plane but different shape deformations, etc.

5.5 MORPHOLOGY OF FERROUS MARTENSITES

The two-shear theory of martensite formation was first confirmed by crystallographic measurements on the two phases, but the existence of the inhomogeneous lattice invariant deformation could only be directly established by microscopic examination. Examination of a number of non-ferrous martensite transformations in the optical microscope revealed that the martensite lamellae contained numerous very fine twins in uniform arrays. For example, the martensite reaction in the indium-thallium system has some similar characteristics to ferrous martensites in so far as the transformation is from fcc to a tetragonal lattice (face-centred). The martensitic lamellae are very uniform, and contain fine twins on a single variant $\{101\}$ $\langle 10\bar{1} \rangle$ in one lamella.

Martensitic plates in steel are frequently not parallel sided, instead they are lenticular as a result of constraints in the matrix which oppose the shape change resulting from the transformation. This is one of the reasons why it is difficult to identify precisely the habit planes in ferrous martensite. However, it is not responsible for the irrational planes, but rather the scatter obtained in experiments. Another feature of higher carbon martensites is the burst phenomenon, in which one martensite plate nucleates a sequence

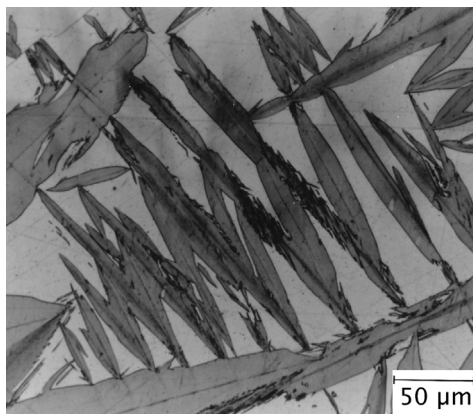


Figure 5.11 Lenticular martensite illustrating the burst phenomenon in a nickel-rich steel.

of plates presumably as a result of stress concentrations set up when the first plate reaches an obstruction such as a grain boundary or another martensite plate (Fig. 5.11).

Perhaps the most striking advances in the structure of ferrous martensites occurred when thin-foil electron microscopy was first used on this problem. The two modes of plastic deformation needed for the inhomogeneous deformation part of the transformation, i.e. slip and twinning, were both observed by Kelly and Nutting. Most ferrous martensites show very high dislocation densities of the order of 10^{11} – 10^{12} cm⁻², Fig. 5.12b, which are similar to those of very heavily cold-worked alloys. Thus, it usually is impossible to analyse systematically the planes on which the dislocations occur or determine their Burgers vectors.

The lower carbon (<0.5 wt% C) martensites on the whole exhibit only dislocations. At higher carbon levels very fine twins (5–10 nm wide) commonly occur (Fig. 5.10c). The twinning plane is $\{112\}_{\alpha'}$ derived from $\{110\}_{\gamma}$, and the twinning direction is $\{111\}_{\alpha'}$ corresponding to the $\{110\}_{\gamma}$ direction. In favourable circumstances the twins can be observed in the optical microscope, but the electron microscope allows the precise identification of twins by the use of the selected area electron diffraction technique. Thus the twin shears can be analysed precisely and have provided good evidence for the correctness of the crystallographic theories discussed above. However, twinning is not always fully developed and even within one plate some areas are often untwinned. The phenomenon is sensitive to composition.

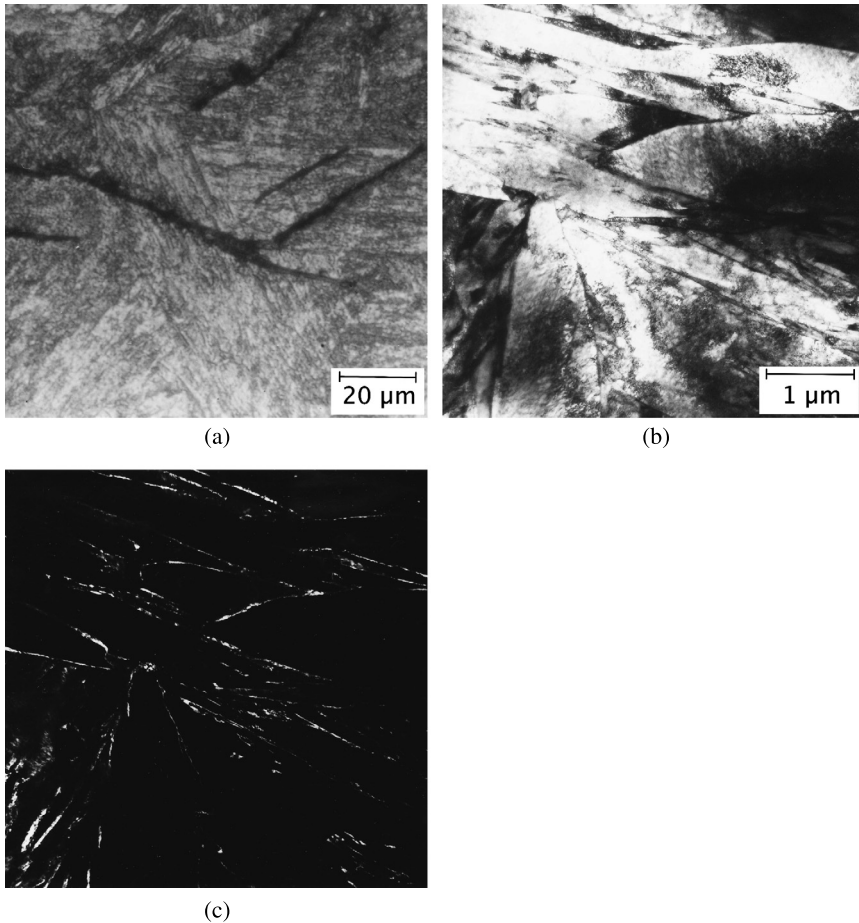


Figure 5.12 A Fe-4Mo-0.2C wt% steel austenitised and quenched into a martensitic microstructure. (a) Optical micrograph of a sample containing cracks. (b) Bright field transmission electron micrograph. The mottled contrast is due to the presence on a large density of dislocations in the martensite. (c) Corresponding dark-field image showing films of retained austenite around the martensite laths (after Bhadeshia [11]).

The evidence suggests that deformation by dislocations and by twinning are alternative methods by which the lattice invariant deformation occurs. Twinning is never the favoured mode from a thermodynamic point of view due to the cost of the twin interfaces. However, the transformation interface between internally twinned martensite and austenite is likely to be more glissile and hence favoured on a kinetic basis when the transformation is rapid [12].

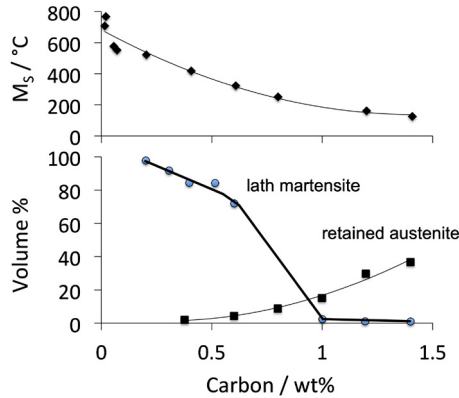


Figure 5.13 Effect of carbon content on the type of martensite and the amount of retained austenite in Fe-C alloys. The plate martensite is simply the total less the laths and retained austenite (adapted from Speich and Leslie [13]).

The morphological and crystallographic characteristics are particularly sensitive to the carbon concentration. Low carbon martensite has a habit plane that is close to $\{111\}_\gamma$ and is found in plain carbon and low alloy steels containing up to about 0.5 wt% carbon. The morphology is lath- or plate-like (Fig. 5.12), where the laths are long and about $0.5\ \mu\text{m}$ wide. These are grouped together in packets with low-misorientation boundaries between each lath, although a minority of laths are separated by high angle boundaries.

At higher carbon concentrations the plates of martensite become more lenticular with habit planes close to $\{225\}_\gamma$, $\{3\ 10\ 15\}_\gamma$ or $\{259\}_\gamma$ (Fig. 5.11). The plates are rather well defined because their shape strains are essentially elastically accommodated at the low M_s temperatures where the parent phase is stronger. Fig. 5.13 shows how the amount of lath martensite decreases relative to the plate form as the carbon concentration is increased and the transformation temperature is reduced. The amount of retained austenite obviously increases with the carbon concentration so the plates of martensite are well-defined when observed using optical microscopy. This is in contrast to the laths in high M_s alloys where the transformation leaves little retained austenite (Equation (5.2)); as a consequence, the individual laths of martensite end up with shapes that are space-filling, determined by physical impingement with other laths.

5.6 KINETICS OF MARTENSITIC TRANSFORMATION

Martensitic transformations are usually described as athermal, since transformation commences at a well-defined temperature M_S , but for transformation to continue the temperature must continue to fall until M_F is reached when the reaction is considered complete. However, there are martensitic reactions which can proceed at constant temperature (e.g. Fig. 5.1).

5.6.1 Nucleation of martensite

Phase and chemical composition fluctuations can occur as random events due to the thermal vibration of atoms. An individual fluctuation may or may not be associated with a reduction in free energy, but it can only survive and grow if there is this reduction beyond its embryonic size. There is a cost associated with the creation of a new phase, the interfacial energy, a penalty which becomes smaller as the particle surface to volume ratio decreases. In a metastable system this leads to a critical size of fluctuation beyond which growth is favoured.

Consider the homogeneous nucleation of martensite from the parent austenite by the classical heterophase fluctuation mechanism. For a spherical particle of radius r with an isotropic interfacial energy $\sigma_{\alpha'\gamma}$, the change in free energy as a function of radius is:

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_{\text{chem}} + \frac{4}{3}\pi r^3 \Delta G_{\text{strain}} + 4\pi r^2 \sigma_{\alpha'\gamma}, \quad (5.5)$$

where $\Delta G_{\text{chem}} = G_V^{\alpha'} - G_V^{\gamma}$, G_V is the Gibbs free energy per unit volume of α' and G_{strain} is the strain energy per unit volume of α' . The activation barrier and critical size obtained using Equation (5.5) are given by:

$$G^* = \frac{16\pi\sigma_{\alpha'\gamma}^3}{3(\Delta G_{\text{chem}} + \Delta G_{\text{strain}})^2} \quad \text{and} \quad r^* = -\frac{2\sigma_{\alpha'\gamma}}{\Delta G_{\text{chem}} + \Delta G_{\text{strain}}}. \quad (5.6)$$

The important outcome is that in classical nucleation the activation energy varies inversely with the square of the driving force. And the mechanism involves random phase fluctuations. It is questionable whether this applies to cases where thermal activation is in short supply. In particular, an activation barrier must be very small indeed if the transformation is to occur at a proper rate at low temperatures – and martensite can form at incredibly low temperatures.

One mechanism in which the barrier becomes sufficiently small involves the spontaneous dissociation of specific dislocation defects which

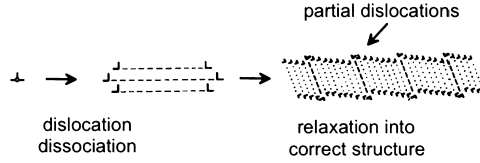


Figure 5.14 Olson and Cohen model for the nucleation of α' martensite. A perfect dislocation $\frac{a_\gamma}{2} \langle 110 \rangle$ undergoes three dimensional dissociation over a set of three close-packed planes. This faulted structure is not yet that of martensite. The fault set then relaxes to a body-centred cubic structure with the introduction of partial dislocations in the interface. Additional lattice-invariant deformations, not illustrated here, occur when the nucleus grows sufficiently large so that it becomes necessary to cancel the long range strain fields of the partial dislocations.

already are present in the parent phase [14,15]. The dislocations are glissile so the mechanism does not require diffusion. The only barrier is the resistance to the glide of the dislocations. The nucleation event cannot occur until the undercooling is sufficient to support the faulting and strains associated with the dissociation process that leads to the creation of the new crystal structure, Fig. 5.14.

The free energy per unit area of fault plane is:

$$G_F = n_\gamma \rho_A (\Delta G_{\text{chem}} + G_{\text{strain}}) + 2\sigma_{\alpha'\gamma} \{n_\gamma\}, \quad (5.7)$$

where n_γ is the number of close-packed planes participating in the faulting process, ρ_A is the spacing of the close-packed planes on which the faulting is assumed to occur. The fault energy can become negative when the austenite becomes metastable.

For a fault bounded by an array of n_γ dislocations each with a Burgers vector of magnitude b , the force required to move a unit length of dislocation array is $n_\gamma \tau_0 b$. τ_0 is the shear resistance of the lattice to the motion of the dislocations. G_F provides the opposing stress via the chemical free energy change ΔG_{chem} ; the physical origin of this stress is the fault energy which becomes negative so that the partial dislocations bounding the fault are repelled. The defect becomes unstable, i.e., nucleation occurs, when

$$G_F = -n_\gamma \tau_0 b. \quad (5.8)$$

Take the energy barrier between adjacent equilibrium positions of a dislocation to be G_o^* . An applied shear stress τ has the effect of reducing the height of this barrier [16,17]:

$$G^* = G_o^* - (\tau - \tau^*) v^* \quad (5.9)$$

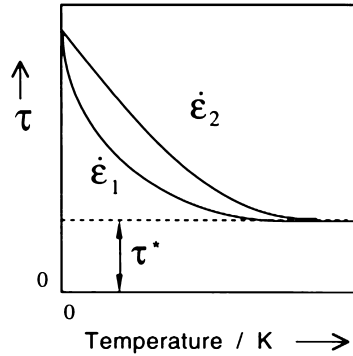


Figure 5.15 Temperature dependence of the applied stress necessary to move a dislocation at two different strain rates ($\dot{\epsilon}_2 > \dot{\epsilon}_1$). τ^* is the athermal resistance which never vanishes (after Conrad [16]).

where ν^* is an activation volume and τ^* is the temperature independent resistance to dislocation motion (Fig. 5.15, Equation (2.1)). In the context of nucleation, the stress τ is not externally applied but comes from the chemical driving force. On combining the last three equations we obtain

$$G^* = G_o^* + \left[\tau^* + \frac{\rho_A}{b} G_{\text{strain}} + \frac{2\sigma}{n_\gamma b} \right] \nu^* + \frac{\rho_A \nu^*}{b} \Delta G_{\text{chem}}. \quad (5.10)$$

It follows that with this model of nucleation the activation energy G^* will decrease *linearly* as the magnitude of the driving force ΔG_{chem} increases. This direct proportionality contrasts with the inverse square relationship of classical theory.

5.6.2 Growth of martensite

Martensitic transformation is diffusionless. We have seen that the interface between martensite and austenite has sufficient of the right kind of coherency to enable it to move without the need for diffusion (section 5.2.3). In other words, the dislocations in the interface can glide without a need for climb. As for the ordinary dislocations involved in slip deformation, the α'/γ interface can glide at speeds limited by that of sound in the metal. The growth of martensite plates has been measured in a Fe-Ni alloy to occur at speeds in excess of 1000 m s^{-1} [5]. But it is emphasised that it need not occur so rapidly if processes such as plastic relaxation damp the growth, or during stress-induced transformations where the driving force for transformation can be small.

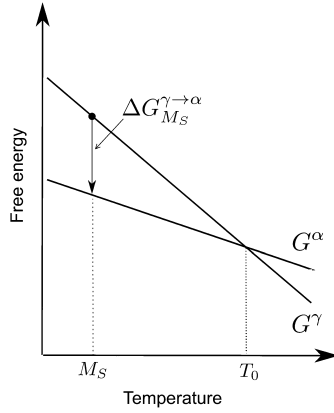


Figure 5.16 An illustration of the driving force $G^\alpha - G^\gamma$ for the transformation of austenite into ferrite of the same chemical composition. This driving force must reach a critical value $\Delta G_{M_S}^{\gamma \rightarrow \alpha}$ at the martensite-start temperature. T_0 is the temperature at which the austenite and ferrite of identical composition have the same free energy. $G^\alpha - G^\gamma$ is negative below T_0 and positive above it.

The rate at which the transformation interface moves is given by [18,19]

$$v_i = v_0 \exp \left\{ -\frac{Q}{kT} \right\} \quad (5.11)$$

where the pre-exponential factor v_0 is a limiting velocity when the activation energy Q is zero, and k is the Boltzmann factor. The interface is defined by its dislocation structure and these dislocations will encounter resistance to their motion such that

$$Q = Q_0 \left(1 - \sqrt{\frac{G_{id}}{G_{id}^*}} \right) \quad (5.12)$$

where Q_0 is that activation free energy necessary to overcome the resistance to dislocation motion with the help of an interfacial driving force G_{id} . The chemical driving force for transformation is illustrated in Fig. 5.16 and the magnitude of G_{id} will be less than that of $\Delta G^{\gamma \rightarrow \alpha} = G^\alpha - G^\gamma$ to allow for the stored energy of martensite.⁷ G_{id}^* represents the maximum glide resistance presented by obstacles to dislocation motion. The velocity of the α'/γ interface will clearly be greater when the driving force is large. In some cases the martensite forms so rapidly that recalescence occurs; the resulting heating of the sample then reduces the driving force, leading to a corresponding decrease in the interfacial velocity. Since the lattice invariant deformation favoured at high velocities is twinning, the early portion of

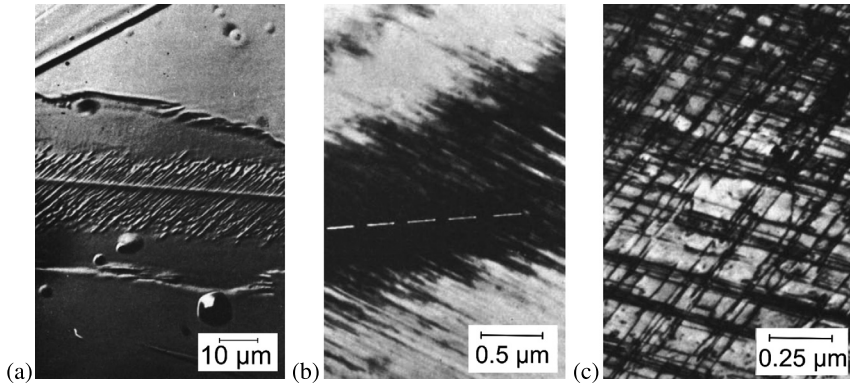


Figure 5.17 The change in the mode of lattice invariant deformation from twinning to slip as a plate of martensite heats up due to the rapid release of the heat of transformation. (a) Optical micrograph showing the twin emanating from the central spine of the plate. (b) Transmission electron micrograph of transformation twins in the central region of the plate. (c) Transmission electron micrographs showing the slip dislocations at the peripheries of the plate. After Patterson and Wayman [20].

the martensite plate has twins but this transitions into slip as the plate grows and interfacial velocity decreases due to recalescence, Fig. 5.17 [20].

A typical elastic strain in a typically stressed metal has a magnitude of 10^{-3} , whereas the transformation strain when a plate of α' -martensite grows in steel is as large as $s = 0.26$ and $\zeta = 0.03$. Given such large strains, the plates of martensite can only be accommodated elastically if the following conditions are satisfied:

1. The austenite is mechanically strong, i.e. has a high yield strength.
2. The austenite has a low elastic modulus because this would permit a larger elastic strain to be accommodated prior to yielding. In some materials, the elastic modulus softens dramatically as the martensite-start temperature is approached.
3. The thickness to length ratio (c/r) of the plate is small because the elastic strain energy per unit volume of martensite scales with this ratio [21]:

$$G_{\text{strain}} \approx \mu \frac{c}{r} (s^2 + \zeta^2). \quad (5.13)$$

In general, ordinary steels do not satisfy these criteria because the M_S temperature tends to be well above ambient so that the austenite is mechanically weak. There will then be a plastic zone around the martensite plate [22,23]. A plate of martensite lengthens until it hits a barrier such as an austenite grain boundary, and then continues to thicken until G_{strain} can no longer

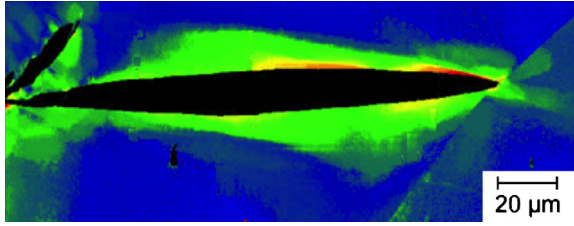


Figure 5.18 A plate of martensite (black) and the crystallographic orientation changes caused in its surrounding austenite due to the plastic accommodation of the shape deformation. The region of austenite far from the plate (blue) is unaffected (after Miyamoto et al. [23], reproduced with permission of Elsevier).

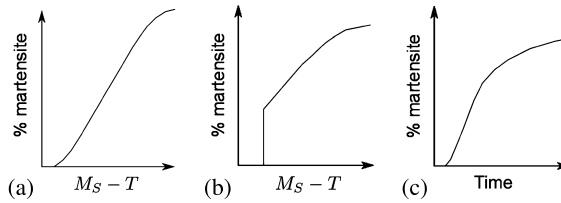


Figure 5.19 Transformation curves for martensite: (a) athermal transformation; (b) athermal with bursts; (c) isothermal transformation (adapted from Christian [10]).

be supported by the chemical driving force. The plastic zone in the austenite typically is much greater in extent than the thickness of the plate, as illustrated in Fig. 5.18.

5.6.3 Overall athermal-transformation kinetics

Looking at the kinetics of martensite formation in broad terms, there are three different types of behaviour which can take place (Fig. 5.19). The first type involves normal athermal transformations with a sigmoidal type of curve where the fraction of austenite transformed is a function solely of the temperature (Fig. 5.19a). This follows approximately the Koistinen and Marburger Equation (5.2), the fundamental basis for which was derived by Magee [24] on the basis of experimental observations that the change in the number of new martensite plates per unit volume of austenite number is proportional to the imposed change in the driving force for transformation:

$$dN_V' = -\phi d(|\Delta G^{\gamma \rightarrow \alpha}|). \quad (5.14)$$

The resulting change in the volume fraction transformed is therefore

$$dV_V^{\alpha'} = \bar{V} dN_V \quad (5.15)$$

where $dN_V = (1 - V_V^{\alpha'})dN_V^{\gamma}$ is the change in the number of plates per unit volume of sample, and $\bar{V}$ is the volume per plate of martensite (assumed constant). It follows that

$$dV_V^{\alpha'} = -\bar{V}(1 - V_V^{\alpha'})\phi \frac{d|\Delta G^{\gamma \rightarrow \alpha}|}{dT} dT. \quad (5.16)$$

On integration between appropriate limits, this gives the familiar form of the Koistinen and Marburger Equation (5.2),

$$1 - V_V^{\alpha'} = \exp \left\{ \bar{V} \phi \left(\frac{d|\Delta G^{\gamma \rightarrow \alpha}|}{dT} \right) (M_S - T_Q) \right\} \quad \text{with} \quad T_Q \leq M_S. \quad (5.17)$$

This analysis gives insight into why this kind of transformation is essentially athermal – the time dependence of rapid growth is neglected by assuming that each plate transforms a fixed amount of austenite. Similarly, there is no nucleation rate as such, rather the number of new plates stimulated is related to the undercooling below M_S . This indicates that there is a potency distribution of embryos that eventually evolve into plates [25,26]. The embryos usually represent different configurations of dislocation clusters.

The second type also involves athermal transformation, but the reaction commences suddenly with a burst phenomenon which effectively causes a proportion of the austenite to transform isothermally (Fig. 5.19b). This occurs because the formation of an initial plate stimulates many others by a process known as *autocatalysis*; the stimulated plates are those which are oriented such that the stress induced by the original plate aids its formation [27]. One such example is illustrated in Fig. 5.11 where the zig-zag array of mutually accommodating plates is clear. Further transformation is again athermal in character.

Finally, with true isothermal transformation (Fig. 5.19c) the proportion of austenite transformed is related to time at a given temperature. The rate of isothermal reaction can be described using the overall transformation kinetics theory outlined in section 3.6.5 if the nucleation and growth functions are known. The isothermal form of martensite is most frequently observed in interstitial-free iron alloys (e.g. [28]) but also in steels (e.g. [29]).

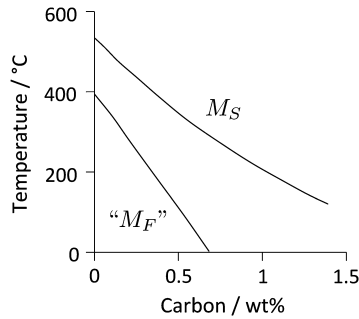


Figure 5.20 The effect of carbon on the martensite-start (M_S) and martensite-finish (M_F) temperatures. The latter is not well defined but can be set to correspond to an arbitrary 95% of transformation. Data from Petty [30].

5.6.4 Effect of alloying elements

Most alloying elements which enter into solid solution in austenite lower the M_S temperature, with the exception of cobalt and aluminium. However, the interstitial solutes carbon and nitrogen have a much larger effect than the metallic solutes. The effect of carbon on both M_S and M_F is shown in Fig. 5.20, from which it can be seen that 1 wt% of carbon lowers the M_F by over 300°C. Note that above 0.7 wt% C the M_F temperature is below room temperature and consequently higher carbon steels quenched into water will normally contain substantial amounts of retained austenite.

The relative effect of other alloying elements is indicated in the following empirical relationship due to Andrews [31]:

$$M_S(^{\circ}\text{C}) = 539 - 423w_{\text{C}} - 30.4w_{\text{Mn}} - 17.7w_{\text{Ni}} - 12.1w_{\text{Cr}} - 7.5w_{\text{Mo}}, \quad (5.18)$$

where w_i represents the weight percent of the element identified by the subscript and the limits of the data on which this equation is based are:

	C	Mn	Si	Ni	Cr	Mo
Minimum / wt%	0.11	0.20	0.11	0.00	0.00	0.00
Maximum / wt%	0.55	1.67	1.74	5.04	3.34	1.00

The uncertainty with relationships such as Equation (5.18) is about $\pm 20^{\circ}\text{C}$, which is associated largely with the noise in conducting experiments that measure the M_S temperature [1].⁸ The assumption that M_S is a linear function of solute concentrations may not be justifiable, and more complex expressions that involve products of concentrations are certainly arbitrary; neural network methods are much better in this respect because the non-linear functions appropriate to represent variations in data are de-

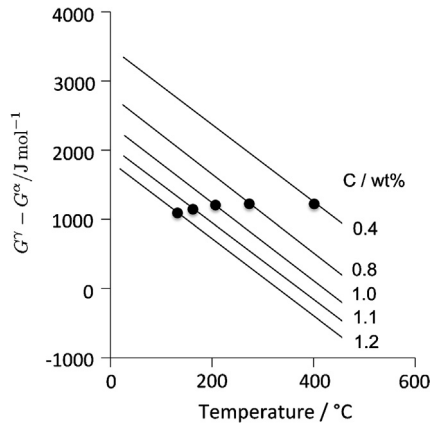


Figure 5.21 Free energy change for the austenite-martensite reaction as a function of temperature and carbon content. The points represent the measured M_S temperatures. Data from Kaufman and Cohen [36].

rived rather than assumed [1]. It is not surprising therefore, that the gradient of the curve in Fig. 5.20 is different from that implied by Equation (5.18), since the relationship between M_S and carbon is not independent of the other solutes.

A better approach is to express M_S in a thermodynamic framework since the influence of solutes on the chemical driving force $\Delta G^{\gamma \rightarrow \alpha}$ is well established and easily calculated using standard thermodynamic databases. Martensite is said to be triggered when this driving force reaches a critical value $\Delta G_{M_S}^{\gamma \rightarrow \alpha}$ (Fig. 5.16). This typically is -1000 J mol^{-1} as illustrated in Fig. 5.21 for iron-carbon alloys. More detailed studies have shown that the critical value depends also on the substitutional solute content [32,33], via the dependence of the strength of austenite on its total solute content [34]. The reason why a large driving force is required before martensite forms is partly the stored energy that has to be accounted for, consisting of the following terms:

- The strain energy due to the shape deformation, about 600 J mol^{-1} . There is also dislocation debris created by the plastic accommodation of the shape deformation, but since this is created by the deformation, it is not an additional term to be added to the 600 J mol^{-1} [35].
- The energy due to the creation of twin interfaces, about 100 J mol^{-1} .
- The α'/γ interfacial energy per unit volume of a plate of martensite, which is a large term at the nucleation stage but becomes negligible at about 1 J mol^{-1} for a fully established plate.

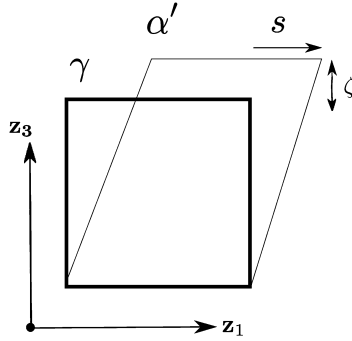


Figure 5.22 Coordinate axes defined by the unit vectors $\mathbf{z}_i$ ($i = 1, 2, 3$) for the derivation of the deformation matrix representing martensitic transformation (α') from austenite (γ).

5.6.5 Stress-induced transformation

Martensitic transformation is also a deformation, described accurately as an invariant-plane strain with a shear s on the habit plane, and a dilatation ζ normal to that plane, Fig. 5.22. Given the orthonormal coordinate system Z defined by the unit vectors $\mathbf{z}_1$ parallel to the direction of shear, and $\mathbf{z}_3$ normal to the habit plane, the deformation matrix $\mathbf{P}$ becomes⁹:

$$\begin{pmatrix} Z & \mathbf{P} & Z \end{pmatrix} = \begin{pmatrix} 1 & 0 & s \\ 0 & 1 & 0 \\ 0 & 0 & 1 + \zeta \end{pmatrix}. \quad (5.19)$$

The effect of the deformation on any vector $\mathbf{u}$ to produce a resultant vector $\mathbf{v}$ is then given by

$$\begin{pmatrix} Z & \mathbf{P} & Z \end{pmatrix} [Z; \mathbf{u}] = [Z; \mathbf{v}]. \quad (5.20)$$

The two vectors will not in general be parallel, but a comparison of the magnitudes gives an impression of the strain expected due to martensitic transformation.

This calculation of strain is along a specific direction $\mathbf{u}$, due to the shape deformation associated with the formation of a plate of martensite. In dealing with TRIP steels, the problem needs to be posed somewhat differently, i.e., what is the strain along a particular direction when a stress is applied to induce martensitic transformation in an otherwise stable austenite. It is necessary therefore to consider the thermodynamics of stress-affected martensitic transformation. Fig. 5.23 shows that in the absence of external

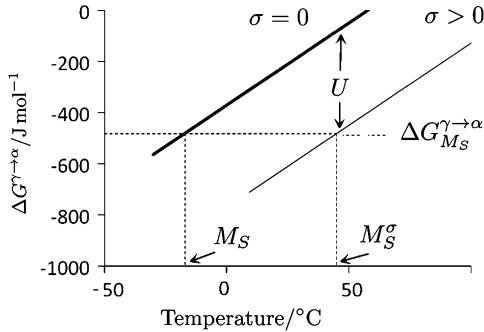


Figure 5.23 Plot of the chemical driving force for martensitic transformation against temperature, with σ representing the applied stress.

stress ($\sigma = 0$), the martensite–start temperature M_S is defined by the temperature at which the free energy change $\Delta G^{\gamma \rightarrow \alpha}$ when austenite decomposes into ferrite of the same composition, reaches a critical value $\Delta G_{M_S}^{\gamma \rightarrow \alpha}$.

In contrast, when transformation occurs under the influence of a stress, the latter interacts with the shape deformation and the interaction energy U is given by [39] to be:

$$U = \tau_r s + \sigma_N \zeta, \quad (5.21)$$

where τ_r is the shear stress on the habit plane and σ_N the stress normal to that plane. Notice that the strains involved are plastic, so the interaction energy is given simply by the product of the stress and strain, rather than half that value as is sometimes assumed on the basis of elastic strains. If the stress is such that it favours the formation of martensite then U supplements $\Delta G^{\gamma \rightarrow \alpha}$ and the martensite–start temperature is raised to M_S^σ which is above ambient temperature, so that stress-induced martensitic transformation becomes feasible (Fig. 5.23).

Each single crystal of austenite can in principle transform into 24 different crystallographic variants of α' -martensite. Each of these variants is associated with a particular value of U depending on its orientation relative to the applied stress. Therefore, those variants with the largest interaction with the stress, i.e., which transform in a manner that relieves the stress, are favoured. This process is known as *variant selection* so that stress-induced martensite results in a biased microstructure with reduced variety. This is illustrated in Fig. 5.24, where the martensite is generated by applying a tensile stress to polycrystalline metastable austenite, resulting in plates which are approximately at 45° to the tensile axis.

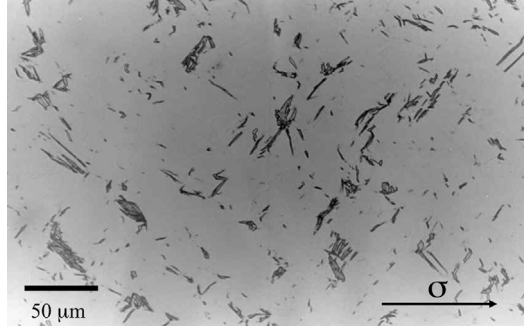


Figure 5.24 A non-random distribution of martensite habit-plane orientations produced by stress-induced martensitic transformation at a temperature between M_S and M_S^σ . The sample is polycrystalline austenite with a grain size of about $30\ \mu\text{m}$.

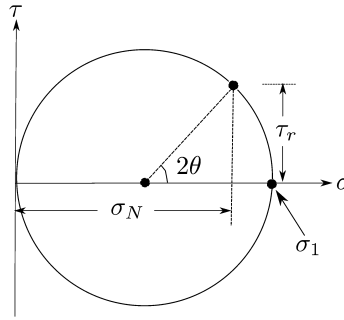


Figure 5.25 Mohr's circle representation of the shear and normal stresses on a habit plane normal inclined at θ to the tensile stress σ_1 .

Assuming that a tensile stress σ_1 is applied, inclined at an angle θ to the habit plane normal, with the stress axis in the plane containing $\mathbf{z}_1$ and $\mathbf{z}_3$, then from Equation (5.21) and the Mohr's circle representation in Fig. 5.25,

$$U = \underbrace{\frac{\sigma_1}{2} \sin 2\theta \times s}_{\tau_o} + \underbrace{\frac{\sigma_1}{2} (1 + \cos 2\theta) \times \zeta}_{\sigma_N},$$

$$\frac{dU}{d\theta} = \frac{\sigma_1}{2} [2s \cos 2\theta - 2\zeta \sin 2\theta]. \quad (5.22)$$

Setting the differential to zero to obtain the maximum value of U is at $\tan 2\theta_{\max} = s/\zeta$, which for typical values of $s = 0.26$ and $\zeta = 0.03$ gives $\theta_{\max} = 46.3^\circ$. Given that there are 24 habit plane orientations within a single austenite grain, it is likely that one close to this value will form first, hence explaining the observation of aligned plates in Fig. 5.24 even though the

sample has many orientations of austenite grains. The tensile axis can be represented as a unit vector

$$[Z; \mathbf{u}] = [\sin \theta_{\max} \quad 0 \quad \cos \theta_{\max}]$$

and using $\theta = 46^\circ$, the elongation obtained along the tensile axis when a single crystal of austenite transforms completely into the most favoured orientation of martensite is, using Equation (5.20), given by:

$$[Z; \mathbf{v}] = [(\sin \theta_{\max} + s \cos \theta_{\max}) \quad 0 \quad (1 + \zeta) \cos \theta_{\max}],$$

$$\% \text{ elongation} = \left(1 - \frac{|\mathbf{v}|}{|\mathbf{u}|} \right) \times 100.$$

This assumes that $\mathbf{v}$ is parallel to $\mathbf{u}$ and a correction would be needed if there is a relative rotation. The elongation due to phase transformation is therefore calculated to be 15% [40]. This impressive value of elongation due to phase transformation alone supplements that due to ordinary dislocation plasticity, which can be a significant boon to the design of strong steels which usually suffer from early plastic instabilities. However, steels which are fully austenitic at ambient temperature can, in the context of iron-based alloys, be expensive. Commercially available TRIP steels are based on ingenious alloy designs that avoid the expense but still rely on the consequences of deformation-induced martensite, as discussed in Chapter 10.

5.6.6 Effect of austenite grain size

It is observed experimentally that a reduction in the austenite grain size causes the depression of the martensite-start temperature (Fig. 5.26). There are two factors that govern this relationship:

- The size of the largest martensite plate that can form is related to the austenite grain size as defined by its mean lineal intercept $\bar{L}_\gamma$.
- Each experimental technique has a detection limit that defines the martensite-start temperature.

Relatively few martensite plates therefore need to form before transformation is detected when the austenite grain size is large. Based on this concept, the Koistinen and Marburger Equation (5.2) becomes [41]:

$$M_S^o - M_S = \frac{1}{b} \ln \left[\frac{1}{\bar{L}_\gamma^3} \left\{ \exp \left(-\frac{\ln(1 - V_V^{\alpha'})}{m} \right) - 1 \right\} + 1 \right], \quad (5.23)$$

where $b = 0.2689$, $\bar{L}_\gamma$ is in mm, $m = 0.05$ is the aspect ratio of martensite plates, and M_S is defined when a fraction $V_V^{\alpha'} = 0.01$ of martensite is

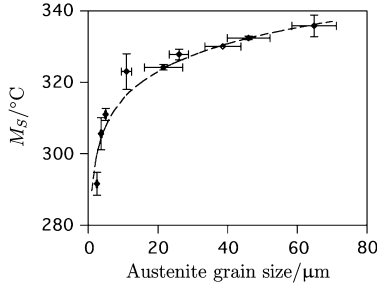


Figure 5.26 Measured variation in the martensite-start temperature as a function of austenite grain size, determined from dilatometric data (after Yang et al. [41]).

obtained. The term M_s^0 is defined as a fundamental martensite-start temperature for an austenite grain size that is so large that the formation of just one martensite plate is detectable using routine methods. It is given by the point where $\Delta G^{\gamma \rightarrow \alpha} = 700 \text{ J mol}^{-1}$, i.e. the stored energy of martensite due to the shape deformation and twin interfaces. M_s^0 is therefore purely a thermodynamic quantity with no consideration given to kinetic effects.

5.6.7 Effect of plastic strain on martensitic transformation

One effect of plastic strain prior to transformation is to alter $\bar{L}_\gamma$ through a change in the shape of the austenite grains. This problem has been dealt with [42,43] for a large variety of deformations in which an equiaxed grain is strained, but for uniaxial tension or compression, the result is:

$$\frac{\bar{L}_0}{\bar{L}} = \frac{(1 + 3\sqrt{3})S_{11}^{0.5} + 3(S_{11}^3 + 2)^{0.5}S_{11}^{-1} + (2 + 2S_{11}^3)^{0.5}S_{11}^{-1}}{3(2\sqrt{3} + 1)}, \quad (5.24)$$

where $S_{11} = \exp\{\pm\epsilon\}$ where $+\epsilon$ and $-\epsilon$ are the plastic strains in tension and compression respectively, and $\bar{L}_0$ and $\bar{L}$ are the lineal intercepts in the undeformed and deformed states respectively.

The second effect of plastic strain is through mechanical stabilisation in which martensitic transformation is suppressed when the deformed austenite contains a large density of dislocations.¹⁰ These dislocations impede the motion of glissile martensite interfaces, thus retarding transformation as illustrated in Fig. 5.27 [44]. The effect is considered by calculating the additional driving force ΔG_{STA} needed in order for the interface to overcome

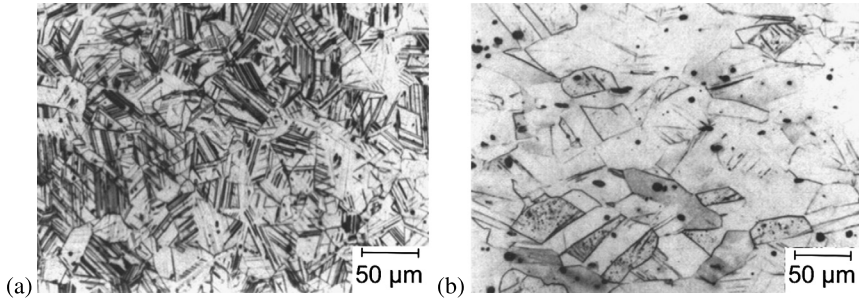


Figure 5.27 Fe-25Mn wt% alloy in which austenite transforms into ϵ -martensite. (a) Sample in which the austenite was not in a plastically deformed state prior to transformation. (b) The austenite was mechanically stabilised by sufficient plastic deformation so the amount of martensite obtained is much reduced relative to (a). After Tomota et al. [44].

the dislocation density (ρ) created by strain prior to transformation [45,46]:

$$\Delta G_{\text{STA}} = \frac{\mu b}{8\pi(1-\nu)}(\rho^{0.5} - \rho_0^{0.5})\text{J m}^{-3},$$

with $\rho = 2 \times 10^{13} + 2 \times 10^{14} \epsilon \text{ m}^{-2}$,

(5.25)

where μ is the shear modulus of austenite at 80 GPa, $b = 0.252 \text{ nm}$ is the magnitude of the Burgers vector of the dislocations, and the Poisson's ratio $\nu = 0.27$. To summarise, the martensite-start temperature independent of grain size effect is obtained from

$$\Delta G^{\gamma \rightarrow \alpha} + U < \Delta G_{M_S}^{\gamma \rightarrow \alpha} - \Delta G_{\text{STA}} \quad (5.26)$$

and this result is then corrected for a grain size effect using Equation (5.23).

5.6.8 Thermal stabilisation

Thermal stabilisation is said to occur when the cooling of a steel is arrested in the $M_S - M_F$ range. When cooling is resumed by lowering the temperature, it does not result in as complete a transformation to martensite as would have been the case if no isothermal pause had occurred. At the chosen delay temperature, the degree of stabilisation increases to a maximum with time, and as the temperature approaches M_F , the extent of stabilisation increases. It appears that stabilisation is at a minimum when only a small amount of martensite is present in the matrix.

The explanation of these complex effects lies in the fact that the formation of martensite plates leads to accommodating plastic deformation in

the surrounding matrix, which can result in high concentrations of dislocations in the austenite. Interaction of some of these dislocations with the glissile dislocations in the martensite plate boundary will then cause it to be no longer mobile, so that the plate cannot grow further. Any phenomena which help to encourage this process will achieve stabilisation. Resting at an intermediate temperature gives time for plastic relaxation, i.e. movement of dislocations, as well as the locking of interfacial dislocations by carbon atoms.

Halting the transformation prior to M_F can lead to the partitioning of carbon from the martensite into the surrounding austenite [47] which may also explain thermal stabilisation. This concept is now widely exploited in the design of the quench and partitioning process where the amount of retained austenite in an otherwise martensitic steel is enhanced by partial transformation into martensite followed by an increase in temperature in order to allow carbon to diffuse into the austenite and hence stabilise it to further transformation [48,49].

5.7 STRENGTH OF MARTENSITE

The high hardness and brittleness of rapidly quenched steels is the result of the formation of martensite, yet many shear transformations in non-ferrous alloy systems do not produce this dramatic hardening. Indeed, if carbon is eliminated from the steel the resulting hardness is very much lower. Fig. 5.28a shows the large effect of carbon content on the hardness of martensite compared with the relatively small consequence on the strength of austenite, retained to room temperature by the addition of nickel.

The strength levels reached depend also on the detailed structure of the martensite, e.g. whether it has remained stable during quenching and testing at room temperature. By addition of nickel to iron carbon alloys, Winchell and Cohen depressed the M_S temperature to -35°C , so that martensite formed only at low temperatures and auto-tempering was eliminated (Chapter 8). In addition, the samples were deformed at 0°C , with the results shown in Fig. 5.28b, indicating that the flow stress of martensite increases with carbon content up to about 0.5 wt% C. Allowing the martensite to rest for 3 h at 0°C , resulted in the upper curve (Fig. 5.28b), demonstrating that martensite can age harden at ambient temperature or below.

The question of the origin of the high strength of martensite is a difficult one, compounded by the complexity of the structure, a tetragonal lattice

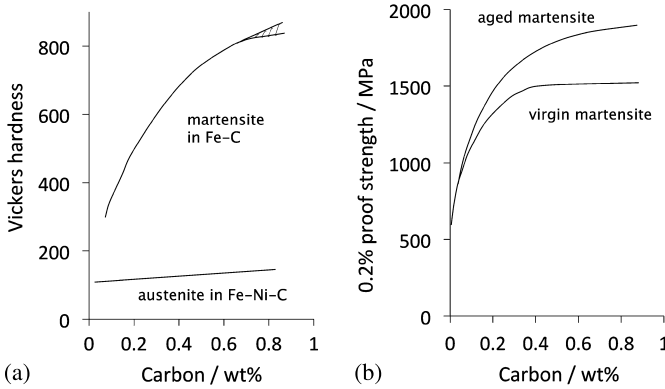


Figure 5.28 (a) The effect of carbon on the hardness of martensite and austenite. (b) Ageing of martensite at 0°C in Fe-Ni-C alloys. Data from Winchell and Cohen [50].

with interstitial carbon in solid solution, formed by shear which leads to high densities of dislocations and fine twins. There are, as a result, several possible strengthening mechanisms:

1. substitutional and interstitial solid solution;
2. dislocation strengthening, i.e. work hardening;
3. fine twins;
4. grain size;
5. segregation of carbon atoms;
6. precipitation of iron carbides.

The interstitial solid solution of carbon which results in the tetragonality of martensite is a prime candidate for the role of major strengthening factor. The work of Winchell and Cohen enabled the determination of the yield stress as a function of carbon content under conditions when the carbon atoms were unable to diffuse to form atmospheres and precipitates. The flow stress was shown to vary as $c^{1/3}$, where c is the carbon concentration, but it was later found that the strength could be shown equally well to vary as $c^{1/2}$.

Fleischer examined the situation theoretically with a model of a dislocation bending away from interstitial solute atoms with short range interactions, and using a parameter $\Delta\epsilon$, the difference in longitudinal and transverse lattice strain caused by an interstitial carbon atom in martensite ($\Delta\epsilon \simeq 0.38$). He found the following expression for the flow stress τ :

$$\tau \propto \frac{2\mu\Delta\epsilon c^{1/2}}{3}, \quad (5.27)$$

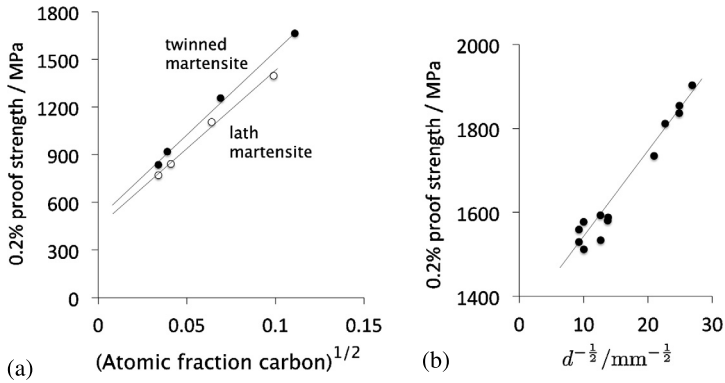


Figure 5.29 (a) Effect of carbon on the strength of martensite. Data from Chilton and Kelly [51]. (b) Plot of the prior austenite grain size versus the strength of martensite. The observed effect reflects the role of the austenite grain size on the size and distribution of martensite plates, rather than a Hall-Petch effect. The alloy is Fe-0.4C-0.7Mn-0.8Cr-1.5Ni-0.25Mo wt%. Data from Grange [52].

predicting that the flow stress should be proportional to $\epsilon^{1/2}$. Other experiments on martensites with low M_S temperatures support the $\epsilon^{1/2}$ relationship, with slight differences in slope depending on whether the martensite is of lath type or twinned (Fig. 5.29a).

The proposal that the fine twins characteristic of higher carbon martensites make a major contribution to strength has not received wide acceptance. Certainly, a large increase in strength is not found when the transition from dislocated martensite to twinned martensite takes place. However, the high dislocation densities of twin-free martensite must make some contribution to strength, estimated to be not greater than 300 MN m^{-2} , and there is reason to believe that the fine twinning makes a similar, but not additive, contribution.

The austenitic grain size determines the maximum size of a martensitic plate, so some dependence of strength on grain size might be expected. In fact, a Petch-type plot has been found for several alloy steels of different austenitic grain sizes tested in the martensitic condition (Fig. 5.29b). However, when the fine structure of martensite is examined, other possible grain sizes much finer than the austenitic grain size can be considered as contributors to strength. Firstly, there is the packet size in lath martensite, or the individual plate in lenticular martensite, and beyond these there is the lath substructure which is usually well below $1 \mu\text{m}$ in thickness. While many of these boundaries are really low angle sub-boundaries, they do present

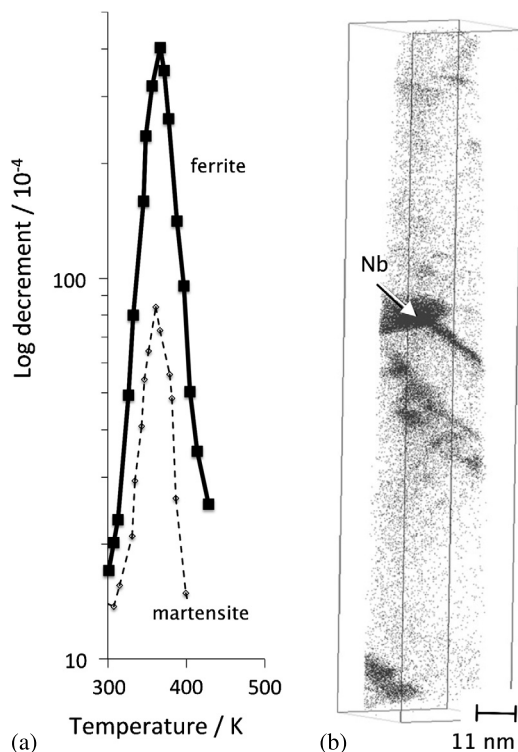


Figure 5.30 (a) Comparison of the internal friction behaviour of low carbon martensite with that of ferrite in the same steel containing 0.026 wt% with the different structures produced by quenching from 1000°C or 710°C. Data from Speich and Leslie [13]. (b) Atom probe tomograph showing the distribution of carbon in a 0.12 wt% C martensitic steel. The carbon is mostly segregated at lath boundaries and dislocations. The niobium rich area illustrated is a NbC particle that did not dissolve during austenitisation; it is not relevant to the present discussion. After Hutchinson et al. [53], reproduced with the permission of Elsevier.

obstacles to dislocation movement and must, therefore, be considered to make some contribution to the overall strength.

It also is to be expected that carbon atoms segregate to the high dislocation populations typical of martensite, bearing in mind the strong interactions found in the case of ferrite. Internal friction measurements by Kurdjumov and co-workers have revealed the well-defined temperature-dependent peak, the Snoek peak (section 1.4.1), which occurs as a result of the stress-induced movement of carbon atoms in ferrite and martensite. Fig. 5.30a shows that the Snoek peak is much lower in a 0.026 wt% C

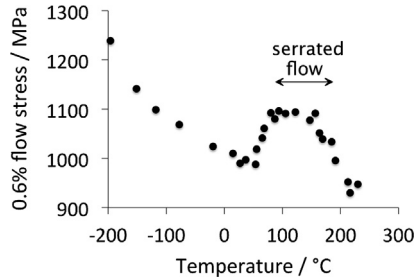


Figure 5.31 Temperature dependence of the flow stress of Fe-21Ni-0.08C wt% martensite tested at a strain rate of $8.3 \times 10^{-4} \text{ s}^{-1}$ (after Owen and Roberts [54]).

martensite than in ferrite of the same composition. This is a direct result of the reduction in free carbon atoms in the martensite structure due to pinning by the high concentration of dislocations. These pinned carbon atoms cannot contribute directly to the Snoek peak, the height of which is proportional to the concentration of free carbon atoms in the lattice. In contrast, ferrite has a very low dislocation density and exhibits a much higher Snoek peak (Fig. 5.30a), because a greater concentration of carbon atoms is available to move interstitially between the octahedral sites. Fig. 5.30b shows an atom-probe tomograph where the segregation of carbon atoms at dislocations and boundaries in martensite is revealed.

Work on the temperature dependence of the flow stress of martensite in Fe-Ni-C alloys has shown a strong temperature dependence, together with a peak in the curve associated with serrated flow in the stress-strain curve (Fig. 5.31). Like the development of the yield point in α -iron, this has been attributed to the Cottrell-Bilby interaction of carbon with dislocations.

However, this phenomenon leads to precipitation of iron carbide on the dislocations which is responsible for the increase in strength shown by martensite aged at room temperature or just above. Martensites with relatively high M_S temperatures will form cementite dispersions during the quench (auto-tempering) which will also make some contribution to the observed strength.

The yield strength of martensite, like that of ferrite, is markedly temperature dependent, but this dependence is little affected by the presence or absence of precipitates, or by the amount of carbon in solution. It is, therefore, likely that the temperature dependence arises from the basic resistance of the lattice to dislocation movement, i.e. it is a result of the temperature dependence of the Peierls-Nabarro force.

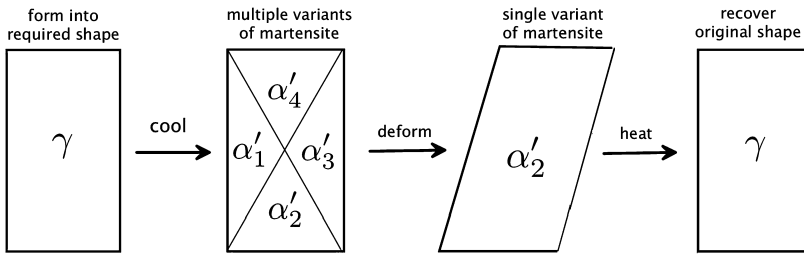


Figure 5.32 Shape memory effect. The alloy is formed into the desired state while austenitic. On cooling, it transforms into multiple variants of martensite without any discernible macroscopic change in shape. Deformation at ambient temperature causes those variants that comply with the stress to grow, thus accomplishing a macroscopic change in shape. To recover the original shape, the material is heated into its austenitic state.

5.8 SHAPE MEMORY EFFECT

The shape deformation accompanying martensitic transformation can be reversed by transforming back to the parent phase. Suppose a crystal of austenite is cooled to form many variants of martensite, in such a way that they accommodate and hence the overall shape is unaffected by transformation. When a stress is applied, the favoured variant of martensite grows, leading to a shape change (Fig. 5.32). On heating the shape change is reversed, thus regaining the original shape. This is the basis of the shape memory effect. The memory can be lost by introducing defects during transformation, e.g. by repeated cycling. Excessive deformation, beyond that required to produce a single martensite variant, will lead to irreversible strain and a loss of memory.

The most successful shape-memory alloys are based on nickel containing titanium and aluminium. A large variety of iron-based shape-memory alloys exist but their recoverable strains are smaller and less reversible. They do have cost advantages and find engineering applications such as pipe-couplings, where the memory effect need operate only once to make an integral joint. Some of these alloys exploit the $\gamma \rightarrow \alpha'$ transformation whereas others rely on $\gamma \rightarrow \epsilon$ martensite. There are even alloys in which the austenite transforms into face-centred tetragonal martensite. The chemical compositions of some of the iron-based shape memory alloys are listed in Table 5.3.

Table 5.3 Compositions of some iron-based shape memory alloys

Composition	Reference
Fe-31Ni-0.4C wt%	[55]
Fe-27Ni-0.8C wt%	[55]
Fe-31Ni-10Co-3Ti wt%	[56]
Fe-20Mn-2Si-7Cr-1Cu wt%	[57]
Fe-30Mn-6.5Si wt%	[58]
Fe-30Pd at%	[59]

5.9 SUMMARY

Martensitic transformation is probably the most understood of all the phase transformations found to occur in the solid state. Virtually every aspect of the phase can be reliably expressed in a quantitative framework that permits the design of alloys. There are two reasons for this. First that it is a simple transformation that does not involve a change in the chemical composition and the second that it involves a highly disciplined motion of atoms so the crystallographic characteristics are reproducible. The transformation benefits from dislocation theory because it is, after all, a mechanism for deformation that happens to change the crystal structure at the same time. Just as in slip, where the slip system is defined by a slip plane and Burgers vector, the deformation system for martensite is its habit plane and shape strain.

The role of substitutional solutes is also easy to understand and predict, since they only influence the relative thermodynamic stabilities of the parent and product phases. Solution hardening also has a role in changing dislocation dynamics and hence the critical driving force for triggering martensitic transformation.

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BACKNOTES

1. The formal thermodynamic definition of trapping is that the chemical potential of the species concerned increases on transfer across the interface.
2. M_S is defined as the highest temperature at which martensite can form. However, the minimum detectable amount of transformation depends on the sensitivity of the equipment used. For example, M_S measured using acoustic emission is known to be greater than that using dilatometry. The proper procedure is, therefore, to state the M_S temperature in conjunction with the sensitivity of the measurement [1]. In this way, the measurements become reproducible and the level of accuracy needed for a particular application, can be assessed.
3. Reconstructive transformation in the solid state with difference in the chemical compositions of the parent and product phases.
4. The body-centred cubic lattice does not have a close-packed plane but $\{0\ 1\ 1\}_\alpha$ is the most densely packed plane.
5. The exact Nishiyama Wasserman orientation relationship would lead only to 12 variants, but the exact relationship does not exist.
6. Tetragonal martensite can occur in interstitial-free iron alloys if substitutional solutes have long-range order in the austenite, or if the austenite contains ordered precipitates [9].

7. This stored energy consists of strain energy due to the accommodation of the shape deformation and that due to defects created during the transformation.
8. Assuming chemically homogeneous samples, the M_S temperature is also dependent on the sensitivity of the measuring technique. Thus, acoustic emission will in general give a greater M_S than dilatometry.
9. The notation and method here is due to Bowles and MacKenzie [37,38]. The deformation matrix in Equation (5.19) is easily derived by inspection of Fig. 5.22. For example, the third column of the matrix represents what happens to the components of the vector $\mathbf{z}_3$ as a consequence of the deformation.
10. Small plastic strains enhance the nucleation rate of martensite, but in contrast, large strains prevent the nuclei from growing into substantial plates.

CHAPTER 6

Bainite

Abstract

There are high temperatures where all atoms are mobile and low-temperatures where none of the atoms can diffuse during the formation of microstructure. However, in an intermediate temperature range the logic becomes fuzzy – it may or may not then be possible for carbon to diffuse during transformation even though the substitutional lattice is displaced into position. This is the regime where bainite forms and hence arguably represents the most difficult solid-state phase transformation to understand. We describe in this chapter, the experimental observations and how they can be used to define the atomic mechanism of transformation. This understanding is the basis of the design of some of the most innovative steels today, as discussed in the remainder of this book.

6.1 INTRODUCTION

Solid-state transformations are interesting precisely because it ordinarily is difficult to appreciate how the arrangement of atoms can change in a substance that after all, is solid to the touch. Steels are doubly fascinating in this respect, since they contain both large and very small atoms. There will be circumstances where the small atoms zip through the space between the large and immobile atoms of iron. We have seen (Chapter 3) that all atoms must diffuse during a reconstructive transformation, but it is possible at lower temperatures to obviate the need for large atoms to diffuse. Such a case is typified by the displacive growth of Widmanstätten ferrite at a rate controlled by the diffusion of carbon in the austenite ahead of the interface.¹ However, further reductions in the transformation temperature, but still above M_S , lead to the possibility that neither carbon nor the large atoms move during the time scale of the evolution of the new phase. It is this regime between the high-temperature transformations (α , P , α_W) and martensite, that the bainite transformation occurs.

Fig. 6.1 illustrates schematically the sequence of transformations expected as a function of the isothermal transformation temperature. Bainite typically occurs in the range 250–550°C, with the lower limit determined by the onset of martensitic transformation. It is now known that there is no lower limit as long as a gap can be maintained between the bainite-start (B_S) and martensite-start temperature, with the possibility that bainite can

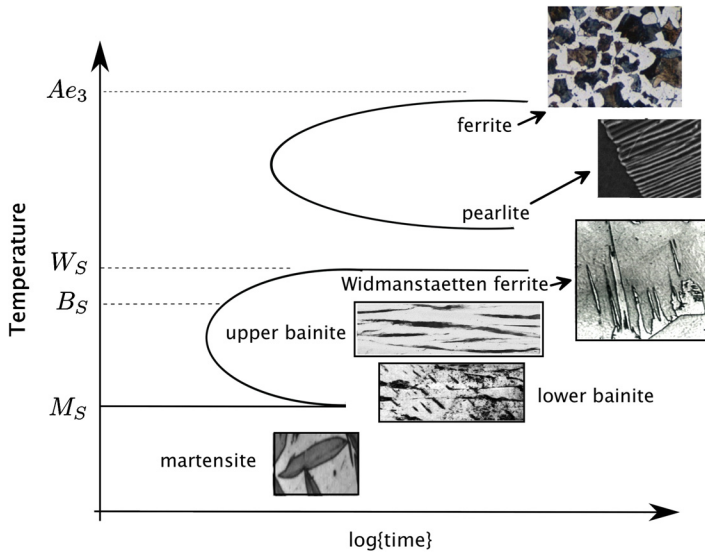


Figure 6.1 An illustration of the variety of microstructures that in principle can be generated during the isothermal transformation of austenite.

actually form at room temperature [2–4]; this will be discussed in more detail in Chapter 14.

Bainite is named after Edgar Bain who with Davenport first isolated these structures during their pioneering systematic studies of the isothermal decomposition of austenite [5,6]. It consists of fine aggregates of ferrite plates and cementite particles. The nature of bainite changes as the transformation temperature is lowered. Two main forms can be identified: *upper* and *lower* bainite.

6.2 UPPER BAINITE ($\approx 550 - 400^\circ\text{C}$)

The microstructure of upper bainite consists of fine plates of ferrite, each of which is about $0.2\ \mu\text{m}$ thick and about $10\ \mu\text{m}$ long. The plates grow in clusters called sheaves Fig. 6.2a. Within each sheaf the plates are parallel and of identical crystallographic orientation, each with a well-defined crystallographic habit. The individual plates in a sheaf are often called the ‘sub-units’ of bainite [7], Fig. 6.2b. They usually are separated by low-misorientation boundaries, cementite particles or austenite.

Upper bainite evolves in distinct stages beginning with the nucleation of ferrite plates at the austenite grain boundaries. The growth of each plate is

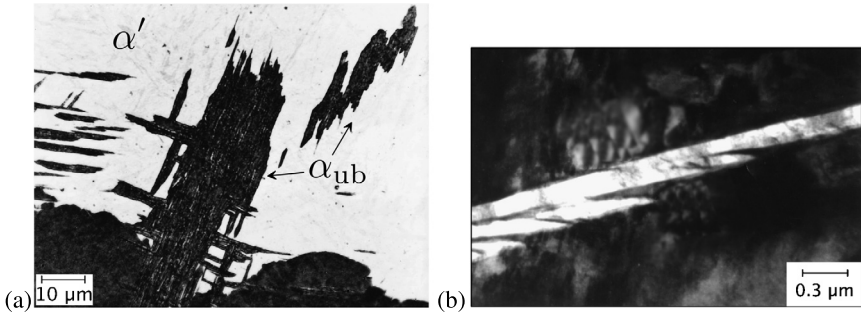


Figure 6.2 Upper bainite. (a) An optical micrograph of upper bainite (α_{ub}) generated in a Fe-0.8C wt% steel by isothermal transformation at 400°C for 20 s followed by quenching so that the remaining austenite transforms into martensite (α'). Micrograph courtesy of Y. Ohmori. (b) Transmission electron micrograph to show the sub-unit structure of a sheaf of bainite.

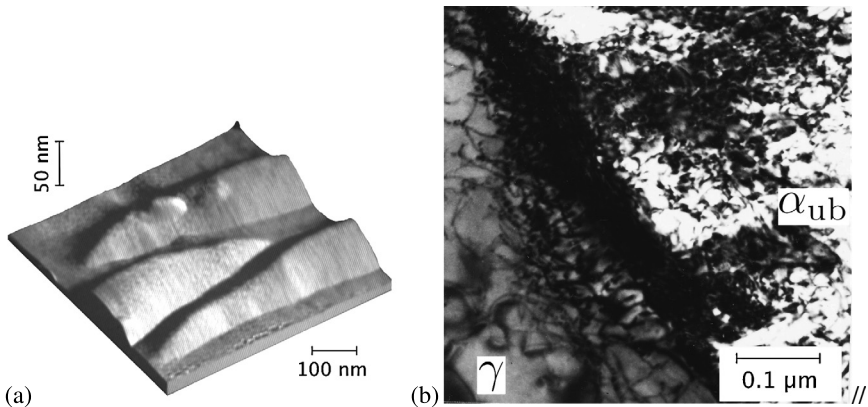


Figure 6.3 Upper bainite. (a) Atomic force micrograph showing the deformation caused by the formation of α_{ub} when a pre-polished sample of austenite is transformed. Image courtesy of M. Peet. (b) Intense dislocation arrays at, and in the vicinity of, the α_{ub}/γ interface.

accompanied by a change in the shape of the transformed region (Fig. 6.3a), a change which can be described precisely as an invariant-plane strain (IPS) with a large shear component, virtually identical to that observed during martensitic transformation [8]. However, bainite grows at relatively high temperatures when compared with martensite. The large strains associated with the shape change cannot be sustained by the austenite, the strength of which decreases as the temperature rises. These strains are relaxed by the plastic deformation of the adjacent austenite. The local increase in dis-

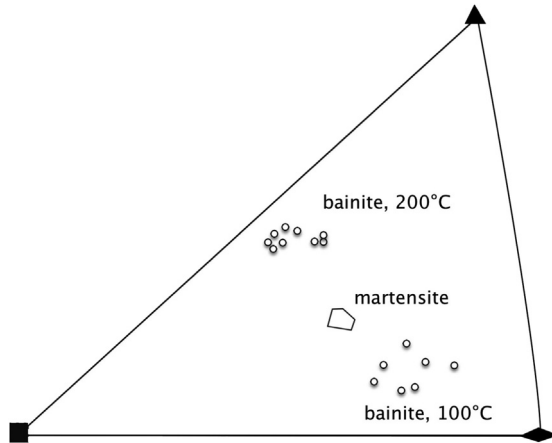


Figure 6.4 Stereographic triangle showing the habit plane of bainite compared with that of martensite in the same steel. Data from Greninger and Troiano [10].

location density caused by the yielding of the austenite blocks the further movement of the glissile transformation interface, Fig. 6.3b [9]. This localised plastic deformation therefore halts the growth of the ferrite plate so that each sub-unit only achieves a limited size, that usually is much less than the size of an austenite grain.

As with martensite, the shape change implies that the mechanism of growth of bainitic ferrite is displacive. It is the minimisation of the strain energy associated with the displacements that ensures that bainite grows in the form of thin plates. Since the crystal structure of bainite is generated by a coordinated movement of atoms, it follows that there must exist an orientation relationship between the austenite and the bainite. This relationship is found experimentally to be of the type where a pair of the most densely packed planes of the two lattices are approximately parallel, as are a corresponding pair of close-packed directions within those planes. This is loosely described by a Kurdjumov-Sachs type orientation relationship.

Bainite forms on particular crystallographic planes, but the indices of the habit plane show considerable scatter (Fig. 6.4). This is because most of the measurements are made using light microscopy, in which case the habit plane determined is not that of an individual sub-unit. It corresponds instead to some average value depending on the number, size and distribution of sub-units within the sheaf. All of these factors can vary with the transformation temperature, time and chemical composition.

It was emphasised earlier that upper bainite forms in two distinct stages, the first involving the formation of bainitic ferrite that eventually retains little carbon in solid solution (<0.02 wt%). The remaining austenite therefore enriches in carbon. Cementite then precipitates from the enriched austenite layers in between the ferrite sub-units. The amount of cementite depends on the carbon concentration of the alloy. High concentrations lead to microstructures in which the ferrite platelets are separated by continuous layers of cementite. Small, discrete particles of cementite form when the alloy carbon concentration is low.

The cementite particles have a ‘Pitsch’ orientation relationship with the austenite from which they precipitate:

$$\begin{aligned} [0 \ 0 \ 1]_{\text{Fe}_3\text{C}} &\parallel [\bar{2} \ 2 \ 5]_{\gamma}, \\ [1 \ 0 \ 0]_{\text{Fe}_3\text{C}} &\parallel [5 \ \bar{5} \ 4]_{\gamma}, \\ [0 \ 1 \ 0]_{\text{Fe}_3\text{C}} &\parallel [\bar{1} \ \bar{1} \ 0]_{\gamma}. \end{aligned}$$

Many variants of carbide may precipitate from the austenite, each particle being indirectly related to the ferrite via the ferrite/austenite orientation relationship.

If sufficient quantities of alloying elements (such as Si or Al) which retard the formation of cementite are added to the steel, then it is possible to suppress the formation of cementite altogether. An upper bainite microstructure consisting of just bainitic ferrite and carbon-enriched retained austenite is obtained instead (Fig. 6.3b). The microstructure may also contain martensite if the residual austenite decomposes on cooling to ambient temperature.

6.3 LOWER BAINITE ($\approx 400 - 250^\circ\text{C}$)

Lower bainite has a microstructure and crystallographic features which are very similar to those of upper bainite. The major distinction is that cementite particles also precipitate inside the plates of ferrite (Fig. 6.5). There are, therefore, two kinds of cementite precipitates: those which grow from the carbon-enriched austenite which separates the platelets of bainitic ferrite, and others which appear to precipitate from supersaturated ferrite. These latter particles exhibit the ‘tempering’ orientation relationship which is found when carbides precipitate during the heat treatment of martensite,

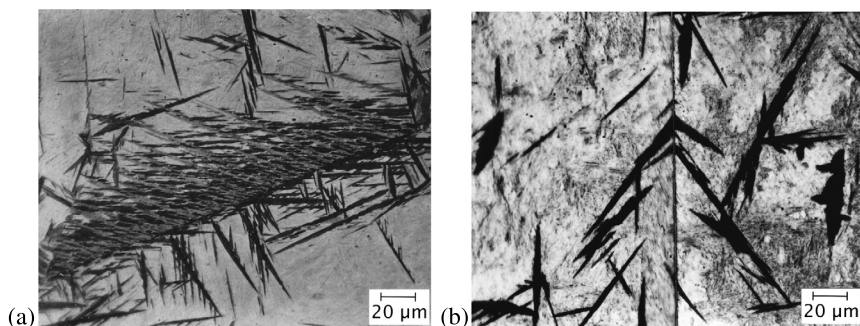


Figure 6.5 Microstructure of lower bainite. (a) Optical micrograph, Fe-0.8C wt% steel transformed at 300°C, showing sheaves of lower bainite. The bainite etches dark relative to the surrounding untempered martensite. (b) Two-surface composite micrograph (courtesy of Ohmori).

often described as the Bagaryatski orientation relationship:

$$[0\ 0\ 1]_{\text{Fe}_3\text{C}} \parallel [\bar{1}\ 0\ 1]_{\alpha},$$

$$[1\ 0\ 0]_{\text{Fe}_3\text{C}} \parallel [1\ 1\ 1]_{\alpha},$$

$$[0\ 1\ 0]_{\text{Fe}_3\text{C}} \parallel [\bar{1}\ 2\ \bar{1}]_{\alpha}.$$

The carbides in the ferrite need not always be cementite. Depending on the chemical composition and the transformation temperature, other transition carbides may precipitate first. For example, in high-carbon steels containing more than about 1 wt% silicon (which retards cementite formation), epsilon carbide is commonly observed to precipitate in the bainitic ferrite.

In contrast to tempered martensite, the cementite particles in lower bainite frequently precipitate in just one variant of the orientation relationship (Fig. 6.6a), such that they form parallel arrays at about 60° to the axis of the bainite plate. In tempered martensite, the carbides tend to precipitate in Widmanstätten arrays.

However, these general observations are not always true. Widmanstätten arrays of cementite are also found in lower bainite when the latter forms in high-carbon steels or when the transformation occurs at low temperatures (Fig. 6.6b). Similarly, martensite in low-carbon steels exhibits only a single variant of carbide on tempering. This is because the carbide precipitation is influenced by the stresses associated with the displacive growth of lower bainite or martensite – those variants of cementite which best comply with the stress are dominant. If the driving force for precipitation is large (i.e.

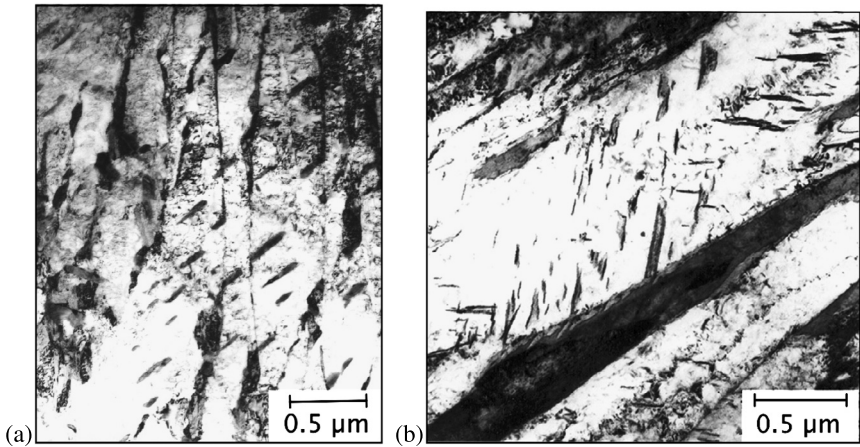


Figure 6.6 (a) Single variant of cementite in lower bainite, Fe-0.3C-4Cr wt%, transformed isothermally at 435°C. (b) Multiple variants of cementite in lower bainite, Fe-0.4C-2Si-3Mn wt%, transformed isothermally at 300°C.

the carbon concentration inherited by the bainite is large) then multiple variants including those which do not comply with the stress are able to precipitate [11].

The carbides in the lower bainite are extremely fine, just a few nanometres thick and about 500 nm long. Because they precipitate within the ferrite, a smaller amount of carbon is partitioned into the residual austenite. This in turn means that fewer and finer cementite particles precipitate between the ferrite plates, when compared with an upper bainitic microstructure. An important consequence is that lower bainite is usually found to be much tougher than upper bainite, in spite of the fact that it also tends to be stronger. The coarse cementite particles in upper bainite are notorious in their ability to nucleate cleavage cracks and voids.

6.4 THE SHAPE DEFORMATION

The IPS surface relief caused by the growth of bainitic ferrite has a large shear strain component of 0.24 in addition to the volume strain (0.03) on transformation. There is, therefore, a coordinated movement of atoms as the transformation occurs. Consistent with this, the iron and substitutional solutes such as Mn, Si, Ni, Mo and Cr, have been demonstrated using high-resolution techniques to be frozen into position during transformation, Fig. 6.7 [12,13]. The change in crystal structure is therefore

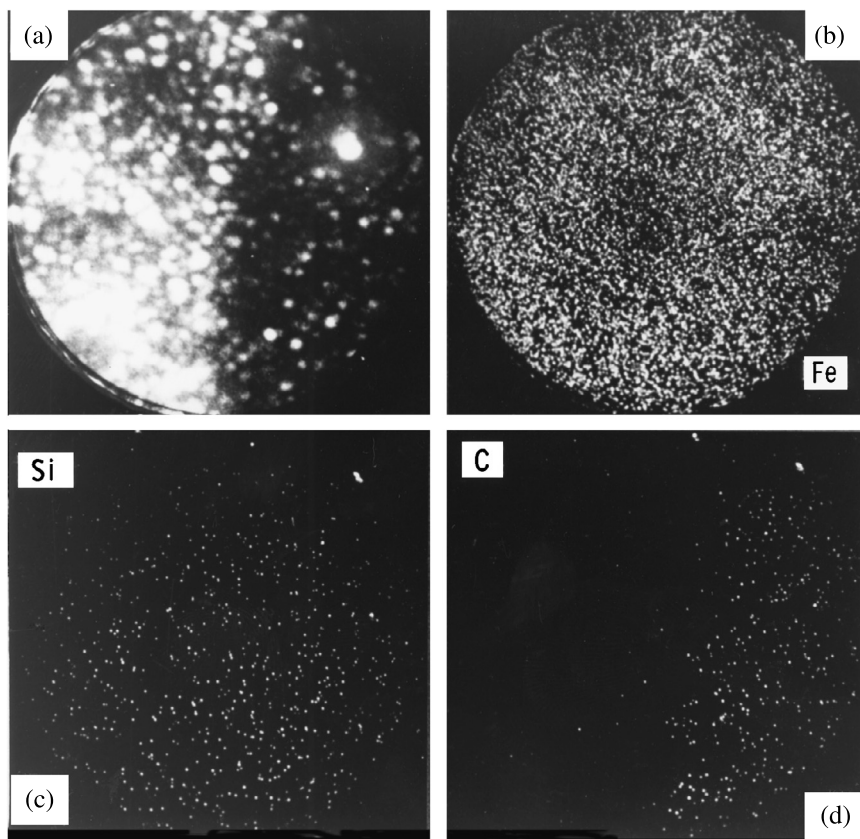


Figure 6.7 Imaging atom-probe micrographs, taken across an austenite-bainitic ferrite interface in a Fe-C-Si-Mn alloy. Substitutional atoms clearly do not diffuse during transformation. (a) Field ion image; each dot corresponds to an atom. The interface is vertical in the image, the austenite located on the right-hand side. (b) Fe atom map. (c) Corresponding Si atom map, showing a uniform distribution. (d) C atom map (Bhadeshia and Waugh, 1982).

achieved by a deformation of the austenite crystal. If the strain is elastically accommodated, then the strain energy of bainitic ferrite amounts to about 400 J mol^{-1} . Some of the strain can be relaxed by plastic deformation in the adjacent austenite.

The movement of interstitial atoms during the change in crystal structure does not influence the development of surface relief [14]. Conversely, the observation of relief cannot yield information about whether or not carbon diffuses during transformation.

6.5 CARBON IN BAINITE

It is simple to establish that martensitic transformation is diffusionless, by measuring the local compositions before and after transformation. Bainite forms at somewhat higher temperatures where the carbon can escape out of the plate within a fraction of a second. Its original composition cannot therefore be measured directly.

There are three possibilities. The carbon may partition during growth so that the ferrite may never contain any excess carbon. The growth may on the other hand be diffusionless with carbon being trapped by the advancing interface. Finally, there is an intermediate case in which some carbon may diffuse with the remainder being trapped to leave the ferrite partially supersaturated. It is therefore much more difficult to determine the precise role of carbon during the growth of bainitic ferrite than in martensite.

Diffusionless growth requires that transformation occurs at a temperature below T_0 , when the free energy of bainite becomes less than that of austenite of the same composition. A locus of the T_0 temperature of the function of the carbon concentration is called the T_0 curve, an example of which is plotted on the Fe-C phase diagram in Fig. 6.8. Growth without diffusion can only occur if the carbon concentration of the austenite lies to the left of the T_0 curve.

Suppose that the plate of bainite forms without diffusion, but that any excess carbon is soon afterwards rejected into the residual austenite. The next plate of bainite then has to grow from carbon-enriched austenite (Fig. 6.9a). This process must cease when the austenite carbon concentration reaches the T_0 curve. The reaction is said to be incomplete, since the austenite has not achieved its equilibrium composition (given by the Ae_3 curve) at the point the reaction stops. If on the other hand, the ferrite grows with an equilibrium carbon concentration then the transformation should cease when the austenite carbon concentration reaches the Ae_3 curve.

It is found experimentally that the transformation to bainite does indeed stop at the T_0 boundary (Fig. 6.9b). The balance of the evidence is that the growth of bainite below the B_S temperature involves the successive nucleation and martensitic growth of sub-units, followed in upper bainite by the diffusion of carbon into the surrounding austenite. The possibility that a small fraction of the carbon is nevertheless partitioned during growth cannot entirely be ruled out, but there is little doubt that the bainite is at first substantially supersaturated with carbon.

These conclusions are not significantly modified when the strain energy of transformation is included in the analysis.

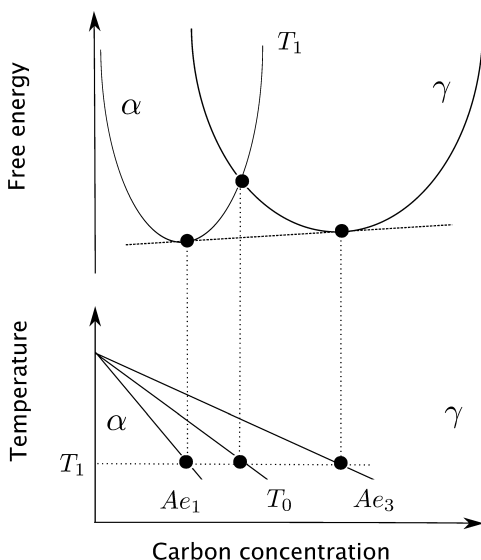


Figure 6.8 Schematic illustration of the origin of the T_0 construction on the Fe-C phase diagram. Austenite with a carbon concentration to the left of the T_0 boundary can in principle transform without any diffusion. Diffusionless transformation is thermodynamically impossible if the carbon concentration of the austenite exceeds the T_0 curve.

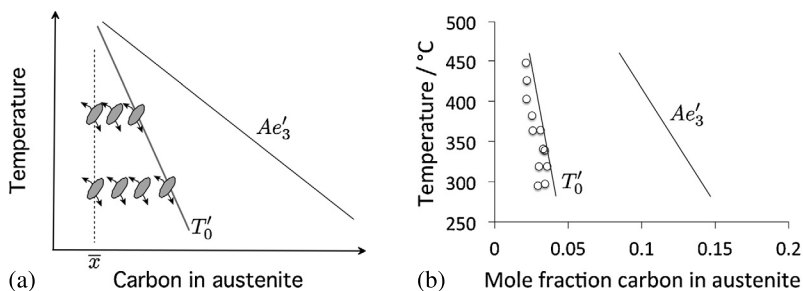


Figure 6.9 (a) Illustration of the incomplete-reaction phenomenon. During isothermal transformation, a plate of bainite grows without diffusion, then partitions its excess carbon into the residual austenite. The next plate therefore has to grow from carbon-enriched austenite. This process continues until diffusionless transformation becomes impossible when the austenite composition eventually reaches the T'_0 boundary, which unlike T_0 , includes the stored energy of transformation. The Ae'_3 curve is for paraequilibrium since substitutional solutes are not partitioned during the bainite reaction. (b) Experimental data showing that the growth of bainite stops when the austenite carbon concentration reaches the T'_0 curve (Fe-0.43C-3Mn-2.12Si wt% alloy).

There are two important features of bainite which can be shown by a variety of techniques, e.g. dilatometry, electrical resistivity, magnetic measurements and by metallography. Firstly, there is a well-defined temperature B_S above which no bainite will form, which has been confirmed for a wide range of alloy steels. The amount of bainite that forms increases as the transformation temperature is reduced below the B_S temperature. The fraction increases during isothermal transformation as a sigmoidal function of time, reaching an asymptotic limit which does not change on prolonged heat treatment even when substantial quantities of austenite remain untransformed. Transformation in fact ceases before the austenite achieves its equilibrium composition, so that the effect is dubbed the ‘incomplete-reaction phenomenon’. These observations are understood when it is realised that growth must cease if the carbon concentration in the austenite reaches the T_0 curve of the phase diagram.

Since this condition is met at ever-increasing carbon concentrations when the transformation temperature is reduced, more bainite can form with greater undercoolings below B_S . But the T_0 restriction means that equilibrium, when the austenite has a composition given by the Ae_3 phase boundary, can never be reached, as observed experimentally. A bainite-finish temperature B_F is sometimes defined, but this clearly cannot have any fundamental significance.

6.6 KINETICS

The rate of the bainite reaction needs to be considered in terms of a number of distinct events (Fig. 6.10). A sub-unit nucleates at an austenite grain boundary and lengthens at a certain rate before its growth is stifled by plastic deformation within the austenite. New sub-units then nucleate at its tip, and the sheaf structure develops as this process continues. The overall lengthening rate of a sheaf is therefore smaller than that of an individual sub-unit because there is an interval between the formation of successive sub-units [15]. The volume fraction of bainite depends on the totality of sheaves growing from different regions in the sample. Carbide precipitation events also influence the kinetics, primarily by removing carbon either from the residual austenite or from the supersaturated ferrite.

Little is known about the nucleation of bainite except that the activation energy for nucleation is directly proportional to the driving force for transformation [16]. This is consistent with the theory for martensite nucleation (Equation (5.10)). However, unlike martensite, carbon must partition into

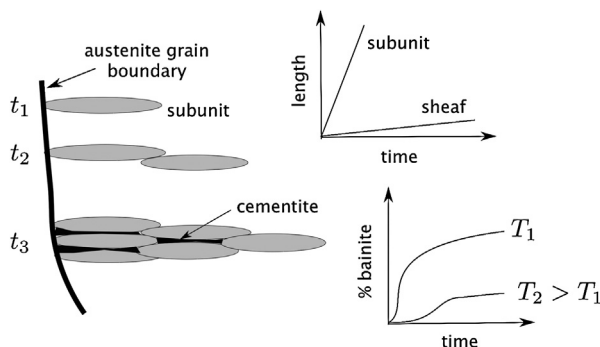


Figure 6.10 Schematic illustration of the microstructural features relevant in the kinetic description of a bainitic microstructure.

the austenite during bainite nucleation, although the nucleus then develops into a sub-unit which grows without diffusion.

The scale of individual plates of ferrite is too small to be resolved adequately using optical microscopy, which is capable only of revealing clusters of plates. Using higher-resolution techniques such as photoemission electron microscopy (Fig. 6.11) it has been possible to study directly the progress of the bainite reaction [17]. Not surprisingly, the lengthening of individual bainite platelets has been found to occur at a rate which is much faster than expected from a diffusion-controlled process. The growth rate is nevertheless much smaller than that of martensite, because the driving force for bainite formation is smaller due to the higher transformation temperatures involved. The platelets tend to grow at a constant rate but are usually stifled before they can traverse the austenite grain.

The lengthening rate of a sheaf is slower still, because of the delay caused by the need to repeatedly nucleate new sub-units. Nevertheless, sheaf lengthening rates are generally found to be about an order of magnitude higher than expected from carbon diffusion-controlled growth. Low-resolution measurements have also been made of the thickening of bainite sheaves, a process which appears to be discontinuous, presumably because of the sub-unit mechanism of growth. The thickening process therefore depends on the rate at which sub-units are nucleated in adjacent locations within a sheaf.

The bainitic reaction has several of the recognised features of a nucleation and growth process. It takes place isothermally, starting with an incubation period during which no transformation is detected, followed by an increasing rate of transformation to a maximum and then a gradual

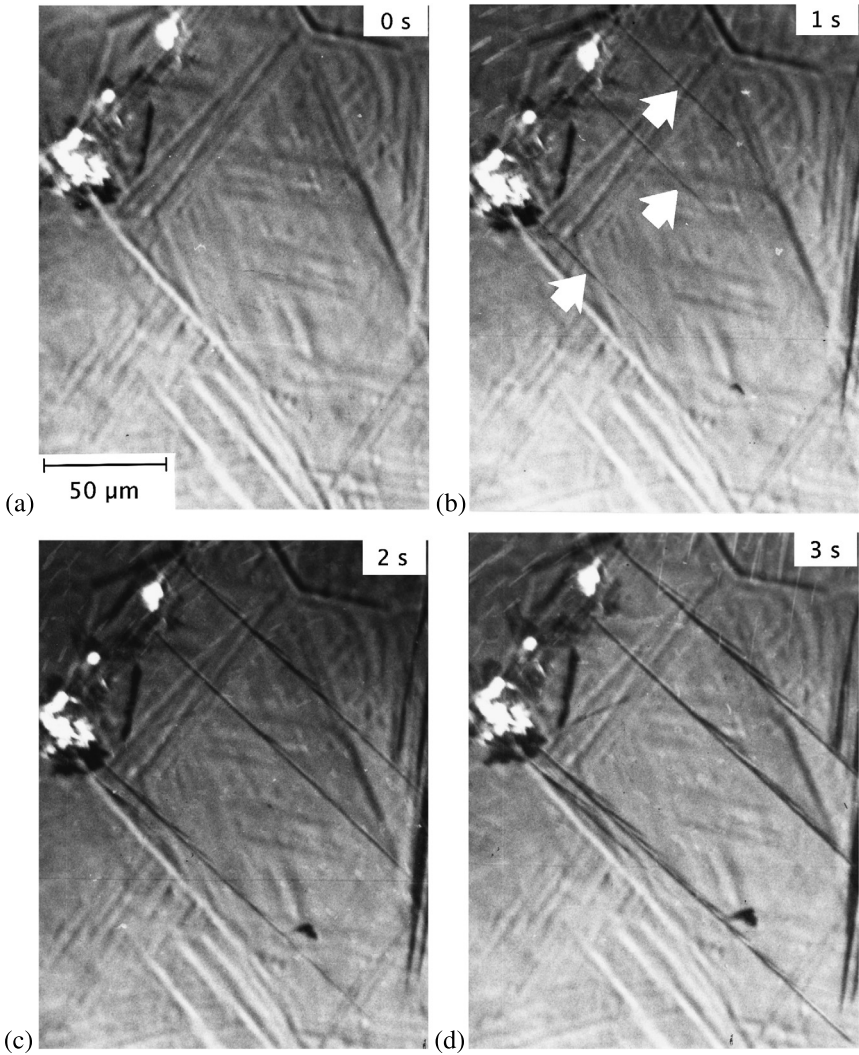


Figure 6.11 Photoemission electron microscope observations on the growth of individual sub-units in a bainite sheaf. The pictures are taken at 1 s intervals [17].

slowing down. These features are illustrated in the dilatometric results of Fig. 6.12a, for three transformation temperatures in the bainitic range for a Fe-1Cr-0.4C wt% steel, the extent of transformation increasing with decreasing temperature. In this steel at 510°C the reaction stops after about 1 h, and the remaining austenite is stable at this temperature for a long time.

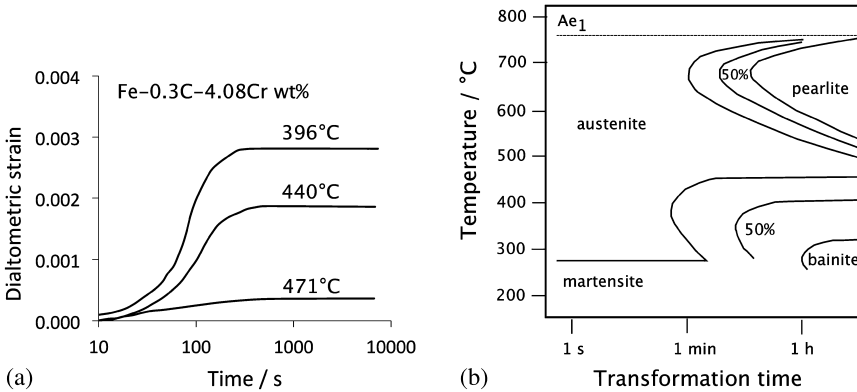


Figure 6.12 (a) Isothermal reaction curves for the formation of bainite, illustrating the incomplete reaction phenomenon. (b) TTT curves for a Fe-3Cr-0.5C wt% steel, adapted from Thelning [18].

These overall transformation characteristics, i.e. the change in the fraction of bainite with time, temperature, austenite grain structure and alloy chemistry are therefore best considered in terms of a TTT diagram (Fig. 6.12b). A simplified view is that the TTT diagram consists of two separable C-shaped curves. The one at higher temperatures describes the evolution of diffusional transformation products such as ferrite and pearlite, whereas the lower C-shaped curve represents displacive reactions such as Widmanstätten ferrite and bainite. In lean steels which transform rapidly, these two curves overlap so much that there is apparently just one curve which is the combination of all reactions. As the alloy concentration is increased to retard the decomposition of austenite, the two overlapping curves begin to become distinct, and a characteristic ‘gap’ develops at about the B_S temperature in the TTT diagram. This gap is important in the design of some high-strength (ausformed) steels which have to be deformed in the austenitic condition at low temperatures before the onset of transformation.

6.7 TRANSITION FROM UPPER TO LOWER BAINITE

As the isothermal transformation temperature is reduced below B_S , lower bainite is obtained in which carbides precipitate in the ferrite, with a correspondingly reduced amount of precipitation from the austenite between the ferrite. This transition from upper to lower bainite can be explained

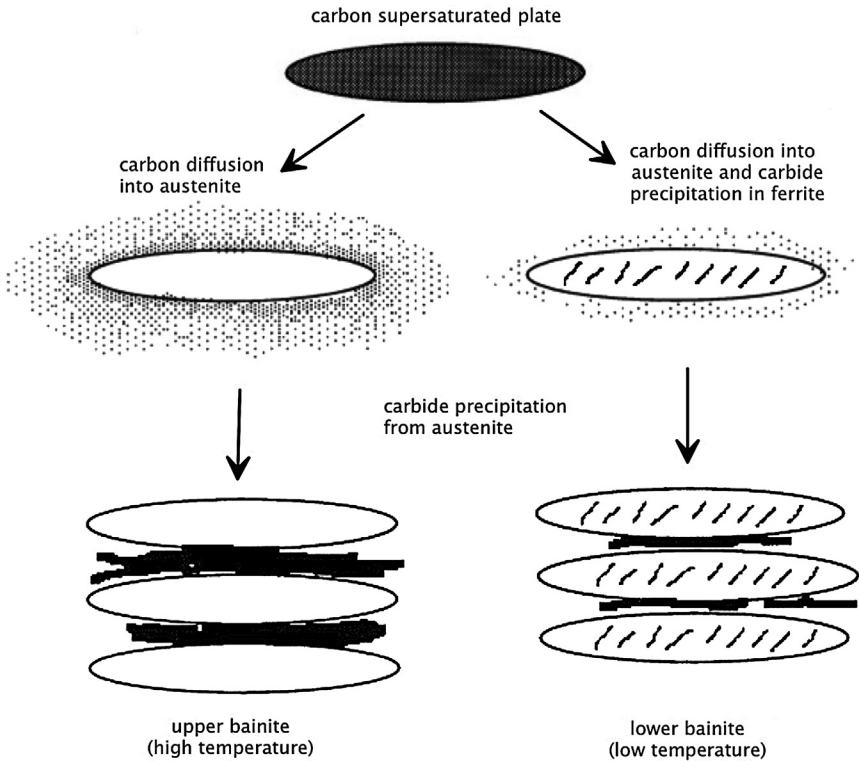


Figure 6.13 Schematic representation of the transition from upper to lower bainite.

in terms of the rapid tempering processes that occur after the growth of a supersaturated plate of bainite, [Fig. 6.13](#) [19]. Excess carbon tends to partition into the residual austenite by diffusion, but the supersaturation may also be reduced by precipitation in the ferrite.

The time required for a supersaturated plate of ferrite to decarburise by diffusion into austenite is illustrated in [Fig. 6.14](#) for a typical steel. At elevated temperatures the diffusion is so rapid that there is no opportunity to precipitate carbides in the ferrite, giving rise to an upper bainitic microstructure. Cementite eventually precipitates from the carbon-enriched residual austenite.

As the transformation temperature is reduced and the time for decarburisation increases, some of the carbon has an opportunity to precipitate as fine carbides in the ferrite, whereas the remainder partitions into the austenite, eventually to precipitate as inter-plate carbides. This is the lower

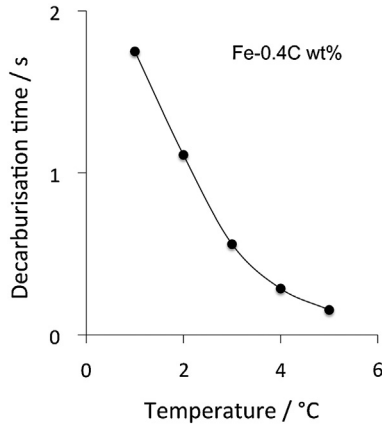


Figure 6.14 The approximate time required to decarburise a supersaturated plate of bainite.

bainite microstructure. Because only a fraction of the carbon partitions into the austenite the inter-plate carbides are much smaller than those associated with upper bainite. This is why lower bainite with its highly refined microstructure is always found to be much tougher than upper bainite, even though it usually has a much higher strength.

A corollary to the mechanism of the transition from upper to lower bainite is that in steels containing high concentrations of carbon, only lower bainite is ever obtained. The large amount of carbon that is trapped in the ferrite by transformation simply cannot escape fast enough into the austenite so that precipitation from ferrite is unavoidable. Conversely, in very low-carbon steels, the time for decarburisation is so small that only upper bainite is obtained by transformation at all temperatures between the pearlite-finish and the martensite-start temperatures.

It is also possible to obtain mixtures of upper and lower bainite by isothermal transformation. As upper bainite forms first, the residual austenite becomes richer in carbon and the tendency to form lower bainite increases as the transformation progresses.

6.8 GRANULAR BAINITE

Granular bainite (Fig. 6.15) describes the bainite that occurs during continuous cooling transformation. This terminology is used widely in industry, where most steels undergo non-isothermal heat treatments. A good exam-

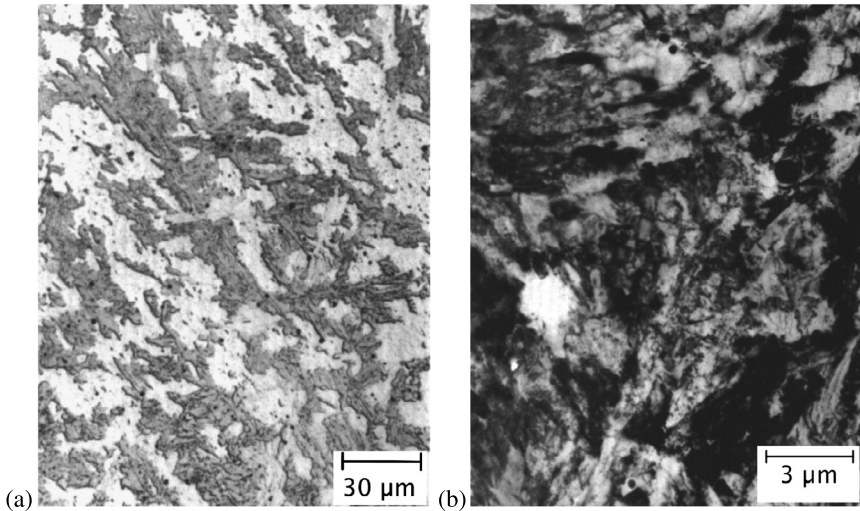


Figure 6.15 Granular bainite in a Fe-0.15C-2.25Cr-0.5Mo wt% steel of the kind used extensively in the energy generation industry. (a) Light micrograph. (b) Corresponding transmission electron micrograph (courtesy of B. Joseffson).

ple is the energy generation industry where larger Cr-Mo steel components are allowed to cool naturally from the austenitic state, to generate bainitic microstructures.

Granular bainite cannot readily be distinguished from ordinary bainite when examined using transmission electron microscopy, because its mechanism of formation is not different. However, because the microstructure forms gradually during cooling, the sheaves of bainite can be rather coarse. The optical microstructure then gives the appearance of blocks of bainite and austenite, so that it is appropriate to use the adjective ‘granular’.

A characteristic (though not unique) feature of granular bainite is the lack of carbides in the microstructure. Instead, the carbon that is partitioned from the bainitic ferrite stabilises the residual austenite, so that the final microstructure contains both retained austenite and some high-carbon martensite in addition to the bainitic ferrite.

6.9 TEMPERING OF BAINITE

The extent and the rate of change of the microstructure and properties during tempering must depend on how far the initial sample deviates from

equilibrium. The behaviour of bainite during tempering is therefore expected to be different from that of martensite.

Unlike martensite, bainitic ferrite usually contains only a slight excess of carbon in solution. Most of the carbon in a transformed sample of bainite is in the form of cementite particles, which in turn tend to be coarser than those associated with tempered martensite. The effects of tempering heat treatments are therefore always milder than is the case when martensite in the same steel is annealed.

Bainite forms at relatively high temperatures where some recovery occurs during transformation. Consequently, when low-carbon bainitic steels are annealed at temperatures as high as 700°C (1 h), there are only minor changes in recovery, morphology or carbide particles. Rapid softening occurs only when the plate-like structure of ferrite changes into equiaxed ferrite. Associated with this change is the spheroidisation and coarsening of cementite. Further tempering has minimal effects.

In marked contrast with martensitic steels, small variations in the carbon concentration (0.06–0.14 wt%) have little effect on the tempering of bainite. Carbon has a very potent solid solution strengthening effect. Thus, the strength of martensite drops sharply as the carbon precipitates during tempering. With bainite the carbon is mostly present as coarse carbides which contribute little to strength. It is not therefore surprising that the tempering response is rather insensitive to the bulk carbon concentration.

Many bainitic microstructures contain appreciable quantities of retained austenite. Tempering, usually at temperatures in excess of 400°C, induces the decomposition of this austenite into a mixture of ferrite and carbides.

Bainitic steels containing strong carbide-forming elements such as Cr, V, Mo and Nb, undergo secondary hardening during annealing at high temperatures. Secondary hardening occurs when fine (more stable) alloy carbides form at the expense of cementite (Chapter 9). Because the cementite in bainite is coarse, the secondary hardening reaction tends to be sluggish when compared with martensite.

There is considerable interest in the use of copper-bearing bainitic steels for applications in heavy engineering. Tempering induces the formation of fine particles of copper which contribute to strength without jeopardising toughness.

To summarise, there are significant differences in the tempering behaviour of bainite and martensite, the most prominent being that there is little carbon in solid solution in bainite. This has the consequence that bainitic microstructures are much less sensitive to tempering, since there

is hardly any loss of strength due to the removal of the small quantity of dissolved carbon. Major changes in strength occur only when the bainite plate microstructure coarsens or recrystallises into one consisting of equiaxed grains of ferrite. Minor changes in strength are due to cementite particle coarsening and a general recovery of the dislocation substructure. Bainitic steels containing strong carbide-forming elements tend to exhibit secondary hardening phenomena rather like those observed in martensitic steels which depends on the precipitation of fine alloy carbides.

6.10 ROLE OF ALLOYING ELEMENTS

Carbon

Carbon has a large effect on the range of temperature over which upper and lower bainite occur. The B_S temperature is depressed by many alloying elements but carbon has the greatest influence, as indicated by the following empirical equation [20]:

$$B_S(^{\circ}\text{C}) = 830 - 270w_{\text{C}} - 90w_{\text{Mn}} - 37w_{\text{Ni}} - 70w_{\text{Cr}} - 83w_{\text{Mo}}, \quad (6.1)$$

where the concentrations w_i are all in wt% and the equation has 90% confidence limits of $\pm 25^{\circ}\text{C}$, over the range of compositions summarised below.

	C	Si	Ni	Cr	Mo
Minimum / wt%	0.10	0.20	0.00	0.00	0.00
Maximum / wt%	0.55	1.70	5.00	3.50	1.00

Carbon has a much larger solubility in austenite than in ferrite, and is a very powerful austenite stabiliser which leads to a general retardation of reaction kinetics. The fraction of carbides to be found in the final microstructure increases in proportion to the carbon concentration, so that the concentration must be kept below about 0.4 wt% to ensure reliable mechanical properties. We have already seen that an increase in carbon makes it easier for lower bainite to form because it becomes more difficult for plates of supersaturated bainitic ferrite to decarburise before the onset of cementite precipitation.

Other alloying elements

In plain carbon steels, the bainitic reaction is kinetically shielded by the reconstructive ferrite and pearlite reactions which commence at higher temperatures and shorter times (Fig. 4.2), so that in continuously cooled

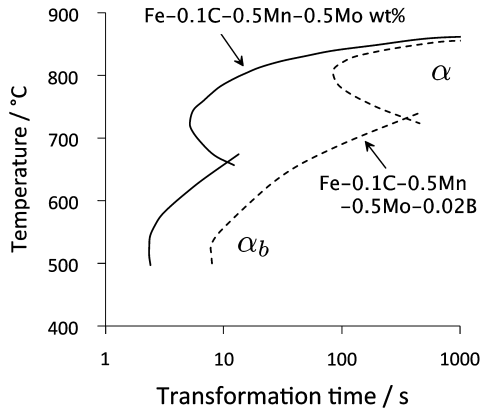


Figure 6.16 Effect of boron on the bainite reaction TTT curves for the initiation of transformation. Adapted from Irvine and Pickering [21].

samples bainitic structures are difficult to obtain. Even using isothermal transformation, difficulties arise if, e.g., the ferrite reaction is particularly rapid. As explained in Chapter 4, the addition of metallic alloying elements usually results in the retardation of the ferrite and pearlite reactions. In addition, the bainite reaction is depressed to lower temperatures. This often leads to a greater separation of the reactions, and the TTT curves for many alloy steels show much more clearly separate C-shaped curves for the pearlite and bainitic reactions (Fig. 4.2). However, it is still difficult to obtain a fully bainitic microstructure because of its proximity to the martensite reaction.

A very effective means of isolating the bainite reaction in low-carbon steels has been found by adding about 0.002 wt% soluble boron to a Mo-containing steel. While the straight molybdenum steel encourages the bainite reaction (Fig. 6.16), the boron markedly retards the ferrite reaction, probably by preferential segregation to the prior austenite boundaries. This permits the bainite reaction to occur at shorter times. At the same time, the bainite C-shaped curve is hardly affected by the boron addition, so that martensite formation is not enhanced. Consequently, by the use of a range of cooling rates, fully bainitic steels can be obtained.

6.11 USE OF BAINITIC STEELS

There are large markets for steels with strengths less than 1000 MPa, and where the total alloy concentration rarely exceeds 2 wt%. Bainitic

steels are well suited for applications within these constraints. However, alloy design must be careful in order to obtain the right microstructures. Steels with inadequate hardenability tend to transform into mixtures of allotriomorphic ferrite and bainite. Attempts to improve hardenability usually lead to partially martensitic microstructures. The solution therefore lies in low-alloy, low-carbon steels, containing small amounts of boron and molybdenum to suppress allotriomorphic ferrite formation. Boron increases the bainitic hardenability. Other solute additions can, in the presence of boron, be kept at sufficiently low concentrations to avoid the formation of martensite. A typical composition might be Fe-0.1C-0.25Si-0.50Mn-0.55Mo-0.003B wt%. Steels like these are found to transform into virtually fully bainitic microstructures with very little martensite using normalising heat treatments.

The most modern bainitic steels are designed with much reduced carbon and other alloying element concentrations. They are then processed using accelerated cooling in order to obtain the necessary bainitic microstructure. The reduced alloy concentration not only gives better weldability, but also a larger strength due to the refined bainitic microstructure.

The range of bainitic alloys available commercially is summarised in Fig. 6.17, and some typical alloy compositions are stated in Table 6.1. The ultra-high-strength steels consist of mixtures of bainite ferrite, martensite and retained austenite. They have an enhanced hardenability using manganese, chromium and nickel, and usually also contain a large silicon concentration (~ 2 wt%) in order to prevent the formation of cementite. High-strength steels are made with very low impurity and inclusion concentrations, so that the steel then becomes susceptible to the formation of cementite particles, which therefore have to be avoided or refined.

Medium-strength steels with the same microstructure but somewhat reduced alloy content have found applications in the automobile industry as crash reinforcement bars to protect against sidewise impact. Another major advance in the automobile industry has been in the application of bainitic forging alloys to the manufacture of components such as cam shafts. These were previously made of martensitic steels by forging, hardening, tempering, straightening and finally stress-relieving. All of these operations are now replaced by controlled cooling from the die forging temperature, to generate the bainitic microstructure, with cost savings which on occasions have made the difference between profit and loss for the entire unit.

Creep-resistant bainitic steels have been used successfully in the power generation industry since the early 1940s. Their hardenability has to be such

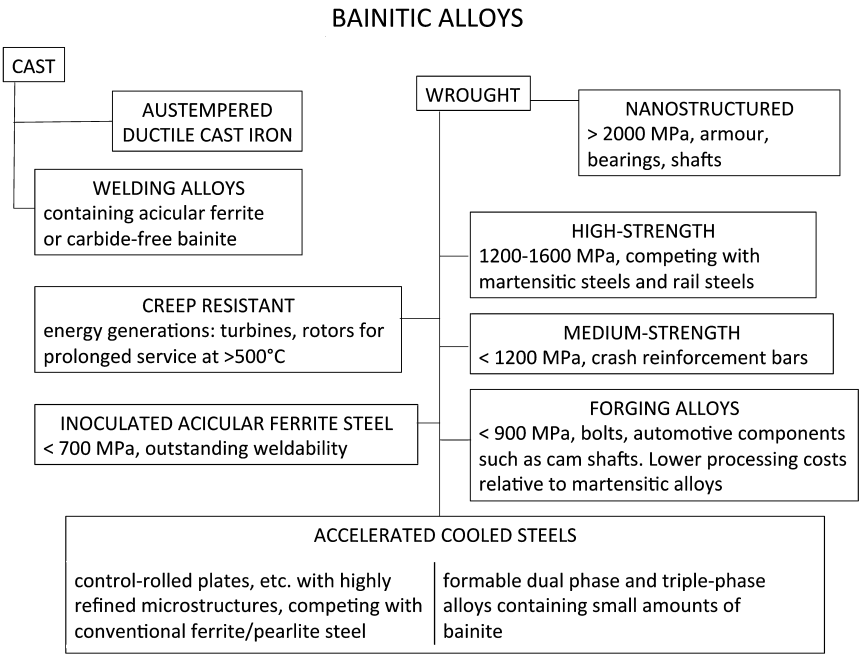


Figure 6.17 Bainitic alloys currently available commercially.

Table 6.1 Chemical composition, wt%, of typical bainitic steels

Alloy	C	Si	Mn	Ni	Mo	Cr	V	B	Nb	Other
Early bainitic steel	0.10	0.25	0.5	–	–	0.003	–	–	–	
Ultra-low carbon	0.02	0.20	2.0	0.3	0.30	–	–	0.010	0.05	
Tough pipeline steel	0.05	0.12	1.55	0.13	–	0.23	–	–	0.10	0.011 Ti
Ultra-high strength	0.20	2.00	3.0	–	–	–	–	–	–	
Creep resistant	0.15	0.25	0.50	–	1.00	2.30	–	–	–	
Forging alloy	0.10	0.25	1.00	0.50	1.00	–	–	–	0.10	
Inoculated	0.08	0.20	1.40	–	–	–	–	–	0.10	0.012 Ti
Bearing alloy	1.0	0.30	0.30	–	–	1.50	–	–	–	
Nanostructured bainite	1.0	1.50	1.90	–	0.26	1.26	0.1	–	–	

that components as large as 1 m in diameter can be cooled continuously to generate a bainitic microstructure throughout the section. The alloys utilise chromium and molybdenum, which serve to enhance hardenability but also, during subsequent heat-treatment, cause the precipitation of alloy carbides which greatly improve the creep resistance.

By inoculating molten steel with controlled additions of non-metallic particles, bainite can be induced to nucleate intragranularly on the inclusions, rather than from the austenite grain surfaces. This intragranularly nucleated bainite is called 'acicular ferrite'. It is a much more disorganised microstructure with a larger ability to deflect cracks. Inoculated steels are now available commercially and are being used in demanding structural applications such as the fabrication of oil rigs for hostile environments.

Advances in rolling technology have led to the ability to cool the steel plate rapidly during the rolling process, without causing undue distortion. This has led to the development of 'accelerated cooled steels' which have a bainitic microstructure, can be highly formable and compete with conventional control-rolled steels.

A much more complete description of the design and exploitation of bainitic steels can be obtained in [4].

6.12 SUMMARY

Bainite can be regarded to form exactly as does martensite, but that it tem-
pers rapidly because of the higher transformation temperatures involved. Thus, excess carbon is able to partition into the residual austenite immediately after transformation, where it either precipitates as cementite or remains in solid solution within the austenite which is then retained to room temperature. The partitioning process is slower when the transformation temperature is reduced, so some carbon has an opportunity to precipitate with the bainitic ferrite to form the lower bainite microstructure.

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BACKNOTES

1. Another case is vanadium hydride, where the crystal structure change is displacive but with hydrogen partitioning to the hydride [1].

CHAPTER 7

Acicular Ferrite

Abstract

Non-metallic inclusions are anathema when it comes to the design of strong steels because they become the initiation sites for fracture. Huge efforts have been made devoted to making clean steels – the oxygen concentration of a hard bearing steel is routinely less than 10 ppm. However, there are other structural steels that have to be welded where the localised heat input generates microstructures in the heat-affected zone that are undesirable. The alloys that are used to deposit the weld must have good properties in the as-cast state. In both of these circumstances, specific non-metallic inclusions are a positive boon in that they provide substrates for the intragranular nucleation of bainite. As a consequence, highly organised sheaves of bainite are altered into a more chaotic arrangement that frequently deflects propagating cracks and hence enhances the toughness. This is the so-called acicular ferrite that is the subject of this chapter.

7.1 INTRODUCTION

Highly organised microstructures can often be found in steels, e.g., ferrite can grow in the form of packets containing parallel plates which are in the same crystallographic orientation (Fig. 7.1a). This can be harmful to mechanical properties because cleavage cracks, or deformation processes, can extend readily across the packets. The effects of the individual plates within these packets then have a minimal effect on the mechanical properties.

Some of the counterintuitive developments in wrought and welded steel technology have involved ‘acicular ferrite’ [1,2]. Far from being organised, this microstructure is better described as chaotic. The plates of acicular ferrite nucleate heterogeneously on small non-metallic inclusions and radiate in many different directions from these ‘point’ nucleation sites (Fig. 7.1b). It is believed that propagating cleavage cracks are frequently deflected as they cross an acicular ferrite microstructure with its many different orientations. This gives rise to superior mechanical properties, especially toughness.

Acicular ferrite is therefore widely recognised to be a desirable microstructure. This chapter deals with the mechanism by which it forms and with the role of inclusions in stimulating its formation.

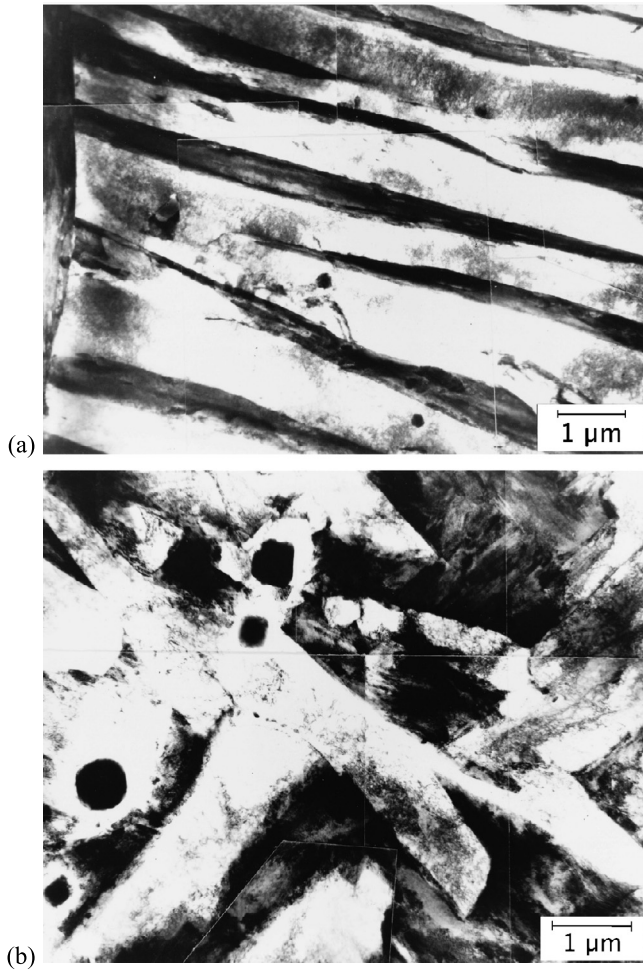


Figure 7.1 Transmission electron micrographs taken from samples transformed at the same temperature but with different austenite grain size. (a) Small austenite grain size leading to plates of ferrite growing in parallel formations. (b) Large austenite grain size with plates of ferrite nucleating intragranularly on non-metallic inclusions and growing along many different directions (courtesy of J.R. Yang).

7.2 MICROSTRUCTURE

The term *acicular* means shaped and pointed like a needle, but it generally is recognised that acicular ferrite has in three dimensions the morphology of thin, lenticular plates (Fig. 7.2). In two-dimensional sections, the acicular ferrite always appears like a plate rather than a section of a rod. Serial sec-

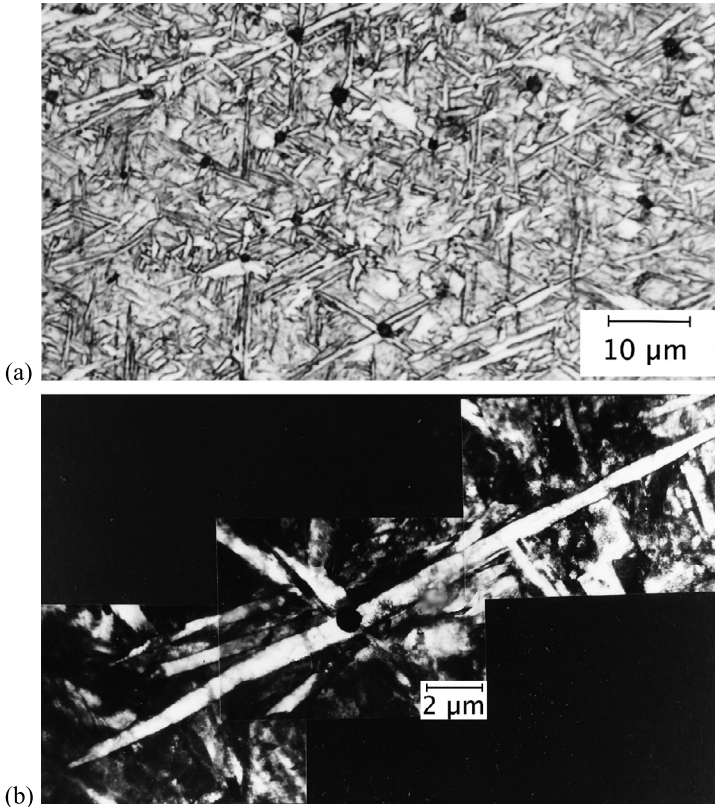


Figure 7.2 (a) Optical micrograph showing multiple plates of acicular ferrite emanating from inclusions. (b) Montage of transmission electron micrograph showing the inclusion as the nucleating point from which the ferrite plates grow (courtesy of Barritte).

tioning experiments which have a depth resolution of about $0.5\text{ }\mu\text{m}$ have confirmed that the shape is between that of a lath or plate, with the length, width and thickness normally less than about 36, 6 and $3\text{ }\mu\text{m}$, respectively [3]. There are difficulties with such experiments. There will be a further loss of resolution in combining the images together to generate a three-dimensional shape. Many of the published images show features such as steps that are known to be artifacts of the reconstruction process.

An optimum method now available for revealing the true shape of fine crystals in a polycrystalline sample involves observation simultaneously on two different surfaces.¹ The technique uses a scanning electron microscope equipped with a focused ion-beam facility that is used to cut a sample of

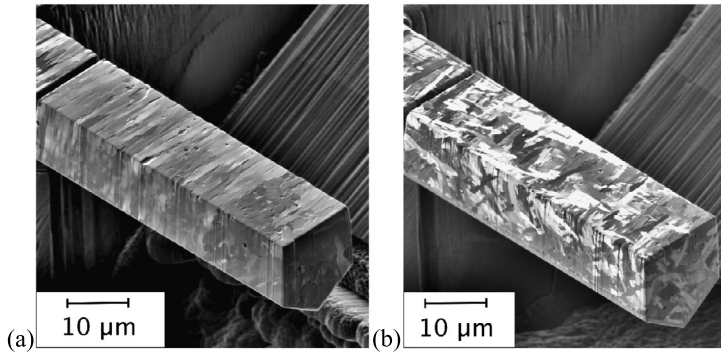


Figure 7.3 Images of samples ion beam machined from a weld, illustrating the three dimensional shapes of (a) bainite and (b) of acicular ferrite in the same steel – reproduced from Costin et al. [5] with permission of Elsevier.

specified shape with incredible accuracy. Fig. 7.3 shows pillars that have been machined out of a weld from two regions of the same chemical composition, one showing the parallel formations of bainite plates and the other the more disorganised arrays of acicular ferrite plates [5]. The individual plates can be followed across the edges between surfaces to verify unambiguously that the shapes are plates in three dimensions.

Although the plates are nucleated heterogeneously on non-metallic inclusions, the chance of observing an inclusion in any given plate is rather small. If the acicular ferrite is approximated as a square plate of side $10\text{ }\mu\text{m}$ and thickness $t = 1\text{ }\mu\text{m}$, containing an inclusion of radius $r = 0.2\text{ }\mu\text{m}$, the ratio of the mean linear intercepts of the two phases is given by $4r/6t$ [6]. If every plate contains an inclusion, some 13% will show the nucleating particle in a plane section which is large enough [7]. It is also likely that once a plate forms on a particle, it stimulates the nucleation of others, an effect known as autocatalysis. Plates generated in this way may not contain any inclusions except those engulfed accidentally by the growing ferrite.

7.3 MECHANISM OF TRANSFORMATION

Acicular ferrite and bainite are in many respects similar in their transformation mechanisms. Their microstructures differ in detail because bainite sheaves grow as a series of parallel platelets emanating from austenite grain surfaces, whereas acicular ferrite platelets nucleate intragranularly at point sites so that parallel formations of plates cannot develop. The nucleation

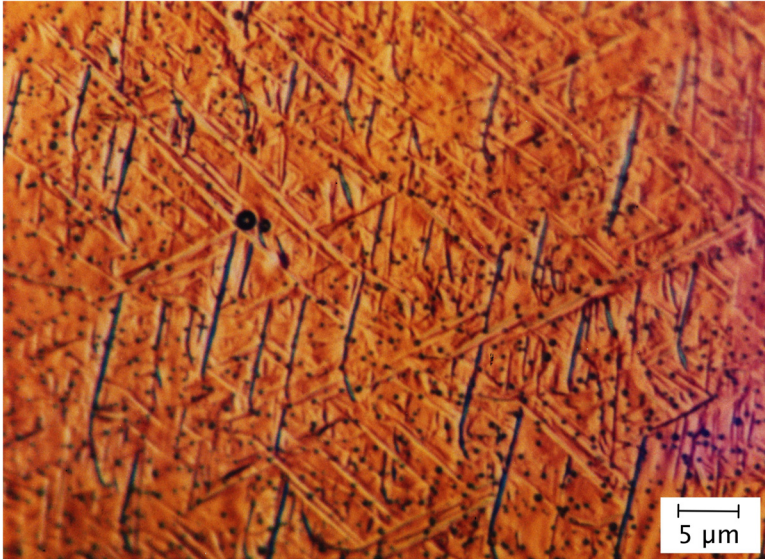


Figure 7.4 Interference contrast micrograph showing the surface relief caused when a metallographically polished sample of steel is transformed to acicular ferrite (courtesy of Strangwood).

site in the latter case is smaller than the thickness of the plate, so that the inclusion is normally engulfed by the plate of ferrite which it stimulates.

The growth of both bainite and acicular ferrite causes an invariant-plane strain shape deformation with a large shear component (Fig. 7.4). Consequently, plates of acicular ferrite cannot cross austenite grain boundaries, because the coordinated movement of atoms implied by the shape change cannot in general be sustained across grains in different crystallographic orientations. The lattice of the acicular ferrite is therefore generated by a deformation of the austenite, so that the iron and substitutional solutes are unable to diffuse during the course of transformation. It is not therefore surprising that the concentrations of substitutional alloying elements are unchanged during the growth of acicular ferrite.

The deformation which changes the austenite into acicular ferrite occurs on particular planes and directions, so that the ferrite structure and orientation are intimately related to that of the austenite. It follows that plates of acicular ferrite, like bainite, must without exception have an orientation relationship with the austenite. This is not necessarily the case when a transformation occurs by a diffusional mechanism, because a grain

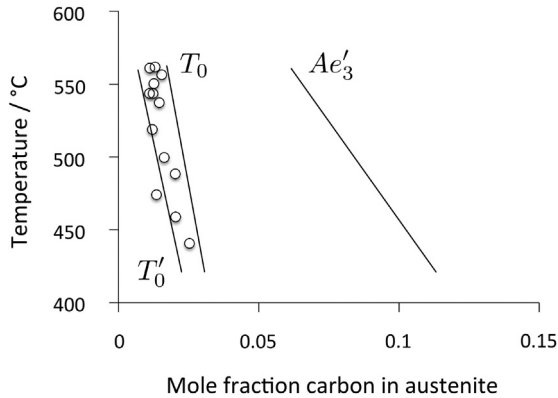


Figure 7.5 Data from experiments in which the austenite is transformed isothermally to acicular ferrite, showing that the reaction stops when the carbon concentration of the austenite reaches the T'_0 curve (courtesy of Strangwood).

of ferrite can easily grow into any adjacent grain of austenite with which it happens to come into contact.

During isothermal transformation, the acicular ferrite reaction stops when the carbon concentration of the remaining austenite makes it impossible to decompose without diffusion. This implies that the plates of acicular ferrite grow supersaturated with carbon, but the excess carbon is shortly afterwards rejected into the remaining austenite. This of course is the incomplete reaction phenomenon described in Chapter 6 for bainite, where the austenite never reaches its equilibrium composition since the reaction stops at the T'_0 curve of the phase diagram, Fig. 7.5 [8]. The obvious conclusion is that acicular ferrite cannot form at temperatures above the bainite-start temperature, and this is indeed found to be the case in practice.

There are many other correlations which reveal the analogy between acicular ferrite and bainite. For example, the removal of inclusions by vacuum arc melting, without changing any other feature, causes an immediate change in the microstructure from acicular ferrite to bainite [9]. The same effect can be obtained by increasing the number density of austenite grain nucleation sites relative to intragranular sites. This can be done by refining the austenite grains to obtain a transition from an acicular ferrite microstructure to one which is predominantly bainitic (Fig. 7.6).

The opposite phenomenon, in which an inclusion-containing steel with bainite can be induced to transform into an acicular ferrite microstructure

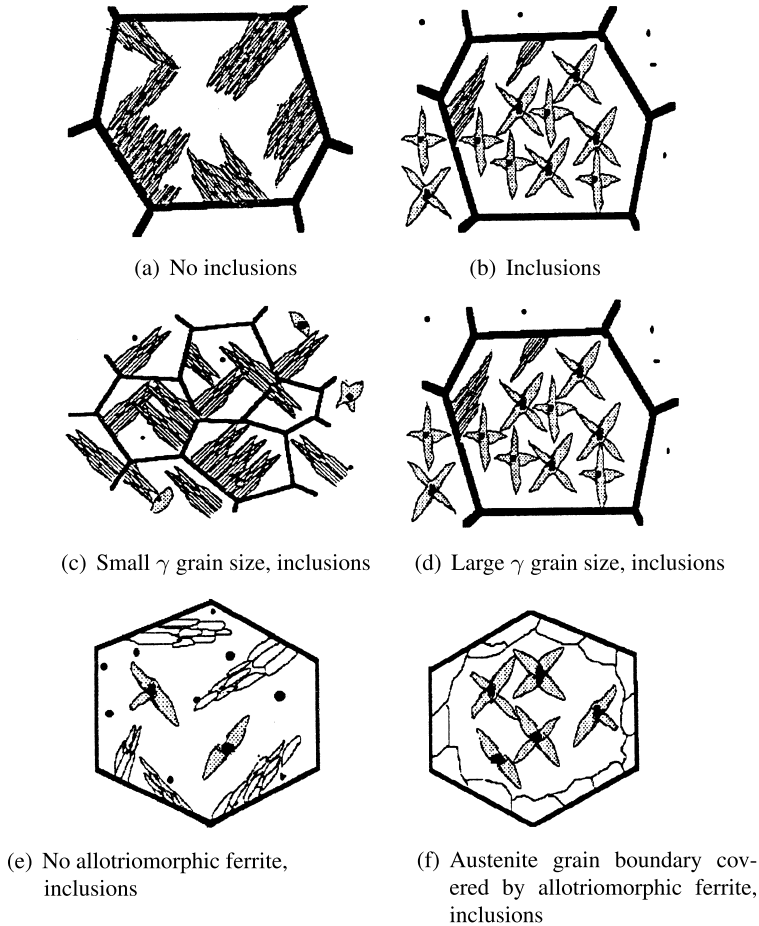


Figure 7.6 The transition from bainite to acicular ferrite because of the change in the ratio of the number density of nucleation sites at austenite grain boundaries to inclusions. (a)→(b) acicular ferrite promoted by introducing inclusions. (c)→(d) acicular ferrite promoted by an increase in the austenite grain size. (e)→(f) acicular ferrite promoted by saturating austenite grain boundaries with allotriomorphic ferrite. Figures courtesy of S.S. Babu.

is also observed. This can be done by rendering the austenite grain surfaces ineffective as nucleation sites, either by decorating the boundaries with a thin layer of inert allotriomorphic ferrite (Fig. 7.7) or by adding a small amount of boron (30 ppm). The boron segregates to the boundaries, thereby reducing the boundary energy and making them less favourable sites for heterogeneous nucleation [10]. In general, any method which

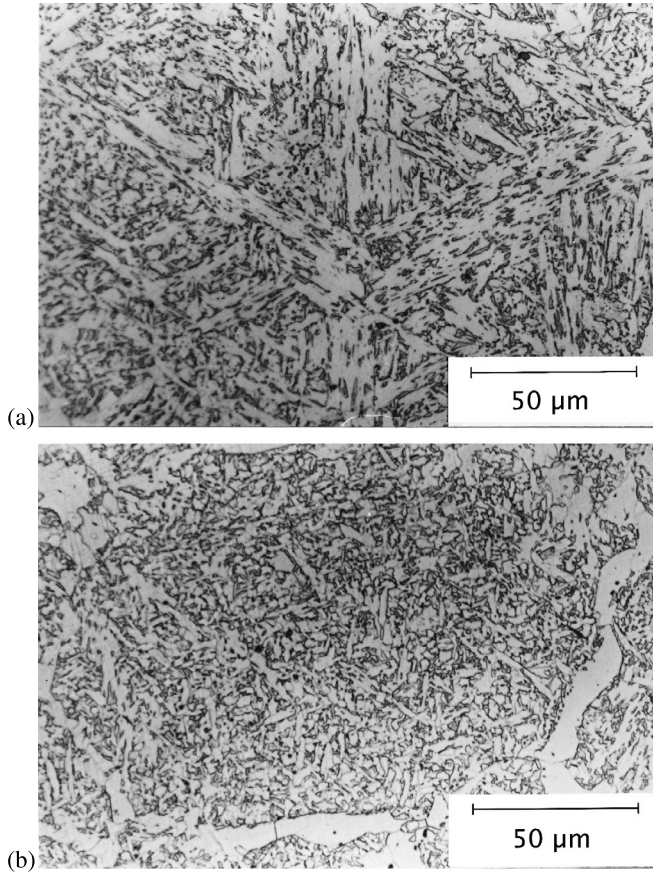


Figure 7.7 The change from a bainitic (a) to an acicular ferrite (b) microstructure when the austenite grain boundaries are eliminated as nucleation sites by decoration with inert layers of ferrite (courtesy of Babu).

increases the number density of intragranular nucleation sites relative to austenite grain boundary sites will favour the acicular ferrite microstructure.

7.4 INCLUSIONS AS HETEROGENEOUS NUCLEATION SITES

Many experiments show that inclusions rich in titanium are most effective in acicular ferrite production (Fig. 7.8). A number of different mechanisms have been proposed. It is rare, however, that the specific titanium com-

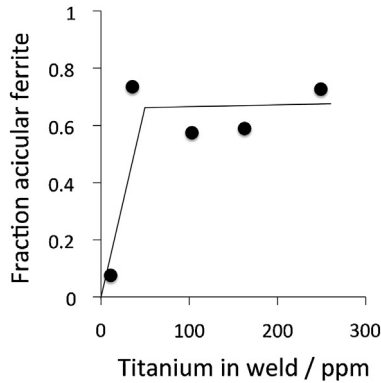


Figure 7.8 Large change in the acicular ferrite content as titanium is introduced into a welding alloy. Data from [11] for manual metal arc weld metal containing about 1.8Mn-0.3Si-0.08C wt%. The sharp initial rise in acicular ferrite content can be attributed directly to the potency of Ti-rich inclusions in stimulating intragranular nucleation, with subsequent smaller changes dependent also on the evolution of other microstructural constituents.

pound responsible for the observed effects is identified. This is because many of the compounds have similar crystal structures and lattice parameters. When microanalysis is used, elements such as C, N and O are either undetectable or cannot be estimated with sufficient accuracy to determine the stoichiometric ratio with respect to Ti. In reality, the non-metallic inclusions tend to consist of many crystalline and amorphous phases, so that it becomes difficult to identify the particular component responsible for nucleation of acicular ferrite.

There are now many results which prove that the inclusions responsible for the heterogeneous nucleation of acicular ferrite are themselves inhomogeneous, as illustrated in Fig. 7.9. The microstructure of the *inclusions* is particularly important from the point of view of developing a clear understanding of their role in stimulating the nucleation of ferrite. As an example, it is sometimes found that the non-metallic particles in some submerged arc weld deposits consist of titanium nitride cores, surrounded by a glassy phase containing manganese, silicon and aluminium oxides, with a thin layer of manganese sulphide (and possibly, titanium oxide) partly covering the surface of the inclusions. The inclusions may therefore be a wide variety of oxides or other compounds, but some can influence the development of microstructure during cooling.

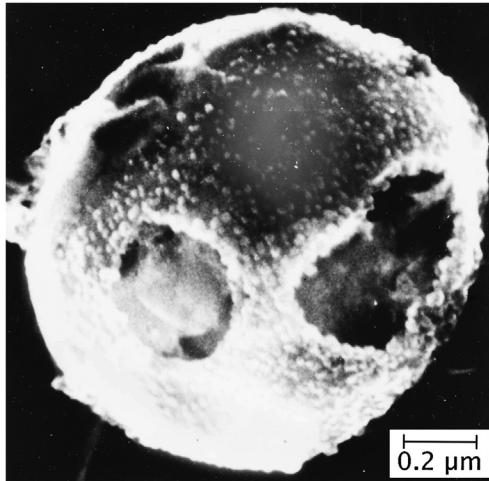


Figure 7.9 Scanning transmission electron micrograph of a non-metallic inclusion in a steel weld metal. The inclusion surface is very irregular, and it features many phases (courtesy of Barritte).

7.5 NUCLEATION OF ACICULAR FERRITE

It has been demonstrated, assuming classical nucleation theory, that inclusions are less effective in nucleating ferrite when compared with austenite grain surfaces. Experiments confirm this since ferrite formation first begins at the austenite grain boundaries. Furthermore, larger inclusions are expected to be more effective since the curvature of the inclusion/ferrite interface will then be reduced. This is confirmed by experimental observations.

7.5.1 Lattice matching theory

Inclusions have long been used to control solidification in aluminium alloys. The aluminium melts are inoculated with particles in order to increase the solid nucleation rate and hence produce a refined grain structure in the fully solidified condition. It is found that inclusions whose lattices match well with solid aluminium are quite effective nucleating agents. This idea has been extrapolated to solid state transformations in steels, where it is argued that those inclusions which show the best 'lattice matching' with ferrite are most effective in nucleating the ferrite.

The lattice matching is expressed in terms of a mean percentage planar misfit κ [12]. To calculate κ , it is assumed that the inclusion is

Table 7.1 Some misfit values between different substrates and ferrite. The data are from a more detailed set published in reference [13] and include all cases where the misfit is found to be less than 5%. The inclusions all have a cubic-F lattice and the ferrite is body-centred cubic (cubic-I)

Inclusion	Orientation	Plane of epitaxy	Misfit (%)
TiO	Bain	$\{1\ 0\ 0\}$	3.0
TiN	Bain	$\{1\ 0\ 0\}$	4.6
γ -alumina	Bain	$\{1\ 0\ 0\}$	3.2
Galaxite	Bain	$\{1\ 0\ 0\}$	1.8
CuS	Cube	$\{1\ 1\ 1\}$	2.8

faceted on a plane $(hkl)_I$, and that the ferrite deposits epitaxially with its plane $(hkl)_\alpha || (hkl)_I$, with the corresponding rational directions $[uvw]_I$, and $[uvw]_\alpha$ being inclined at an angle ϕ to each other. The interatomic spacings d along three such directions ($j = 1, 2, 3$) within the plane of epitaxy are examined to obtain:

$$\kappa = \frac{100}{3} \sum_{j=1}^3 \frac{|d_j^I \cos \phi - d_j^\alpha|}{d_j^\alpha}. \quad (7.1)$$

Data calculated in this manner, for a variety of inclusions phases, are presented in Table 7.1.

To enable the lattice matching concept to be compared against experiments, it is necessary not only to obtain the right orientation relationship, but the inclusion must also be faceted on the correct plane of epitaxy. Many compounds, including some of the titanium oxides, show good matching with ferrite, and indeed seem effective in nucleating ferrite. However, there are other compounds, such as γ -alumina, which show good fit but are ineffective nucleants. It is likely that there is more than one mechanism which helps make a nonmetallic phase a potent heterogeneous nucleation site.

7.5.2 Other possibilities

Other ways in which inclusions may assist the formation of acicular ferrite include stimulation by thermal strains or by the presence of chemical heterogeneities in the vicinity of the inclusion/matrix interface. Alternatively, the inclusions may simply act as inert sites for heterogeneous nucleation. Chemical reactions are also possible at the inclusion matrix interface (Table 7.2). Those minerals which are natural oxygen sources are found to be very effective in stimulating nucleation, probably by inducing decarburisation in the adjacent steel. This effect seems to be independent of the

Table 7.2 List of ceramics which have been tested for their potency in stimulating the nucleation of ferrite plates [14]

Effective: oxygen sources	Effective: other mechanisms	Ineffective
TiO ₂ , SnO ₂	Ti ₂ O ₃	TiN, CaTiO ₃
MnO ₂ , PbO ₂	TiO	SrTiO ₃ , α -Al ₂ O ₃
KNO ₃		NbC

crystallographic nature of the mineral, except in the ability of the mineral to tolerate oxygen vacancy defects, or to thermally decompose. Ti₂O₃ has the ability to cause a dramatic reduction in the manganese concentration of the adjacent steel, and this in turn stimulates nucleation since manganese is an austenite stabiliser. TiO is puzzling in the sense that it is an effective nucleant and yet does not cause any pronounced modification of the adjacent steel. It does have a good lattice match with ferrite, but so does TiN, which is not an effective nucleant.

7.6 SUMMARY

Bainite and acicular ferrite have essentially the same transformation mechanism, but their microstructures differ in detail because the former nucleates at grain surfaces and hence grows in the form of sheaves of parallel platelets. Acicular ferrite, on the other hand, nucleates intragranularly on non-metallic inclusions, which are in effect point nucleation sites. The platelets of acicular ferrite therefore radiate from the individual inclusions, thus generating a microstructure which is much more disorganised with adjacent platelets pointing in different directions. There are many kinds of non-metallic inclusions which are effective in stimulating intragranular nucleation, but some titanium compounds are found to be particularly potent. The exact mechanism of nucleation remains to be resolved.

Acicular ferrite grows without diffusion, but the excess carbon is not retained in the supersaturated ferrite. It is partitioned into the residual austenite shortly after growth. The transformation is accompanied by shear, and rather smaller dilatational displacements which together with the reproducible orientation relationship, the plate shape and lack of chemical composition change fit a displacive mechanism of transformation.

We have now dealt with all the major solid-state transformations that occur in steels and their characteristics can be summarised as in [Table 7.3 \[15\]](#).

Table 7.3 Key transformation characteristics in steels. Martensite α' , lower bainite α_{lb} , upper bainite α_{ub} , acicular ferrite α_a , Widmanstätten ferrite α_w , allotriomorphic ferrite α , idiomorphic ferrite α_i , pearlite P , substitutional solutes X . Consistency of a comment with the transformation concerned is indicated by =, inconsistency by $\neq$; a bullet $\bullet$ identifies the case where the comment is only sometimes consistent with the transformation. The term *parent* γ implies the γ grain from which the product phase grows. Adapted from [15]

Comment	α'	α_{lb}	α_{ub}	α_a	α_w	α	α_i	P
Nucleation and growth reaction	=	=	=	=	=	=	=	=
Plate shape	=	=	=	=	=	$\neq$	$\neq$	$\neq$
IPS shape change with large shear	=	=	=	=	=	$\neq$	$\neq$	$\neq$
Lattice correspondence during growth	=	=	=	=	$\neq$	$\neq$	$\neq$	$\neq$
Co-operative growth of ferrite and cementite	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	=
High dislocation density	=	=	=	=	$\bullet$	$\neq$	$\neq$	$\neq$
Necessarily has a glissile interface	=	=	=	=	=	$\neq$	$\neq$	$\neq$
Always has an orientation within the Bain region	=	=	=	=	=	$\neq$	$\neq$	$\neq$
Grows across austenite grain boundaries	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	=	=	=
High interface mobility at low temperatures	=	=	=	=	=	$\neq$	$\neq$	$\neq$
Acoustic emissions during transformation	=	=	=					
Reconstructive diffusion during growth	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	=	=	=
Bulk redistribution of X atoms during growth	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$\bullet$	$\bullet$	$\bullet$
Displacive transformation mechanism	=	=	=	=	=	$\neq$	$\neq$	$\neq$
Reconstructive transformation mechanism	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	=	=	=
Diffusionless nucleation	=	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$
Only carbon diffuses during nucleation	$\neq$	=	=	=	=	$\neq$	$\neq$	$\neq$
Reconstructive diffusion during nucleation	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	=	=	=
Often nucleates intragranularly on defects	=	$\neq$	$\neq$	=	$\neq$	$\neq$	=	$\neq$
Diffusionless growth	=	=	=	=	$\neq$	$\neq$	$\neq$	$\neq$
Local equilibrium at interface during growth	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$\bullet$	$\bullet$	$\bullet$
Local paraequilibrium at interface during growth	$\neq$	$\neq$	$\neq$	$\neq$	=	$\bullet$	$\bullet$	$\neq$
Diffusion of carbon during transformation	$\neq$	$\neq$	$\neq$	$\neq$	=	=	=	=
Carbon diffusion-controlled growth	$\neq$	$\neq$	$\neq$	$\neq$	=	$\bullet$	$\bullet$	$\bullet$
Incomplete reaction phenomenon	$\neq$	=	=	=	$\neq$	$\neq$	$\neq$	$\neq$

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BACKNOTES

1. This is a high-resolution equivalent of two surface analysis using optical microscopy, for example, the classic work of Srinivasan and Wayman [4].

CHAPTER 8

Heat Treatment of Steels: Hardenability

Abstract

A heat treatment that causes steel to harden is so much more than the mere plunging of hot metal into a fluid that is often a liquid. The initial red-hot state represents the austenitic condition and the subsequent cooling results in a variety of transformations that depend on the chemical composition of the steel. If the intention is to produce a martensitic structure, then the constituents of the steel must be such that the phase is obtained over the depth required. This leads to the definition of hardenability, but it also is necessary to describe the complex phenomena involved in the quench, that depend on the properties of the quenchant and whether or not it is agitated. Heat treatment leads to non-uniform microstructures although the extent of the variation can be controlled. But in addition, there are more subtle effects that leave the final component in a state of stress that can sometimes be beneficial. If the residual stress is allowed to relax then the component may distort. These and other complexities that form the science of heat treatment are introduced in this Chapter.

8.1 INTRODUCTION

The traditional route to high strength in steels is by quenching to form martensite which is subsequently reheated or *tempered* at an intermediate temperature below A_{e1} , increasing the toughness of the steel without too great a loss in strength. Therefore, for the optimum development of strength, a steel must first be fully converted into martensite. To achieve this, the steel must be quenched at a rate sufficiently rapid to avoid the decomposition of austenite during cooling to such products as ferrite, pearlite and bainite. The effectiveness of the quench in a given medium will depend primarily on two factors: the geometry of the specimen, and the composition of the steel.

A large diameter rod quenched in a particular medium will obviously cool more slowly than one with a smaller diameter subjected to a similar treatment. Therefore, the small rod is more likely to become fully martensitic. With the exception of cobalt and aluminium, the addition of common alloying elements to a steel usually moves the time-temperature-transformation curve to longer times, thus making it easier to pass the nose of the curve during a quenching operation, i.e. there is a reduction in the

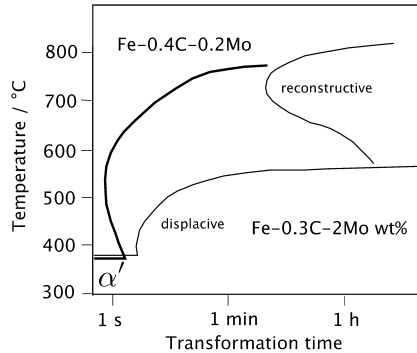


Figure 8.1 TTT diagrams for two steels, one of which is richly alloyed with molybdenum. For clarity, only the curves for the initiation of transformation (5%) are shown. Adapted from [2].

critical rate of cooling needed to make a steel specimen fully martensitic. If this critical cooling rate is not achieved a steel rod will be martensitic in the outer regions which cool faster but, in the core, the slower cooling rate will give rise to bainite, ferrite and pearlite depending on the exact circumstances.

The ability of a steel to form martensite on quenching is referred to as its *hardenability*. This can be simply expressed for steel rods of standard size, as the distance below the surface at which there is 50% transformation to martensite after a standard quenching treatment, and is thus a measure of the depth of hardening.

8.2 USE OF TTT AND CONTINUOUS COOLING DIAGRAMS

TTT diagrams provide a good starting point for an examination of hardenability, but as they are statements of the kinetics of transformation of austenite carried out isothermally, they can only be a rough guide. To take one example, the effect of increasing molybdenum, Fig. 8.1 shows the TTT diagrams for a Fe-0.4C-0.2Mo wt% steel and another that has the composition Fe-0.3C-2Mo wt%. The 0.2 wt% Mo steel begins to transform in about 1 s at 550°C, but on increasing the molybdenum to 2 wt% the whole C-shaped curve is raised and the reaction substantially slowed so that the nose is above 700°C, the reaction starting after 4 min. The high-Mo steel will clearly have a greatly enhanced hardenability over that of the 0.2 wt% Mo steel. Also noticeable is the fact that in the high hardenability alloy, the

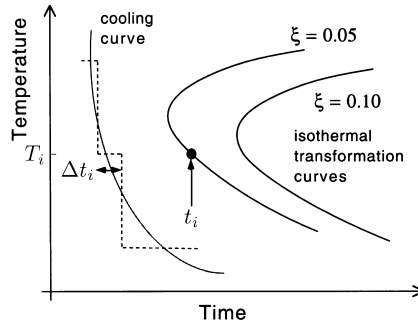


Figure 8.2 The Scheil method for converting between isothermal and anisothermal transformation data.

curves for the reconstructive and displacive transformations are well separated, but because of the rapidity of the reactions in the low-molybdenum steel, there is an overlap of information resulting in an apparently single C-curve over the whole transformation temperature range (cf. Fig. 4.2). If the experimental techniques used has sufficient time resolution, then even the diagram for the low-molybdenum steel will show the two C-curves [1].

The obvious limitations of using isothermal diagrams for situations involving a variety of cooling rates through the transformation temperature range have led to efforts to develop more representative diagrams, i.e. continuous cooling transformation (CCT) diagrams. These diagrams record the progress of the transformation with falling temperature for a series of cooling rates. They are determined using cylindrical rods which are subjected to different rates of cooling, and the onset of transformation is detected by dilatometry, magnetic permeability or some other physical technique. The products of the transformation, whether ferrite, pearlite or bainite, are assessed partly by reference to isothermal diagrams but confirmed by metallographic examination. The results are then plotted on a temperature/cooling time diagram, which records, e.g. the time to reach the beginning of the pearlite reaction over a range of cooling rates.

There is an approximate relationship between TTT and CCT curves based on the so-called additive reaction rule due to Scheil [3]. In this, the cooling curve is treated as a series of isothermal steps. Referring to Fig. 8.2, if the i th step has anisothermal interval Δt_i at a temperature T_i , and if the time taken to achieve $\xi = 0.05$ of isothermal transformation at T_i is t_i , then the same degree of reaction is obtained during continuous cooling when a

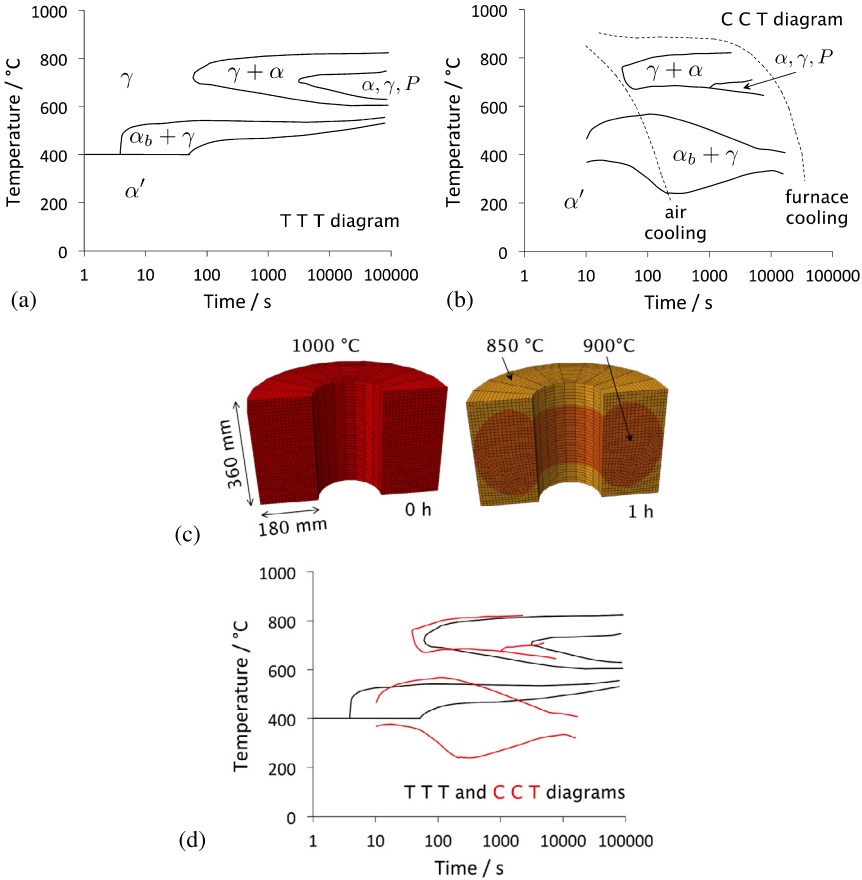


Figure 8.3 $2\frac{1}{4}\text{Cr1Mo}$ steel. (a) TTT diagram. (b) Corresponding CCT diagram. (c) Large components do not cool uniformly. Here, the core of a $2\frac{1}{4}\text{Cr1Mo}$ steel cylinder lags behind the surface temperature by 50°C. The internal diameter of the cylinder is 180 mm (calculations courtesy of S.W. Ooi). (d) Superposed CCT and TTT diagrams. The data for plotting the transformation diagrams are from Lundin et al. [4].

temperature is reached at step j where

$$\sum_{i=1}^j \frac{\Delta t_i}{t_i} = 1 \quad (8.1)$$

with the summation beginning as soon as the parent phase cools below the equilibrium temperature Ae_3 . The method may fail when the transformation rate is determined by multiple functions that vary differently with temperature.

Fig. 8.3a, b show the TTT and corresponding CCT diagrams for a $2\frac{1}{4}\text{Cr1Mo}$ steel used typically as a creep resistant alloy in power plant or petroleum engineering. Such applications require large components, which cannot be transformed isothermally; the thick cylindrical pipe shown in Fig. 8.3c following austenitisation and cooling in air for one hour contains large temperature variations from the core to the surface. The surface experiences air cooling leading eventually to a bainitic microstructure whereas the core is akin to furnace cooling and will contain primarily allotriomorphic ferrite and pearlite.

Fig. 8.3d shows an interesting superposition of the TTT and CCT diagrams. Continuous cooling at slow rates in general accelerates transformation because the incubation of transformation begins immediately the material is cooled below the A_{e3} temperature, whereas in the isothermal case, the steel is cooled too rapidly to the transformation temperature for its cooling history to have any influence.

8.3 HARDENABILITY TESTING

The rate at which austenite decomposes to form ferrite, pearlite and bainite is dependent on the composition of the steel, as well as on other factors such as the austenite grain size, and the degree of homogeneity in the distribution of the alloying elements. It is now possible to estimate hardenability using pragmatic versions of phase transformation theory, but for generic use there are very useful practical tests that allow the hardenability of any steel to be readily determined.

8.3.1 The Grossman test

Much of the earlier systematic work on hardenability was done by Grossman and co-workers who developed a test involving the quenching, in a particular cooling medium, of several cylindrical bars of different diameter of the steel under consideration. Transverse sections of the different bars on which hardness measurements have been made will show directly the effect of hardenability. In Fig. 8.4, which plots these hardness data for bars of different diameters, oil-quenched from the austenitisation temperature of 815°C . It is evident that the full martensitic-hardness is obtained only in the smaller sections, while for larger diameter bars the hardness drops off markedly towards the centre of the bar. The softer and harder regions of the section can in addition be resolved clearly by etching.

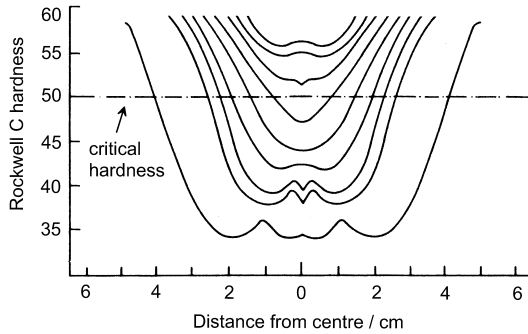


Figure 8.4 Fe-0.4C-1.1Ni-0.75Crwt% steel. Hardness data from transverse sections through water-quenched bars of increasing diameter. For this particular steel, 50% martensite corresponds to the critical hardness illustrated (after Grossman et al. [5]).

Table 8.1 *H*-coefficients of quenching media

Agitation	Cooling medium		
	Oil	Water	Brine
None	0.25–0.30	1.0	2.0
Moderate	0.35–0.40	1.2–1.3	
Violent	0.8–1.1	4.0	5.0

By combining the metallographic and hardness data, the bar diameter that has 50% martensite at its centre is designated the critical diameter D_0 , which will depend on the severity of the quench. However, this dimension is of no absolute value in expressing the hardenability as it will vary if the quenching medium is changed, e.g. from water to oil. It is necessary therefore to assess quantitatively the effectiveness of the different quenching media, by determining the so-called *H*-coefficients (Table 8.1). The value for quenching in still water is set at 1, as a standard against which to compare other modes of quenching.

Using the *H*-coefficients, it is possible to determine in place of D_0 , an ideal critical diameter D_i which has 50% martensite at the centre of the bar when the surface is cooled at an infinitely rapid rate, i.e. when $H = \infty$. Obviously, in these circumstances $D_0 = D_i$, thus providing the upper reference line in a series of graphs for different values of *H* (Fig. 8.5). In practice, *H* varies between about 0.2 and 5.0, so that if a quenching experiment is carried out at an *H*-value of, say, 0.4, and D_0 is measured, then the graph of Fig. 8.5 can be used to determine D_i . This value will be

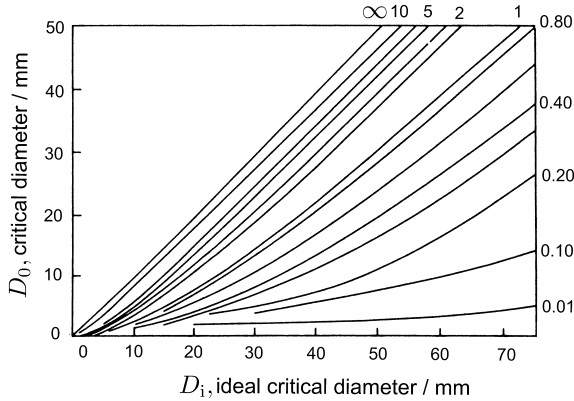


Figure 8.5 Chart for determining ideal diameter (D_i) from the critical diameter (D_0) and the severity of quench (H) for carbon and medium alloy steels (after Grossman and Bain [6]).

a measure of the hardenability of a given steel, which is independent of the quenching medium used.

8.3.2 The Jominy end quench test

While the Grossman approach to hardenability is reliable, other less elaborate tests have been devised to provide hardenability data. Foremost amongst these is the Jominy test, in which a standardised round bar (25.4 mm diameter, 102 mm long) is heated to the austenitising temperature, then placed on a rig in which one end of the rod is quenched by a standard jet of water (Figs. 8.6a). This results in a progressive decrease in the rate of cooling along the bar from the quenched end; the temperature as a function of time and the distance (z) from the quenched end is described roughly by the equation [7]:

$$T - T_o = (T_\gamma - T_o) \operatorname{erf} \frac{z}{2\sqrt{D_{th}t}} \quad (8.2)$$

where T_γ is the austenitisation temperature, T_o that of the quenchant, and D_{th} the thermal diffusivity (radiation heat losses and recalescence effects due to phase change are neglected). The equation assumes conduction heat transfer and that the end of the sample away from the quenchant stays at T_γ , i.e., the sample is semi-infinite in length. Fig. 8.6b shows a finite element calculation of the temperature contours following one minute since the beginning of the water quench. This method avoids most of the approximations associated with the analytical equation for the dissipation of heat;

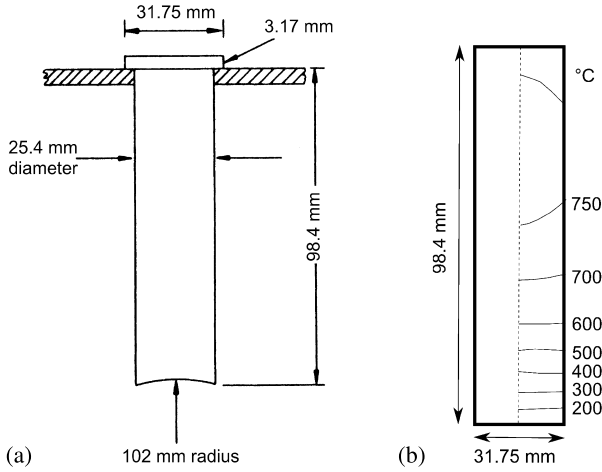


Figure 8.6 (a) The Jominy sample. Following austenitisation, a water jet is directed at the lower end of the sample. (b) Finite element calculation of the temperature profile following one minute of operation of the water jet. The contours are symmetrical about the centreline (adapted from Buchmayr and Kirkaldy [8]).

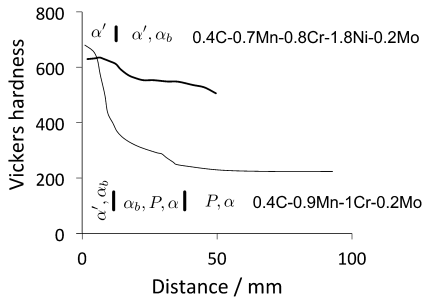


Figure 8.7 Jominy sample hardness data for two steels whose approximate chemical compositions are stated in wt% (adapted using selected data from Buchmayr and Kirkaldy [8] and Kandpal et al. [10]).

for example, the contour at the top of the sample reflects the loss of heat through radiation effects.

The effects of the variations in cooling rate along the length of the test sample generate corresponding variations in microstructure and hardness as illustrated in Fig. 8.7. The two steels illustrated have different hardenabilities in spite of their identical carbon concentration because one of them contains a large nickel concentration which enhances the stability of the austenite. Therefore, only martensite and bainite are obtained to a depth of

some 50 mm, making the steel suitable for relatively deep hardening applications. In any steel that is quenched, the appearance of ferrite and pearlite corresponds to a large reduction in hardness, as expected from the following empirical equations that have been derived from a large experimental database [9]:

$$\begin{aligned}
 \text{HV}_{\alpha'} &= 127 + 949w_{\text{C}} + 27w_{\text{Si}} + 11w_{\text{Mn}} + 8w_{\text{Ni}} + 16w_{\text{Cr}} + 21 \log \dot{T} \\
 \text{HV}_{\alpha_b} &= -323 + 185w_{\text{C}} + 330w_{\text{Si}} + 153w_{\text{Mn}} + 65w_{\text{Ni}} + 144w_{\text{Cr}} + 191w_{\text{Mo}} \\
 &\quad + (89 + 53w_{\text{C}} - 55w_{\text{Si}} - 22w_{\text{Mn}} - 10w_{\text{Ni}} - 20w_{\text{Cr}} - 33w_{\text{Mo}}) \\
 &\quad \times \log \dot{T} \\
 \text{HV}_{\alpha/p} &= 42 + 223w_{\text{C}} + 30w_{\text{Mn}} + 12.6w_{\text{Ni}} + 7w_{\text{Cr}} + 19w_{\text{Mo}} \\
 &\quad + (10 - 19w_{\text{Si}} + 4w_{\text{Ni}} - 8w_{\text{Cr}} + 130w_{\text{V}}) \times \log \dot{T} \quad (8.3)
 \end{aligned}$$

where $\dot{T}$ is the cooling rate in $^{\circ}\text{C h}^{-1}$. The equation applies over the range $0.1 < w_{\text{C}} < 0.5$, $w_{\text{Si}} < 1$, $w_{\text{Mn}} < 2$, $w_{\text{Ni}} < 4$, $w_{\text{Cr}} < 3$, $w_{\text{Mo}} < 1$, $w_{\text{V}} < 0.2$, $(w_{\text{Mn}} + w_{\text{Ni}} + w_{\text{Cr}} + w_{\text{Mo}}) < 5$. w_i represents the wt% of the solute identified in the subscript.

The Jominy test is now used widely to determine hardenabilities in the range $D_i = 1\text{--}6\text{ cm}$; beyond this range the test is of limited use. The results can be readily converted to determine the largest diameter round bar which can be fully hardened. Fig. 8.8 plots bar diameter against the Jominy positions at which the same cooling rates as those in the centres of the bars are obtained for a series of different quenches. Taking the ideal quench ($H = \infty$), the highest curve, it can be seen that at 1.25 cm along the Jominy bar gives a cooling rate equivalent to that at the centre of a 7.5 cm diameter bar. This diameter reduces to just over 50 mm for a quench in still water ($H = 1$). With, e.g., a steel which gives 50% martensite at 19 mm from the quenched end after still oil quenching ($H = 0.3$), the critical diameter D_0 for a round rod will be 5.1 cm.

The diagram in Fig. 8.8 can also be used to determine the hardness at the centre of a round bar of a particular steel, provided a Jominy end quench test has been carried out. For example, if the hardness at the centre of a 5 cm diameter bar, quenched in still water, is required, Fig. 8.8 shows that this hardness will be achieved at about 1.2 cm along the Jominy test specimen from the quenched end. Reference to the Jominy hardness distance plot then gives the required hardness value. If hardness values are required for other points in round bars, e.g. surface or at half-radius, suitable diagrams are available for use.

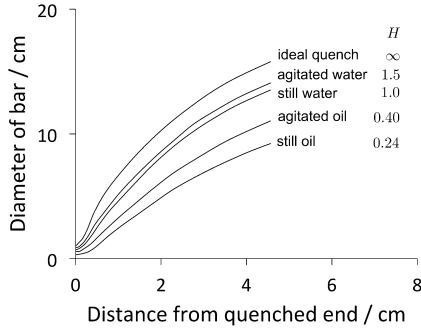


Figure 8.8 Equivalent Jominy positions and bar diameter, where the cooling rate for the bar centre is the same as that for the point in the Jominy specimen. Curves are plotted for a range of cooling rates (after Grossman and Bain [6]).

8.4 EFFECT OF GRAIN SIZE AND CHEMICAL COMPOSITION ON HARDENABILITY

Two important variables which influence hardenability are austenite grain size and chemical composition. The hardenability increases with increasing austenite grain size, because the grain boundary area per unit volume decreases. The sites for the nucleation of ferrite and pearlite are then reduced in number, with the result that these transformations are slowed down, and the hardenability therefore increases. Alloying elements which slow down the ferrite and pearlite reactions increase hardenability as described in Chapter 4.

From a practical point of view, experimental data have been measured as a function of the austenite grain size and carbon concentration, as illustrated in Fig. 8.9. The diagram provides a base hardenability, D_{iC} , which is then modified to account for any additional alloying elements. This is done by using multiplying factors which have been determined experimentally for the familiar alloying elements. The ideal critical diameter D_i is then found from the empirical relationship:

$$D_i = D_{iC} \times 2.21w_{Mn} \times 1.40w_{Si} \times 2.13w_{Cr} \times 3.275w_{Mo} \times 1.47w_{Ni} \text{ mm.} \quad (8.4)$$

8.5 HARDENABILITY AND HEAT TREATMENT

While alloying elements are used for various reasons, they are important in achieving the strength in the required shapes, and often in very large sections. The sections may be up to a metre or more in diameter in the

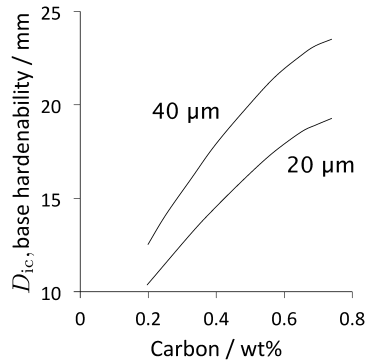


Figure 8.9 Effect of carbon content and grain size on base hardenability (selected data from Moser and Legat [11]). The austenite grain size represents a mean lineal intercept in micrometres.

case of large shafts and rotors. Hardenability is, therefore, of the greatest importance, and one must aim for the appropriate concentrations of alloying element needed to harden fully the section of steel under consideration. Equally, there is little point in using too high a concentration of expensive alloying elements, i.e. more than that necessary for full hardening of the required sections. Carbon has a marked influence of hardenability, but its use at higher levels is limited, because of the lack of toughness which results, as well as the greater difficulties in fabrication and, more important, increased probability of distortion and cracking during heat treatment and welding.

The most economical way of increasing the hardenability of a plain carbon steel is to increase the manganese content; chromium and molybdenum are also very effective, and amongst the cheaper alloying additions per unit of increased hardenability. Boron has a particularly large effect when added to a fully deoxidised low carbon steel, even in concentrations of the order of 0.001 wt%, and would be more widely used if its distribution in steel could be more easily controlled. The role of grain size should not be overlooked because an increase from 0.02 to 0.125 mm can enhance the hardenability by as much as 50%, which is acceptable provided the toughness is not adversely affected.

High hardenability is not always desirable for many tool and machine parts, where a hard wear-resistant surface is best combined with a tough core. Such shallow hardening situations are additionally preferred because, on quenching, the core develops a tensile internal stress while the surface becomes stressed in compression. This situation is desirable because any fa-

tigue cracks nucleated at surface stress concentrations will find propagation more difficult when a compressive stress is present.

8.6 QUENCHING STRESSES AND QUENCH CRACKS

The act of quenching is quite complex because it involves a red-hot sample of steel being plunged into a fluid that usually is at ambient temperature. The instant effect is for the fluid to vaporise; the cooling rate at this stage is slow because the vapour shields the sample from the fluid (Fig. 8.10a). Once the vapour envelope has collapsed, the heat transfer rate increases dramatically due to the rapid removal of heat as the liquid that touches the sample is boiled off. In the final stage, when the sample has a temperature less than the boiling temperature of the fluid, heat transfer slows down because it occurs primarily by conduction and convection.

It frequently is impossible to achieve uniform cooling at all locations on the sample that is quenched. Even when something as simple as a straight bar is plunged into water, the end that enters the water first will cool more rapidly than the opposite end. Having a complex shape does not help – the shaft illustrated in Fig. 8.10b, c has a keyway parallel to its length, which gives rise to non-uniform cooling. As a result, the shaft is distorted on quenching. Distortion must be minimised in production processes for engineering components in order to maintain tolerances and preserve the intended shape of the sample. One method of minimising distortion by using more gentle quenching, for example in water containing polymeric additives, in oil or air-hardening. All of these lead to more uniform cooling of components.

Quenching processes are in general used when producing strong components based on martensitic microstructures. Strong steels are necessarily less tolerant to plastic relaxation during the quench. As a result of the quench stresses, the component may develop serious quench cracks. Fig. 8.11a shows large cracks in a bearing steel that in the quenched state typically has a hardness in excess of 750 HV. Since the interiors of the prior austenite grains are so hard, the sample gives way at the prior austenite grain boundaries so that the cracks meander between those boundaries with occasional excursions into the martensitic matrix.

Fig. 8.11b shows a different kind of cracking induced by quenching. Microscopic cracks form through the thickness of untempered, high-carbon martensite plates. These cracks can be minimised by reducing the

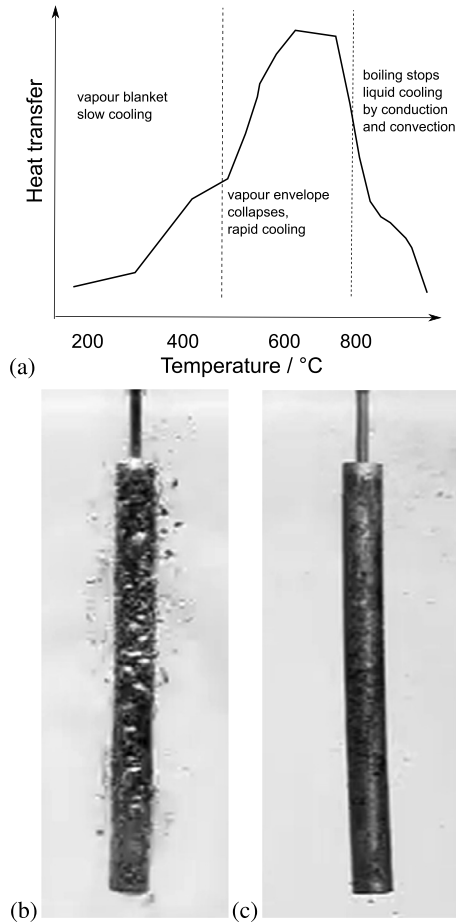


Figure 8.10 (a) Variation in the heat transfer mechanism during a quench (courtesy of Hala Salman Hasan). (b) The moment a red-hot steel shaft containing a keyway parallel to its length, is plunged into water, leading to localised boiling and bubbles. (c) The same shaft at ambient temperature, showing significant distortion. The images are courtesy of M. Narasaki and K. Arimoto of Usunomiya University. The full movie for this can be found on the YouTube channel 'bhadeshia123' and more detail in Arimoto [12].

austenite grain size, which in turn limits the martensite plate size. Small martensite plates are less prone to cracking [13].

To summarise, cracking is a consequence of the internal stresses which develop during quenching from two sources:

1. *Thermal stresses* arising directly from the different cooling rates experienced by the surface and the interior of the steel.

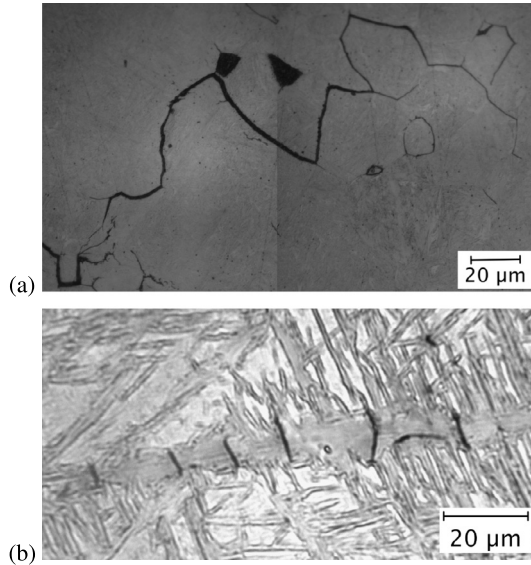


Figure 8.11 (a) Crack in bearing steel containing 1C-1.5Cr wt%, austenitised at 1100°C and quenched into water at 0°C (courtesy of W. Alvarez-Solano). (b) Microscopic cracks in a plate of untempered martensite containing 1C wt% amongst other elements (courtesy of S. Chatterjee).

2. *Transformation stresses* due to the volume changes which occur when austenite transforms to other phases.

An example of the effect of thermal stresses is given in Fig. 8.12 for a 100 mm diameter steel bar quenched into water from 850°C. The temperature-time relationship for the surface and the core are given in Fig. 8.12a, from which it is seen that the maximum temperature difference occurs after a time t , when it is about 500°C, which could give rise to a stress in excess of 1000 MPa, if no relaxation took place. Under these conditions, the surface stress-time relationship would be that of curve A, Fig. 8.12b. However, the maximum stress level is not sustained because plastic deformation takes place and the stress-time relationship in reality is that indicated by curve B. The tensile stress in the surface is balanced by a compressive stress in the core as shown by curve C. At some lower temperature t_2 the compressive and tensile stresses will both fall to zero but as the temperature drops further to room temperature the stress situation reverses and the core goes into tension and the surface into compression. Fig. 8.12c shows the stress distribution through the bar at room temperature.

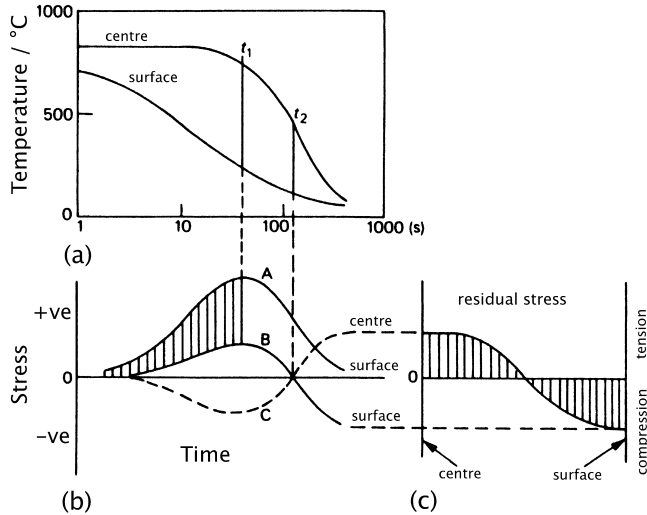


Figure 8.12 Development of thermal stresses during cooling of a 100-mm diameter bar quenched into water from 850°C (after Rose [14]).

The more rapid the quench, the higher the temperature difference between core and surface during quenching and, therefore, the greater the resulting stresses at room temperature. In practical terms this means that avoidance of distortion involves the use of less drastic quenching media, e.g. oil instead of water, and consequently adjustments have to be made to the hardenability if full hardening through the section is required.

Transformation stresses arise from the change in volume associated with the formation of a new phase. The expansion coefficient of austenite is much greater than that of ferrite (Fig. 8.13). This means that transformations that occur at high temperatures lead to a smaller volume change than those that occur at lower temperatures. For example, when austenite transforms into martensite in a 1 wt% carbon steel, there is an increase in volume of 4%, while the transformation to pearlite results in a smaller increase of 2.4%.¹

The effect of these volume changes on the stress pattern developed depends on whether the reactions at the surface and the core start simultaneously, and whether the hardenability is sufficient to permit full hardening or not. If the martensite reaction starts at the surface, a tensile stress is generated there and a compressive stress occurs at the centre, a situation which is accentuated by having the martensite reaction throughout the diameter, i.e. in small sections, or in steels of high hardenability. The presence of a

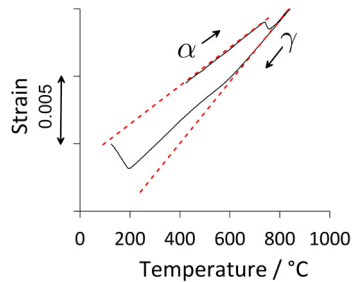


Figure 8.13 A typical heating and cooling curve showing the linear transformation strain, i.e. the vertical distance at any temperature between the dashed lines, as a function of temperature. It is clear that the austenite expansion coefficient (slope of the cooling dashed line) is much greater than that of ferrite. Data courtesy of Nibedita Behara.

tensile stress in the surface region is clearly undesirable, so it is clear that in some cases high hardenability can create problems. This can be avoided by the use of steels which provide only a relatively thin hardened layer at the surface which can be maintained in a state of compression. Surface treatment methods such as carburising and nitriding (section 1.4.3), where the interstitial element concentration is substantially increased by a diffusive process, not only lead to hard wear resistant surfaces, but also surfaces which resist crack propagation by being subject to compressive stresses.

Martensite becomes more brittle with increasing carbon content. In high carbon martensites, which tend to exhibit the burst phenomenon in which individual martensite plates are successively nucleated by previous plates, cracks are often observed in plates at points of impact of later plates upon them. These micro-cracks provide obvious nuclei for the propagation of major cracks. In broader terms, quench cracking is likely to occur when quenching stresses have not been sufficiently released by plastic deformation at elevated temperatures, and they therefore reach the fracture stress of the steel. As in the case of fatigue cracking, the safest situation is to have the most sensitive region of the steel in a state of compression.

There are some fairly obvious precautions which can be taken to avoid such cracking, including the use of the slowest quench compatible with the achievement of adequate hardness. Also stress concentrations in the form of notches, heavy machining grooves and sudden changes in cross section should be avoided where possible, as these will all encourage quench-crack nucleation.

The composition of the steel is important because the transformation characteristics will influence the incidence of cracking. The effect of carbon has already been referred to but, additionally, the M_S temperature decreases with increasing carbon content. Thus, in higher carbon steels, the quenching stresses are less likely to be relieved than would be the case if the martensite begins to form at a higher temperature where the steel is more able to relieve stresses by flow than by fracture. Further, the lower the M_S temperature the larger the change in volume during the transformation and, therefore, the higher the transformation stresses developed. Metallic alloying elements also depress the M_S , but by substantially increasing the hardenability they allow the use of less drastic quenching which greatly reduces the probability of distortion and cracking.

8.7 CRYOGENIC TREATMENT

Liquid nitrogen is cheap and boils at -196°C so this temperature is in practice the lowest used to implement cryogenic treatments. However, many applications do not require such a low temperature so other fluid mixtures are used when sub-zero temperatures are required.

The major use of such treatments is to control retained austenite content. In components containing large concentrations of alloying elements an excessive amount of retained austenite can reduce dimensional stability if the austenite transforms during service. Rotating bearings in particular require dimensional stability because they are press-fitted on to shafts, a fit that can be compromised if the diameter of the bearing increases when the austenite transforms into martensite [17]. Cooling below ambient temperature can, according to the Koistinen and Marburger Equation (5.2), reduce the amount of retained austenite before the bearing is put into service. Although this equation does not contain time, it is necessary to allow sufficient time permit the sample to reach a homogeneous temperature; it also is possible that martensite can form isothermally at low temperatures (Chapter 5).

Excessive retained austenite can compromise the hardness so many tool steels are given sub-zero treatments to induce more martensite to form. It is also possible that some transition carbides form during the cryogenic treatment so the combined effect of martensite and fine precipitates increases the hardness and the tool wear-performance [18]. The formation of carbides at such low temperatures is intriguing and not fully understood.

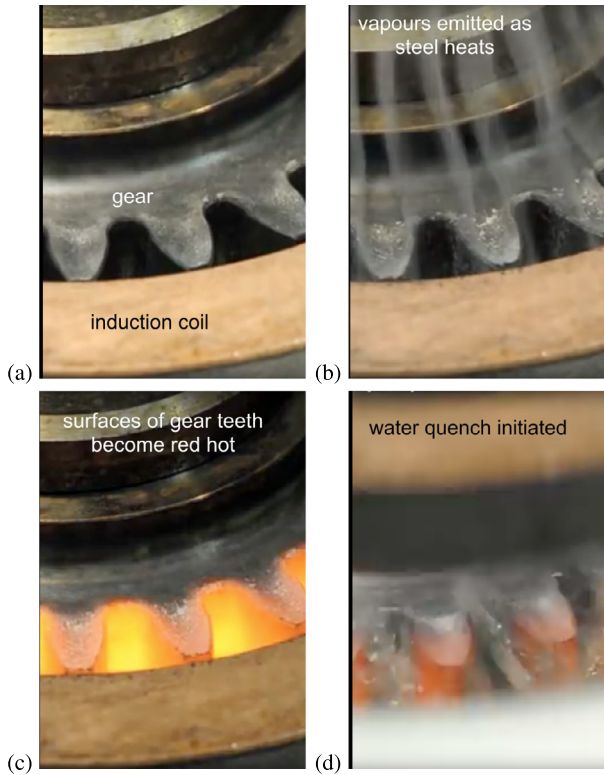


Figure 8.14 Automated inductive hardening of a static gear. The sequence of images is from a movie courtesy of Hans-Werner Zoch of Bremen University. The full movie is available on YouTube channel ‘bhadeshia123’.

In the context of carbide-free steels containing only bainitic ferrite and carbon-enriched retained austenite, cryogenic treatment in liquid nitrogen for 2 h has been found to lead to an overall refinement of the austenite regions due to partial transformation into martensite [19]. As a result, the hardness increased from 640 to 670 HV.

8.8 SUMMARY

There are many historical records on the heat treatment of steel dating back to as long ago as the 12th century [20]; some of this relates to mythology but there are some underlying truths that survive to this day. For example, it was known in the 16th century that quenching in urine is effective in

hardening red-hot iron because of the salt it contains. In the modern context, quenching fluids based on water may contain additives to achieve the most effective cooling conditions. Much is understood about the intimately connected roles of steel composition, the quenching medium and the consequences of the process. These consequences go well beyond the hardness of the steel. The quenching may introduce states of stress in the material that must be accounted for in service. The reproducibility of the process has increased dramatically with the emphasis on automation. Fig. 8.14 illustrates one automated process where carburised gear teeth are heated inductively to that only the regions that require heat treatment experience it, with an automated water quench initiated at the appropriate stage in the sequence.

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BACKNOTES

1. When the austenite is crystallographically textured, the much larger shear strains associated with displacive transformation also manifest [15,16]. But in random microstructures the shear components cancel, leaving only the volume changes.

CHAPTER 9

Tempering of Martensite

Abstract

Martensite in steels can be a very strong but in its virgin condition is rather brittle. It is then necessary to ameliorate this difficulty by heat treatment in the range 150–700°C. This process is called *tempering*, which in plain English means *to moderate*. Tempering compromises the strength so the art is to obtain a good combination of strength and toughness. The mechanism of tempering involves the thermally activated approach to equilibrium, for example by the redistribution of carbon or its precipitation, the rearrangement or elimination of crystal defects and the relief of stresses. These and other aspects of the approach to equilibrium are described in this Chapter.

9.1 INTRODUCTION

Tempering is used to optimise properties for particular applications, but it is driven entirely by the fact that martensite is not an equilibrium phase, which, of course, is why it does not appear on equilibrium phase diagrams. The tendency of the microstructure to react to a tempering heat treatment depends on how far it deviates from equilibrium. The data in [Table 9.1](#) show the components of the excess free energy of martensite in a typical low-alloy steel of chemical composition Fe-0.2C-1.5Mn wt%. The reference state is the equilibrium mixture of ferrite, graphite and cementite, defined here as having a zero stored energy. Graphite precipitates incredibly slowly in steels and is almost never observed during tempering – not surprising given that the reduction in free energy when it forms from a mixture of ferrite and cementite is small (70 J mol^{-1} , [Table 9.1](#)). Preventing the substitutional solute, manganese, from partitioning between the ferrite and the austenite adds a substantial amount of energy, but the greatest stored energy increase comes from the trapping of carbon in supersaturated ferrite. Martensite is in [Table 9.1](#) distinguished from supersaturated ferrite by including the strain and interfacial energies due to its mechanism of transformation.

The general trend during the tempering of martensite therefore begins with the rejection of excess carbon to precipitate carbides but the substitutional solutes do not diffuse during this process. The end result of tempering is a dispersion of coarse carbides in a ferritic matrix which bears little resemblance to the original martensite.

Table 9.1 Stored free energies of a variety of microstructures, adapted from [1]

Phase mixture in Fe-0.2C-1.5Mn wt% at 300 K	Stored energy / J mol ⁻¹
Ferrite, graphite and cementite	0
Ferrite and cementite	70
Para-equilibrium ferrite and para-equilibrium cementite	385
Supersaturated ferrite	1214
Martensite	1914

It should be borne in mind that in many steels, the martensite reaction does not go to completion on quenching, resulting in varying amounts of retained austenite which does not necessarily remain stable during the tempering process.

9.2 TEMPERING INVOLVING CEMENTITE AND TRANSITION CARBIDES

The as-quenched martensite possesses a complex structure which has been referred to in Chapter 5. The laths or plates are heavily dislocated to an extent that individual dislocations are very difficult to observe in thin-foil electron micrographs. A typical dislocation density for a 0.2 wt% carbon steel in its martensitic state is between 0.3 and $1.0 \times 10^{12} \text{ cm}^{-2}$. As the carbon content rises above about 0.3 wt%, fine transformation-twins about 5–10 nm wide are also observed. Often carbide particles, usually rods or small plates, are observed (Fig. 9.1). These occur in the first-formed martensite, i.e. the martensite formed near M_s , which has the opportunity of tempering during the remainder of the quench. This phenomenon, which is referred to as *auto-tempering*, is clearly more likely to occur in steels with a high martensite-start temperature.

On reheating as-quenched martensite, the tempering takes place in four identifiable but overlapping stages¹:

Stage 1, up to 250°C: precipitation of ϵ -iron carbide or other transition carbides; partial loss of tetragonality in the martensite. Excess carbon in the martensite may partition slowly into residual austenite.

Stage 2, between 200°C and 300°C: decomposition of retained austenite.

Stage 3, between 200°C and 350°C: replacement of transition carbides by cementite; martensite loses tetragonality.

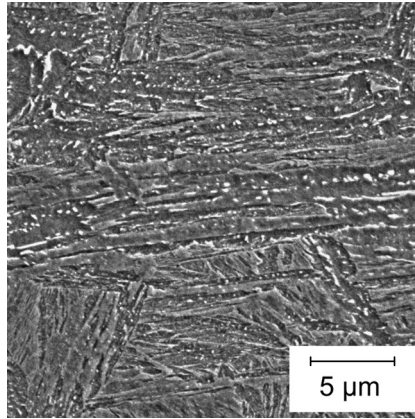


Figure 9.1 A nuclear pressure vessel steel containing just 0.17 wt% carbon, showing autotempered martensite that has formed below the measured M_S temperature of 410°C. The fine particles are cementite (courtesy of H. Pous-Romero). For more details, see [2].

Stage 4, above 350°C: cementite coarsens and spheroidises; recrystallisation of ferrite.

9.2.1 Tempering: stage 1

Martensite formed in medium and high-carbon steels (0.3–1.5 wt% C) is not stable at room temperature because interstitial carbon atoms can diffuse in the tetragonal martensite lattice at this temperature [5]. Direct observations using the atom-probe show that the carbon atoms tend to segregate to defects and form small clusters at temperatures as low as 22°C [6]. Fig. 9.2a shows that the segregation leads to a steady reduction in the carbon that remains in solid solution, as some of the total amount is attracted to defects or into clusters; direct observations of the heterogeneous distribution of carbon in quenched martensite are shown in Fig. 9.2b.

This instability in the distribution of carbon increases between room temperature and 250°C, when ϵ -iron carbide precipitates in the martensite (Fig. 9.3). This carbide has a close-packed hexagonal structure, and precipitates as narrow plates in the matrix, with a well-defined orientation relationship (Jack):

$$\begin{aligned}(101)_{\alpha'} &\parallel (10\bar{1}1)_{\epsilon}, \\ (011)_{\alpha'} &\parallel (0001)_{\epsilon}, \\ [11\bar{1}]_{\alpha'} &\parallel [1\bar{2}10]_{\epsilon}.\end{aligned}$$

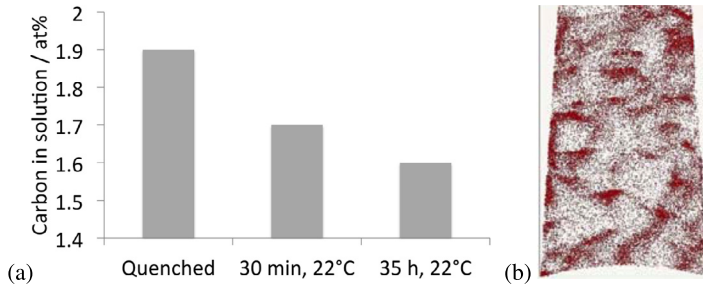


Figure 9.2 (a) Atom-probe observations on a Fe-Ni-C alloy containing 2.08 at% of carbon, with $M_s = -50^\circ\text{C}$, aged at room temperature. The carbon in the matrix is depleted with time as segregation and clustering occurs. Data from Miller et al. [6]. (b) Atom probe tomograph of a quenched Fe-C-Si alloy, showing the heterogeneous distribution of carbon in the martensite. The horizontal extent of the image is about 60 nm and each red dot represents the position of a carbon atom. After Sherman et al. [7], with permission of Springer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this chapter.)

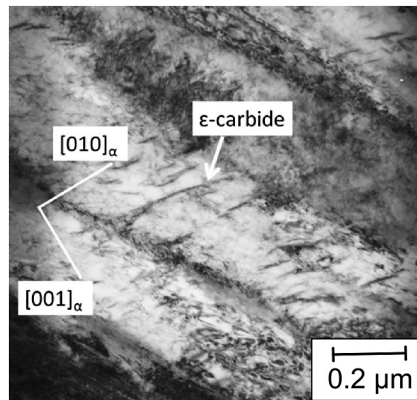


Figure 9.3 ϵ -carbide in a quenched and tempered steel of composition Fe-0.3C-1.6Si-3.5Mn wt% (after Hajyakbary et al. [8], reproduced with permission of Elsevier).

X-ray measurements indicate that the lattice spacings of $(101)_\alpha$ and $(10\bar{1}1)_\epsilon$ are within about 0.5%, so lattice coherency is likely in the early stages of precipitation. In fact, in the higher-carbon steels, an increase in hardness has been observed on tempering in the range $50\text{--}100^\circ\text{C}$, which is attributed to precipitation hardening of the martensite by ϵ -carbide. At the end of stage 1 the martensite still possesses a tetragonality, indicating a carbon content of around 0.25 wt%. It follows that steels with lower carbon contents are unlikely to precipitate ϵ -carbide.

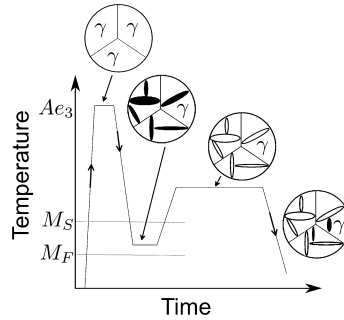


Figure 9.4 The heat treatment used in the quenching and partitioning process. After austenitisation the steel is quenched to produce a mixture of untempered martensite and austenite, which is then heated to allow some of the excess carbon in the martensite to partition into the austenite. On further cooling, a considerable amount of austenite is retained, the remainder decomposing to untempered martensite.

It is possible for some carbon to partition from the supersaturated martensite into the adjacent austenite during tempering [9–11]. This is because the carbon has a lower free energy within the austenite, where its concentration is far less than demanded by equilibrium with ferrite. A modern variant of this partitioning, which exploits the process to stabilise the austenite in order to improve properties, is known as the “quench and partitioning” method [12–15]. The steel is transformed partly into martensite by quenching to a temperature between M_S and M_F (Fig. 9.4). The resulting mixture of martensite and residual austenite is then heated to a higher temperature where some of the excess carbon in the martensite precipitates as carbides, but a significant portion diffuses into the austenite. The enriched austenite is then retained on cooling to ambient temperature and confers a work-hardening capacity to the steel due to deformation-induced martensitic transformation.

9.2.2 Tempering: stage 2

During stage 2, austenite retained during quenching tends to decompose, usually in the temperature range 230–300°C. Cohen and coworkers were able to detect this stage by X-ray diffraction measurements as well as dilatometric and specific volume measurements. In martensitic plain carbon steels with less than 0.5 wt% carbon, the amount of retained austenite is often below 2%, rising to around 6% at 0.8 wt% C and over 30% at 1.25 wt% C. The available evidence suggests that in the range 230–300°C, retained austenite decomposes into bainitic ferrite and cementite. Fig. 9.5 shows how retained

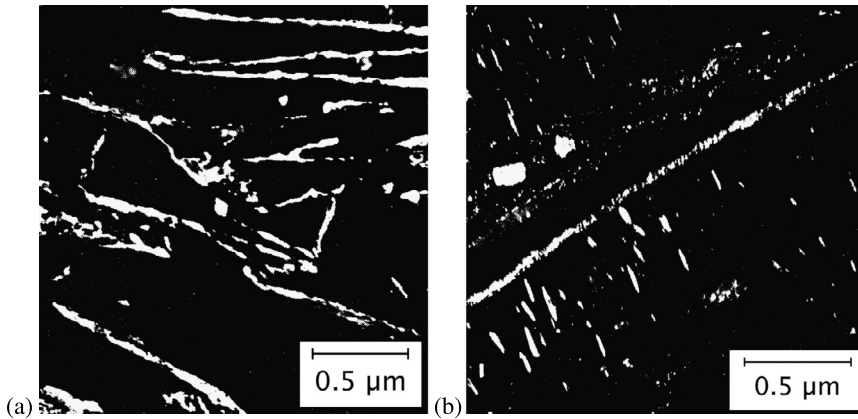


Figure 9.5 Fe-4Mo-0.2C wt% steel. (a) Dark field transmission electron micrograph showing retained austenite films between martensite plates in the as-quenched condition. (b) Dark field transmission electron micrograph showing that the retained austenite has decomposed into an array of discrete particles of cementite at the plate boundaries, following tempering at 295°C for 1 h.

austenite films decompose on tempering into discrete particles of cementite, which can be detrimental to mechanical properties (Chapter 11).

9.2.3 Tempering: stage 3

During the third stage of tempering, cementite first appears in the microstructure as a Widmanstätten distribution of plates which have a well-defined orientation relationship with the matrix which has now lost its tetragonality and become ferrite. The relationship is that due to Bagaryatski:

$$\begin{aligned}(211)_{\alpha'} &\parallel (001)_{\text{Fe}_3\text{C}}, \\ [01\bar{1}]_{\alpha'} &\parallel [100]_{\text{Fe}_3\text{C}}, \\ [\bar{1}11]_{\alpha'} &\parallel [010]_{\text{Fe}_3\text{C}}.\end{aligned}$$

This reaction commences at temperatures as low as 100°C and is fully developed at 300°C (e.g. Fig. 9.5b), with particles up to 200 nm long and ~15 nm in thickness. Similar structures are often observed in lower-carbon steels as-quenched, as a result of the formation of Fe₃C during the quench. During tempering, the most likely sites for the nucleation of the cementite are the ϵ -iron carbide interfaces with the matrix (Fig. 9.3), and as the Fe₃C particles grow, the ϵ -iron carbide particles gradually disappear.

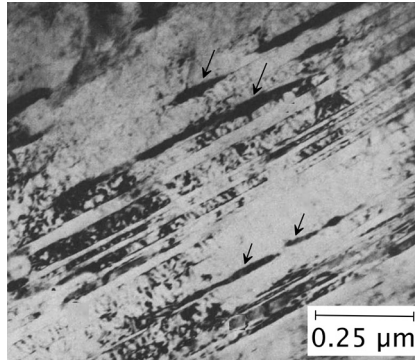


Figure 9.6 Cementite particles (arrows) precipitating on twin boundaries in tempered martensite. After Kraševic et al. [16], with permission from Elsevier.

The twins occurring in the higher carbon martensites are also sites for the nucleation and growth of cementite which tends to grow along the twin boundaries, Fig. 9.6. This is because the atomic arrangement of iron atoms at the twin boundaries is not dissimilar to that found in cementite [16]. The orientation relationship adopted is

$$(211)_{\alpha'} \parallel (\bar{1}01)_{\text{Fe}_3\text{C}},$$

$$[\bar{1}11]_{\alpha'} \approx \parallel [010]_{\text{Fe}_3\text{C}}.$$

A third site for the nucleation of cementite is the martensite lath boundaries (Fig. 9.7a), and precipitation may also occur at the prior austenite grain boundaries (Fig. 9.7b). The cementite can form as very thin films which are difficult to detect but which gradually spheroidise to give rise to well-defined particles of Fe_3C in the grain boundary regions. There is some evidence to show that these grain boundary particles or films can adversely affect ductility. However, they can be modified by addition of alloying elements.

During the third stage of tempering the tetragonality of the matrix disappears and it is then, essentially, ferrite, not supersaturated with respect to carbon, although the consequences of the shape deformation are not yet eliminated. Subsequent changes in the morphology of the cementite particles occur by an Ostwald ripening type of process, where the smaller particles dissolve in the matrix providing carbon for the selective growth of the larger particles.

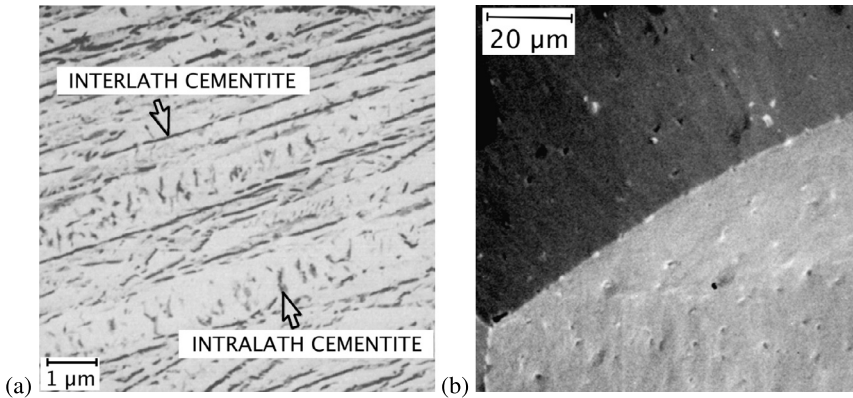


Figure 9.7 (a) Interlath cementite in a quenched and tempered (350°C, 1 h), Fe-0.38C-0.8Mn-0.5Si-1.7Ni-0.8Cr-0.3Mo wt% steel. Adapted from B.C. Kim et al. [17], with permission of Springer. (b) Cementite precipitates at the prior austenite grain boundaries, in a Fe-0.3C-3.5Ni-1.7Cr wt% steel, quenched and tempered at 350°C, 1 h. After Briant and Banerjee [18], with permission of Springer.

9.2.4 Tempering: stage 4

It is useful to define a fourth stage of tempering in which the cementite particles undergo a coarsening process and essentially lose their crystallographic morphology, becoming spheroidised. The coarsening commences between 300°C and 400°C, while spheroidisation takes place increasingly up to 700°C. At the higher end of this range of temperature the martensite lath boundaries are replaced by more equiaxed ferrite grain boundaries in a process which is best described as recrystallisation. The final result is an equiaxed array of ferrite grains with coarse spheroidised particles of Fe_3C (Fig. 9.8), partly, but not exclusively, at the grain boundaries.

The spheroidisation of the Fe_3C is encouraged by the resulting decrease in total interfacial energy per unit volume. The particles which preferentially grow and spheroidise are located mainly at interlath boundaries and prior austenite boundaries, although some particles remain in the matrix. The boundary sites are preferred because of the greater ease of diffusion in these regions. The growth of cementite into ferrite is associated with a decrease in density so vacancies are required to accommodate the growing cementite. Vacancies will diffuse away from cementite particles which are redissolving in the ferrite and towards cementite particles which are growing, so that the rate-controlling process is likely to be the diffusion of vacancies. The measured activation energies are much higher (210–315 kJ mol⁻¹),

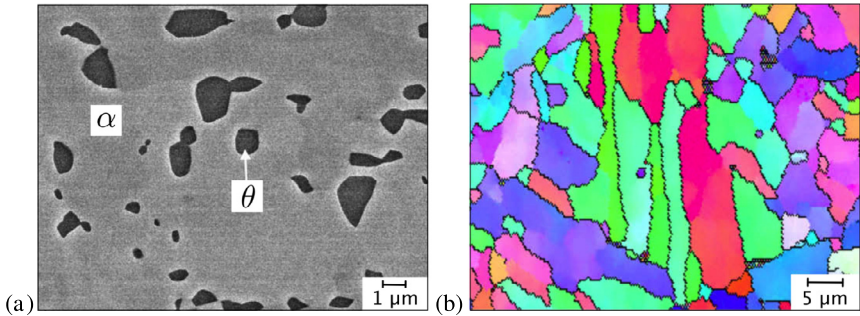


Figure 9.8 Iron-0.6C wt% steel, quenched to martensite and then tempered at 650°C for 1.5 h. (a) Coarse, spheroidised cementite particles. (b) Electron backscatter diffraction orientation image showing the coarsened state of the original martensite plates which would typically have been only 0.24 μm thick. After Miyamoto et al. [19], with permission of Elsevier.

than that for diffusion of carbon in ferrite ($\sim 84 \text{ kJ mol}^{-1}$), and much closer to the activation energy for self diffusion in α -iron ($\sim 240 \text{ kJ mol}^{-1}$).

The original martensite lath boundaries remain stable up to about 600°C, but in the range 350–600°C, there is considerable rearrangement of the dislocations within the laths and at those lath boundaries which are essentially low angle boundaries. This leads to a marked reduction in the dislocation density and to lath-shaped ferritic grains closely related to the packets of similarly oriented laths in the original martensite. This process, which is essentially one of recovery, is replaced between 600°C and 700°C by recrystallisation which results in the formation of equiaxed ferrite grains with spheroidal Fe_3C particles in the boundaries and within the grains. This process occurs most readily in low-carbon steels. At higher carbon contents the increased density of Fe_3C particles is much more effective in pinning the ferrite boundaries, so recrystallisation is much more sluggish. The final process is the continued coarsening of the Fe_3C particles and gradual ferrite grain growth (Fig. 9.9).

9.2.5 Role of carbon content

Carbon has a profound effect on the behaviour of steels during tempering. Firstly, the hardness of the as-quenched martensite is largely influenced by the carbon content (Fig. 5.13), as is the morphology of the martensite laths which have an approximately $\{111\}_\gamma$ habit plane up to 0.3 wt% C, changing to $\{225\}_\gamma$ at higher carbon contents. The M_s temperature is reduced as the carbon content increases, and thus the probability of the occurrence

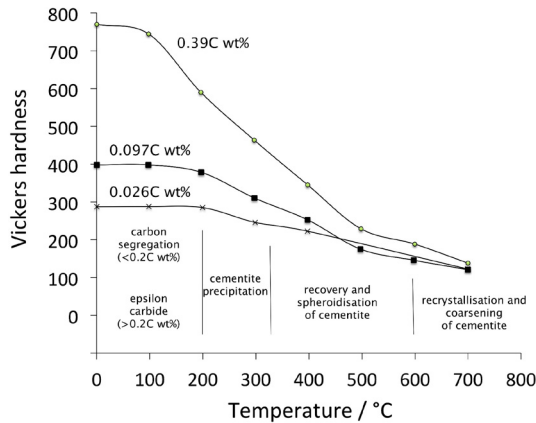


Figure 9.9 Hardness of iron-carbon martensites tempered 1 h at 100–700°C. Adapted from Speich [20].

of auto-tempering is less. During fast quenching in alloys with less than 0.2 wt% C, the majority (up to 90%) of the carbon segregates to dislocations and lath boundaries, but with slower quenching some precipitation of cementite occurs. On subsequent tempering of low-carbon steels up to 200°C further segregation of carbon takes place, but no precipitation has been observed. Under normal circumstances it is difficult to detect any tetragonality in the martensite in steels with less than 0.2 wt% C, a fact which can also be explained by the rapid segregation of carbon during quenching or because M_S exceeds the Zener ordering temperature.²

The hardness changes during tempering are also very dependent on carbon content, as shown in Fig. 9.9 for steels up to 0.4 wt% C. Above this concentration, an increase in hardness has been observed in the temperature range 50–150°C, as ϵ -carbide precipitation strengthens the martensite. However, the general trend is an overall softening, as the tempering temperature is raised. The diagram indicates the main physical processes contributing to the change in mechanical properties.

9.3 MECHANICAL PROPERTIES OF TEMPERED MARTENSITE

The intrinsic mechanical properties of tempered plain carbon martensitic steels are difficult to measure for several reasons. Firstly, the absence of other alloying elements means that the hardenability of the steels is low, so a fully martensitic structure is only possible in thin sections. However, this may

Table 9.2 Mechanical properties of plain carbon steels, both as-quenched and tempered (after Irvine et al. [24])

Steel (wt% C)	Property	Tempered			
		As-quenched	Tempered 7 h at		
			100°C	200°C	300°C
0.2	0.2% Proof strength (MPa)	1270	1460	1235	1110
0.3		1360	1370	1270	1140
0.4			1670	1410	
0.2	UTS (MPa)	1470	1690	1450	1340
0.3		1580	1605	1460	1240
0.5				2040	1600
0.2	Elongation (%)	5	6	6	9
0.3		5	7	7	10
0.5				4	7
0.2	Vickers hardness	446	444	446	357
0.3		564	517	502	420
0.5		680	666	571	470

not be a disadvantage where shallow hardened surface layers are all that is required. Secondly, at lower carbon levels, the M_S temperature is rather high, so auto-tempering is likely to take place. Thirdly, at the higher carbon levels the presence of retained austenite will influence the results. Added to these factors, plain carbon steels can exhibit quench cracking which makes it difficult to obtain reliable test results. This is particularly the case at higher carbon levels, i.e. above 0.5 wt% carbon.

Provided care is taken, very good mechanical properties, in particular proof and tensile stresses, can be obtained on tempering in the range 100–300°C. However, the elongation is frequently low and the impact values poor. Table 9.2 shows some typical results for plain carbon steels with between 0.2 and 0.5 wt% C, tempered at low temperatures.

Plain carbon steels with less than 0.25 wt% are not normally quenched and tempered, but in the range 0.25–0.55 wt% C heat treatment is often used to upgrade mechanical properties. The usual tempering temperature is between 300°C and 600°C allowing the development of tensile strengths between 1700 and 800 MPa, the toughness increasing as the tensile strength decreases. This group of steels is very versatile as they can be used for crankshafts and general machine parts as well as hand tools, such as screw-drivers and pliers.

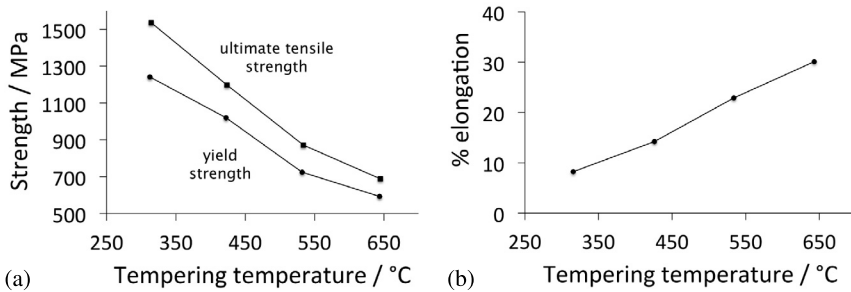


Figure 9.10 Fe-0.52C-0.93Mn wt% steel, quenched into a martensitic state and then tempered at the temperatures indicated, in each case for 1 h. (a) Strength. (b) Ductility. Selected data from the Metals Handbook [25].

The high-carbon steels (0.5–1.0 wt%) are much more difficult to fabricate and are, therefore, particularly used in applications where high hardness and wear resistance are required, e.g. axes, knives, hammers, cutting tools. Typical mechanical properties as a function of tempering temperature are shown in Fig. 9.10 for a steel at the lower level (0.5 wt% C) of this range. Another important application is for springs, where often the required mechanical properties are obtained simply by heavy cold work, i.e. hard drawn spring wire. However, carbon steels in the range 0.5–0.75 wt% C are quenched, then tempered to the required yield stress.

9.4 STEELS WITH STRONG CARBIDE-FORMING ELEMENTS

The addition of alloying elements to a steel has a substantial effect on the kinetics of the $\gamma \rightarrow \alpha$ transformation, and also of the pearlite reaction. Most common alloying elements move the time-temperature-transformation curves to longer times, with the result that it is much easier to ‘miss’ the nose of the curve during quenching. This essentially gives higher hardenability, since martensite structures can be achieved at slower cooling rates and, in practical terms, thicker specimens can be made fully martensitic. Alloying elements have also been shown to have a substantial effect in depressing the M_s temperature (Equation (5.18)). In this section, we will examine the further important effects of alloying elements during the tempering of martensite, where not only the kinetics of the basic reactions are influenced but also the products of these reactions can be substantially changed, e.g. cementite can be replaced by other carbide phases. Several of

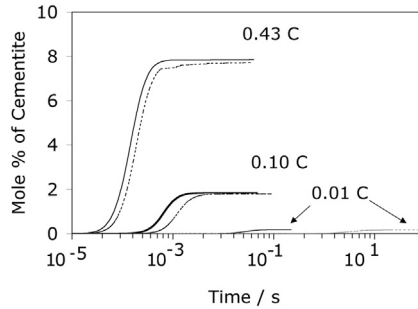


Figure 9.11 Kinetics of paraequilibrium cementite precipitation from supersaturated Fe-0.4C-0.7Mn-0.28Si-0.8Cr-1.8Ni-0.25Mo wt% (continuous curves) and Fe-0.4C-0.7Mn-1.6Si-0.8Cr-1.8Ni-0.25Mo wt% (dotted curves) steels as a function of carbon concentration.

the simpler groups of alloy steels will be used to provide examples of the general behaviour.

9.4.1 The effect of alloying elements on the formation of iron carbides

The structural changes during the early stage of tempering are difficult to follow. However, it is clear that certain elements, notably silicon, can stabilise the ε -iron carbide to such an extent that it is still present in the microstructure after tempering at 400°C in steels with 1–2 wt% Si, and at even higher temperatures if the silicon is further increased. The evidence suggests that both the nucleation and growth of the carbide is slowed down and that silicon enters into the ε -carbide structure. It is also clear that the transformation of ε -iron carbide to cementite is delayed considerably. Fig. 9.11 shows calculated kinetics of cementite precipitation from supersaturated ferrite, assuming that the Fe/X ratio remains constant, as a function of the silicon and carbon concentrations; the effect of silicon, not illustrated here, is much more significant when cementite precipitates from austenite [26].

While the tetragonality of martensite disappears by 300°C in plain carbon steels, in steels containing some alloying elements, e.g. Cr, Mo, W, V, Ti, Si, the tetragonal lattice is still observed after tempering at 450°C and even as high as 500°C. In contrast manganese and nickel decrease the stability of the tetragonal state (Fig. 9.12).

Alloying elements also greatly influence the proportion of austenite retained on quenching. Typically, a steel with 4 wt% molybdenum,

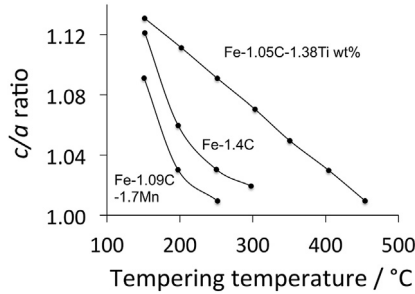


Figure 9.12 Effect of Ti and Mn on the tetragonality of martensite during tempering. Data from Kurdjumov [27].

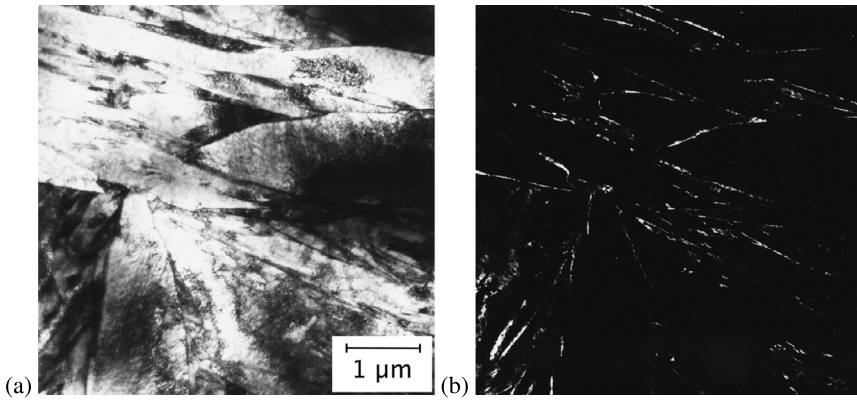


Figure 9.13 Fe-4Mo-0.2C wt% steel austenitised and quenched to produce martensite. (a) Bright field image. (b) Corresponding dark field image showing films of austenite retained between the martensite platelets.

0.2 wt% C, in the martensitic state contains less than 2 vol.% austenite, and about 5 vol.% is detected in a steel with 1 wt% vanadium and 0.2 wt% C.³ The austenite can be revealed as a fine network around the martensite laths, by using dark field electron microscopy (Fig. 9.13). On tempering each of the above steels at 300°C, the austenite decomposes to give thin grain boundary films of cementite which, in the case of the higher concentrations of retained austenite, can be fairly continuous along the lath boundaries. It is likely that this interlath cementite (Fig. 9.5b) is responsible for *tempered martensite embrittlement*, frequently encountered as a toughness minimum in the range 300–350°C, by leading to easy nucleation of cracks, which then propagate across the tempered martensite laths.

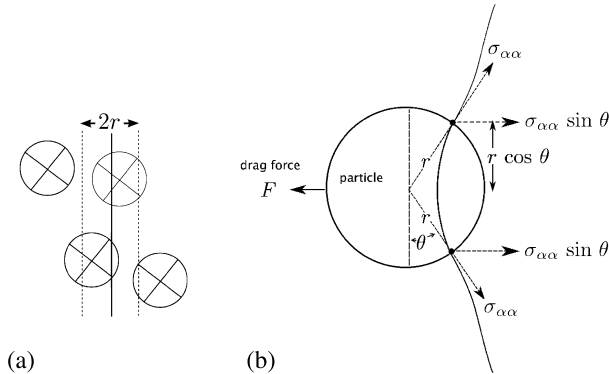


Figure 9.14 (a) Particles whose centres are located a distance r from the boundary intersect it. (b) The pinning geometry when a boundary intersects a particle.

Alloying elements can also restrain the coarsening of cementite in the range 400–700°C, a basic process during the fourth stage of tempering. Several alloying elements, notably silicon, chromium, molybdenum and tungsten, cause the cementite to retain its fine Widmanstätten structure to higher temperatures, either by entering into the cementite structure or by segregating at the carbide–ferrite interfaces. Whatever the basic cause may be, the effect is to delay significantly the softening process during tempering. This influence on the cementite dispersion has other effects, in so far as the carbide particles, by remaining finer, slow down the reorganisation of the dislocations inherited from the martensite, with the result that the dislocation substructures refine more slowly. The cementite particles are also found on ferrite grain boundaries, where they control the rate at which the ferrite grains grow.

Recrystallisation and grain growth involve the movement of grain boundaries. The motion will be inhibited by second phase particles. The drag on the boundary due to an array of insoluble, incoherent spherical particles is because the grain boundary area decreases when a boundary intersects the particle. Therefore, to move away from the particle requires the creation of new surface. To deal with this, we need a net drag force on a boundary of energy $\sigma_{\alpha\alpha}$ per unit area due to a particle of radius r is given by (Fig. 9.14)

$$F = \sigma_{\alpha\alpha} \sin\{\theta\} \times 2\pi r \cos\{\theta\} \quad (9.1)$$

where $\sigma_{\alpha\alpha} \sin\{\theta\}$ is the force per unit length in the direction of boundary motion, and the remaining term on the right represents the length of the

intersection of the boundary plane with the particle. By differentiating this the maximum force occurs at so that at $\theta = 45^\circ$, with $F_{\max} = \sigma_{\alpha\alpha}\pi r$.

Suppose now that there is a random array of particles, volume fraction V_V with N_V particles per unit volume then

$$N_V = \frac{V_V}{\frac{4}{3}\pi r^3}. \quad (9.2)$$

Only those particles within a distance $\pm r$ can intersect a plane. The number of particles intersected by a plane of area 1 m^2 will therefore be

$$n = 2r \times N_V = \frac{3V_V}{2\pi r^2}. \quad (9.3)$$

The drag pressure P is then often expressed as

$$P = F_{\max}n = \frac{3\sigma_{\alpha\alpha}V_V}{2r}. \quad (9.4)$$

This may be a significant pressure if the particles are fine. Anisotropic particles may have a larger effect if they present a greater surface area for interaction with the boundary.

The pinning force $F_{\max}$ opposes the movement of a boundary, whereas the need to minimise the total interfacial energy per unit volume drives the motion. A grain size given by a mean lineal intercept $\bar{L}$ has an amount $S_V = 2/\bar{L}$ of surface per unit volume. It follows that the energy locked as grain boundaries, per unit volume, is $\sigma_{\alpha\alpha}S_V$ so that the force driving the grain boundary motion is $2\sigma_{\alpha\alpha}/\bar{L}$. Grain growth stops when the particle pinning force equals this driving force, i.e.

$$\frac{3\sigma_{\alpha\alpha}V_V}{2r} = \frac{2\sigma_{\alpha\alpha}}{\bar{L}} \quad \text{or when the grain size becomes} \quad \bar{L} = \frac{4r}{3V_V}. \quad (9.5)$$

The theory presented here roughly follows Zener; more sophisticated models are reviewed in [28].

In plain carbon steels cementite particles begin to coarsen in the temperature range $350\text{--}400^\circ\text{C}$, and addition of chromium, silicon, molybdenum or tungsten delays the coarsening to the range $500\text{--}550^\circ\text{C}$. It should be emphasised that up to 500°C , the only carbides to form are those of iron. However, they will take varying amounts of alloying elements into solid solution and may reject other alloying elements as they grow.

9.4.2 The formation of alloy carbides: secondary hardening

A number of the familiar alloying elements in steels form carbides which are thermodynamically more stable than cementite. It is interesting to note

that this also is true of a number of nitrides and borides. Nitrogen and boron are increasingly used in steels in small but significant concentrations. The enthalpies of formation of some of these compounds are shown in Fig. 4.9, in which iron carbide is the least stable compound situated at the right of the diagram. The alloying elements Cr, Mo, V, W and Ti all form carbides with substantially higher enthalpies of formation, while the elements nickel, cobalt and copper do not form carbide phases. Manganese is a weak carbide former, found in solid solution in cementite and not in a separate carbide phase.

It would, therefore, be expected that when strong carbide-forming elements are present in a steel in sufficient concentration, their carbides would be formed in preference to cementite. Nevertheless, during the tempering of all alloy steels, alloy carbides do not form until the temperature range 500–600°C, because below this the metallic alloying elements cannot diffuse sufficiently rapidly to allow alloy carbides to nucleate. The metallic elements diffuse substitutionally, in contrast to carbon and nitrogen which move through the iron lattice interstitially, with the result that the diffusivities of carbon and nitrogen are several orders of magnitude greater in iron than those of the metallic alloying elements (Table 1.3). Consequently, higher temperatures are needed for the necessary diffusion of the alloying elements prior to the nucleation and growth of the alloy carbides and, in practice, for most of the carbide-forming elements this is in the range 500–600°C.

The coarsening of carbides in steels is an important phenomenon which influences markedly the mechanical properties. The free energy per atom of a spherical particle that is small is greater than that of a particle which has a larger radius. When an atom is added to a spherical particle of radius r , its surface area increases by $2V_m/A_v r$, where V_m is the molar volume of precipitate and V_m/A_v is the volume per atom since A_v is Avogadro's constant. Therefore, the free energy increases by $\Delta G = 2\sigma_{\theta\alpha} V_m/A_v r$, where $\sigma_{\theta\alpha}$ is the interfacial energy of cementite/ferrite interface per unit area. For a very large particle of radius r_∞ , this excess free energy due to interface would essentially be zero. Therefore, diffusion will occur from the small to the large particle, with the former dissolving and the latter growing; the flux is driven by ΔG which we have seen is proportional to $1/r$. For a set of spherical particles, the interparticle spacing is also proportional to $1/r$. It follows that the rate of coarsening, $dr/dt \propto 1/r^2$, which on integration gives an r^3 dependence on time. A more thorough derivation by Lifshitz

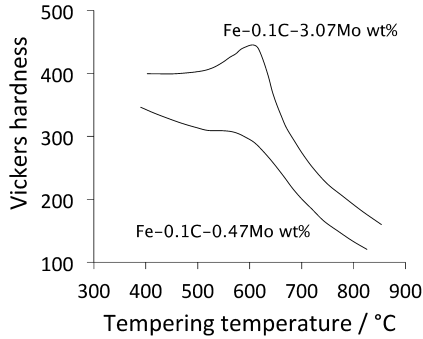


Figure 9.15 The effect of molybdenum on the tempering for 1 h, of quenched 0.1 wt% C steels. Selected data from Irvine and Pickering [29].

and Wagner [30,31] leads to this dependence as follows:

$$\bar{r}_t^3 - \bar{r}_o^3 = \frac{C_3}{RT} V_m^2 D \sigma_{\theta\alpha} t, \quad (9.6)$$

where $\bar{r}_o$ is the mean particle radius in the initial distribution of particles, $\bar{r}_t$ is the corresponding mean particle radius at time t , D diffusion coefficient of solute in matrix, and C_3 is a constant.

The coarsening rate is dependent on the diffusion coefficient of the solute and, under the same conditions, at a given temperature, cementite would coarsen at a greater rate than any of the alloy carbides once formed. This occurs in alloy steels in which cementite and an alloy carbide coexist, where the cementite dispersion is always much coarser. It is this ability of certain alloying elements to form fine alloy carbide dispersions in the range 500–600°C, which remain very fine even after prolonged tempering, that allows the development of high strength levels in many alloy steels. Indeed, the formation of alloy carbides between 500°C and 600°C is accompanied by a marked increase in strength, often in excess of that of the as-quenched martensite (Fig. 9.15). This phenomenon, which is referred to as *secondary hardening*, is best shown in steels containing molybdenum, vanadium, tungsten, titanium and also in chromium steels at higher alloy concentrations.

This secondary-hardening process is a type of age-hardening reaction, in which a relatively coarse cementite dispersion is replaced by a new and much finer alloy carbide dispersion. In Fig. 9.15 the effect of increasing molybdenum content is thus effectively demonstrated in a series of steels containing 0.1 wt% carbon. Significantly, non-carbide-forming elements such as nickel, cobalt, silicon, do not give secondary hardening. However,

some elements, e.g. silicon, by delaying the coarsening of cementite, lead to a plateau on the tempering curve in the range 300–500°C.

9.4.3 Nucleation and growth of alloy carbides

The dispersions of alloy carbides which occur during tempering can be very complex, but some general principles can be discerned which apply to a wide variety of steels. The alloy carbides can form in at least three ways:

1. *In-situ* nucleation at pre-existing cementite particles – it has been shown that the nuclei form on the interfaces between the cementite particles and the ferrite. As they grow, carbon is provided by the adjacent cementite which gradually disappears.
2. By separate nucleation within the ferrite matrix – usually on dislocations inherited from the martensitic structure.
3. At grain boundaries and sub-boundaries – these include the former austenite boundaries, the original martensitic lath boundaries (now ferrite), and the new ferrite boundaries formed by coalescence of sub-boundaries, or by recrystallisation.

In-situ nucleation at pre-existing cementite particles is a common occurrence but, because these particles are fairly widely spaced at temperatures above 500°C, the contribution of this type of alloy carbide nucleation to strength is very limited. Fig. 9.16a shows, in a 4 wt% molybdenum steel tempered 4.5 h at 550°C, the relatively coarse Widmanstätten precipitation of Fe_3C , which at this stage has largely transformed to fine Mo_2C particles. These are readily identified by dark field microscopy. On further tempering, the positions of the original cementite particles are indicated by small necklaces of alloy carbides which tend to be coarser than the matrix precipitation.

Fig. 9.16a also illustrates the dislocation network characteristic of tempered steels as inherited from the martensite, although there has been considerable rearrangement and reduction in dislocation density. Dark field electron microscopy reveals that these dislocations are the sites for very fine precipitation of the appropriate alloy carbide. On further ageing the particles are more readily resolved, e.g. in Mo steels as a Widmanstätten array, comprising Mo_2C rodlets lying along $\langle 001 \rangle_\alpha$ directions. Fig. 9.16b illustrates this stage in a single martensitic lath. Heavier precipitation is evident at the lath boundaries.

The nucleation of carbides at the various types of boundary is to be expected because these are energetically favourable sites which also provide

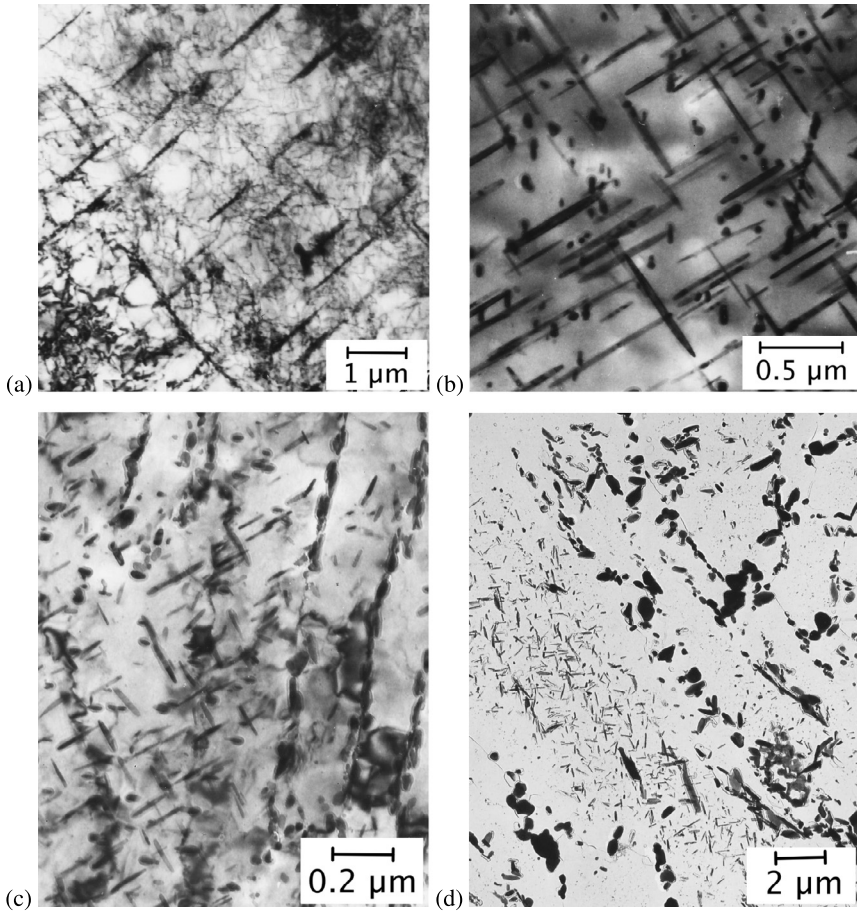


Figure 9.16 Fe-4Mo-0.2C wt% steel, quenched into a martensitic microstructure and then tempered. (a) Tempered at 563°C for 4½ h, showing cementite transforming *in situ* into Mo₂C (courtesy of Raynor). The structure remains heavily dislocated. (b) Tempered at 675°C for 15 h, showing three variants of Mo₂C needles growing along $\langle 001 \rangle_\alpha$ directions. One of these variants appears in cross-section (Raynor). (c) Tempered at 700°C for 30 min showing fine Mo₂C within the laths and M₆C at lath boundaries (courtesy of Irani). (d) Extraction replica image of the sample in (c) showing with greater clarity, the two kinds of precipitates (Irani).

paths for relatively rapid diffusion of solute. Consequently the ageing process is usually more advanced in these regions and the precipitate is more massive (Fig. 9.16c). In many alloy steels, the first alloy carbide to form is not the final equilibrium carbide and, in some steels, as many as three alloy carbides can form successively. In these circumstances, the equilibrium alloy

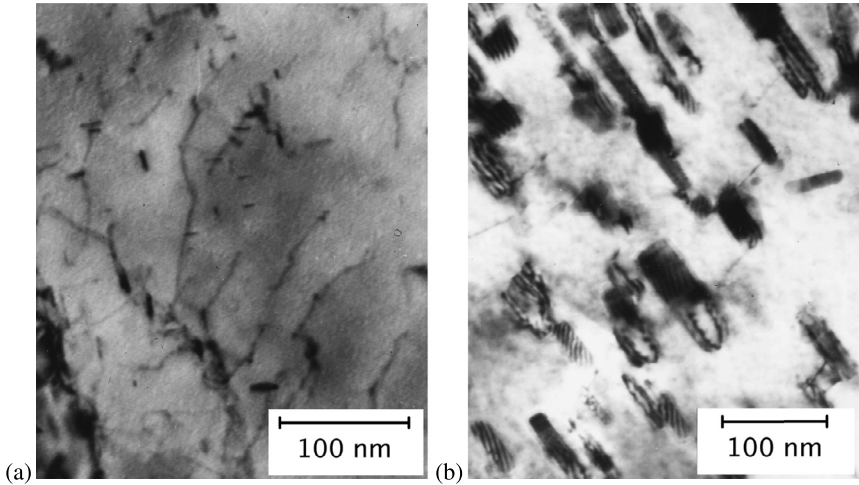


Figure 9.17 Fe-1V-0.2C wt% quenched and tempered. Thin-foil electron micrographs: (a) 72 h at 550°C, VC nucleation on dislocations (courtesy of Raynor); (b) 50 h at 700°C. Plates of VC (courtesy of Irani).

carbide frequently nucleates first in the grain boundaries, grows rapidly and eventually completely replaces the Widmanstätten non-equilibrium carbide within the grains. This is illustrated in Fig. 9.16c for a 4 wt% Mo steel tempered 30 min at 700°C, in which M_6C equiaxed particles are growing at the grain boundaries but Widmanstätten Mo_2C is still visible within the grains. It is interesting to note that the structure still possesses the lath-shaped ferrite grains inherited from the martensite. Recrystallisation occurs after longer times at 700°C.

9.4.4 Tempering of steels containing vanadium

Vanadium is a strong carbide former and, in steel with as little as 0.1 wt% V, the face-centred cubic vanadium carbide (VC) is formed. It is often not of stoichiometric composition, being frequently nearer V_4C_3 , but with other elements in solid solution within the carbide. Normally, this is the only vanadium carbide formed in steels, so the structural changes during tempering of vanadium steels are relatively simple.

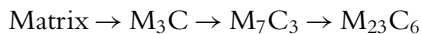
Vanadium carbide forms as small platelets, initially less than 5 nm across and not more than 1 nm thick. These form within the ferrite grains on dislocations (Fig. 9.17a) in the range 550–650°C, and produce a marked secondary-hardening peak. There is a well-defined orientation relation–

ship (Baker/Nutting) with the ferrite matrix: $(100)_\alpha \parallel (100)_{VC}$ and $[010]_\alpha \parallel [011]_{VC}$. In the early stages of precipitation at 550°C , the particles are coherent with the matrix, there being only a 3% misfit between $\langle 010 \rangle_\alpha$ and $\langle 110 \rangle_{VC}$. However, at 700°C , the platelets coarsen rapidly (Fig. 9.17b) and begin to spheroidise. However, the original martensite laths can still be recognised, and are only replaced by equiaxed ferrite grains after long periods at 700°C .

Many steels containing vanadium, e.g. $\frac{1}{2}\text{Cr}\frac{1}{2}\text{Mo}\frac{1}{4}\text{V}$, $1\text{Cr}\frac{1}{4}\text{V}$, $3\text{Cr}1\text{Mo}\frac{1}{4}\text{V}$, $1\text{Cr}1\text{Mo}\frac{3}{4}\text{V}$, will exhibit extensive vanadium carbide precipitation on tempering, because of the stability of this carbide, not only with respect to cementite but also the several chromium carbides and molybdenum carbide (Fig. 4.9). Because of its ability to maintain a fine carbide dispersion, even at temperatures approaching 700°C , vanadium is an important constituent of steels for elevated temperature service.

9.4.5 Tempering of steels containing chromium

In chromium steels, two chromium carbides are very often encountered: Cr_7C_6 (trigonal) and Cr_{23}C_6 (cubic). The normal carbide sequence during tempering is:



where as usual 'M' represents a mixture of iron and chromium atoms, although the M_7C_3 and M_{23}C_6 are rich in Cr. While this sequence occurs in higher-chromium steels, below about 7 wt% Cr, Cr_{23}C_6 is absent unless other metals such as molybdenum are present. Chromium is a weaker carbide former than vanadium, which is illustrated by the fact that Cr_7C_3 does not normally occur until the chromium content of the steel exceeds 1 wt% at a carbon level of about 0.2 wt%.

In steels up to 4 wt% Cr, the transformation from Fe_3C to Cr_7C_3 occurs mainly by nucleation at the Fe_3C /ferrite interfaces. Steels up to 9 wt% Cr do not show secondary-hardening peaks in tempering curves (Fig. 9.18). However, these curves do exhibit plateaus at the higher chromium contents, which are associated with the precipitation of Cr_7C_3 . Chromium diffuses rapidly in ferrite and is usually present in relatively large concentration, with the result that Cr_7C_3 is detected during tempering at temperatures as low as 500°C , and in comparison with vanadium carbide, chromium carbide coarsens rapidly. Thus, in a 2 wt% Cr-0.2 wt% C steel, continuous softening will normally occur on tempering between 500°C

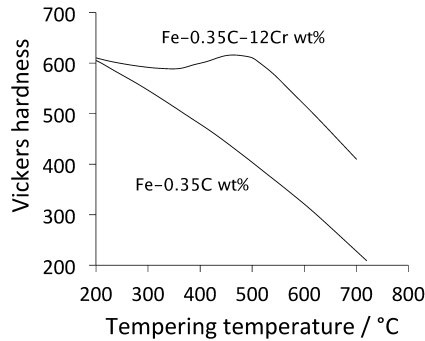


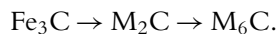
Figure 9.18 The effect of chromium on the tempering of a 0.35 wt% C steel. Selected data from Bain and Paxton [32].

and 700°C, although addition of other alloying elements, e.g. Mo, can reduce the rate of coarsening of Cr_7C_3 .

In contrast, a 12 wt% Cr steel will exhibit secondary hardening in the same temperature range (Fig. 9.18) due to precipitation of Cr_7C_3 . Additionally, Cr_{23}C_6 nucleates at about the same time but at different sites, particularly former austenite grain boundaries and at ferrite lath boundaries. This precipitate grows at the expense of the Cr_7C_3 which eventually disappears from the microstructure, at which stage the steel has completely overaged. This transition from Cr_7C_3 to Cr_{23}C_6 in high-chromium steels is by separate nucleation and growth. Further alloying additions can promote one or other of these carbide reactions, e.g. addition of tungsten encourages formation of Cr_{23}C_6 by allowing it to nucleate faster, while vanadium tends to stabilise Cr_7C_3 . In doing so, it decreases the rate of release into solution of chromium and carbon needed for the growth of Cr_{23}C_6 . Clearly, vanadium would be a preferred addition to tungsten, if a fine stable chromium carbide dispersion is needed in the temperature range 550–650°C.

9.4.6 Tempering of steels containing molybdenum and tungsten

When molybdenum or tungsten is the predominant alloying element in a steel, a number of different carbide phases are possible, but for composition between 4 and 6 wt% of the element the carbide sequence is likely to be:



The carbides responsible for the secondary hardening in both the case of tungsten and molybdenum are the isomorphous hexagonal carbides Mo_2C

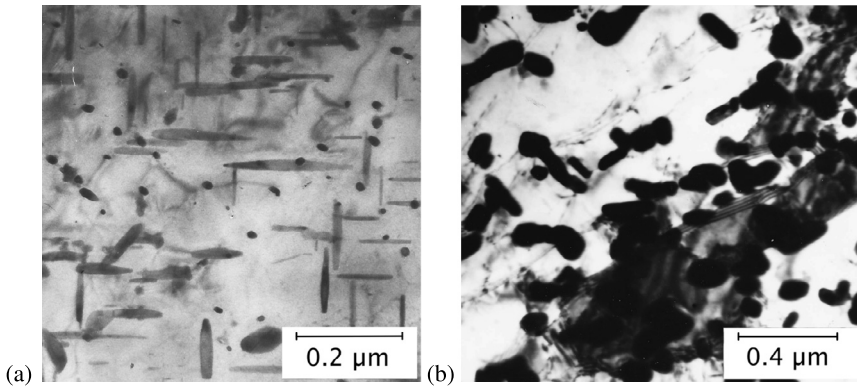


Figure 9.19 Fe-6W-0.23C wt%, quenched into a martensitic microstructure and then tempered. (a) Tempered for 100 h at 600°C, showing needles of W_2C along the $\langle 100 \rangle_\alpha$ directions. (b) Tempered for 5 h at 700°C, showing coarse precipitates of M_6C . Courtesy of Davenport.

and W_2C , both of which, in contrast to vanadium carbide, have a well-defined rodlet morphology (Fig. 9.19a). When formed in the matrix, M_2C adopts a Widmanstätten distribution lying along $\langle 100 \rangle_\alpha$ directions. In molybdenum steels, peak hardness occurs after about 25 h at 550°C, when the rods are about 10–20 nm long and 1–2 nm in diameter. The orientation relationship is:

$$\begin{aligned} (0001)_{M_2C} &\parallel (011)_\alpha, \\ [11\bar{2}0]_{M_2C} &\parallel [100]_\alpha \text{ (rod growth direction)}. \end{aligned}$$

M_2C also nucleates at former austenite and ferrite lath boundaries. As in the case of vanadium steels, M_2C precipitate nucleates both on dislocations in the ferrite, and at the Fe_3C /ferrite interfaces, but the secondary hardening arises primarily from the dislocation-nucleated dispersion of M_2C .

On prolonged tempering at 700°C, the complex cubic M_6C forms predominantly at grain boundaries as massive particles which grow quickly, while the M_2C phase goes back into solution. The equilibrium microstructure is equiaxed ferrite with coarse M_6C in the form of faceted particles at grain boundaries, and plates, illustrated in Fig. 9.19b for a 6 wt% tungsten steel tempered 26 h at 700°C.

For similar atomic concentrations, the secondary hardening response in the case of tungsten steels is less than that of molybdenum steels. The M_2C dispersion in the former case is coarser, probably because the slower

diffusivity of tungsten allows a coarsening of the dislocation network prior to being pinned by the nucleation of M_2C particles.

At lower concentration of tungsten and molybdenum (0.5–2 wt%), two other alloy carbides are interposed in the precipitation sequences, i.e. the complex cubic $M_{23}C_6$ and the orthorhombic M_4C_b , probably Fe_2MoC . These carbides are found as intermediate precipitates between M_2C and M_6C .

9.4.7 Complex alloy steels

The presence of more than one carbide-forming element can complicate the precipitation processes during tempering. In general terms, the carbide phase which is the most stable thermodynamically will predominate, but this assumes that equilibrium is reached during tempering. This is clearly not so at temperatures below 500–600°C. The use of pseudo-binary diagrams for groups of steels, e.g. Cr-V, Cr-Mo, can be a useful guide to carbide phases likely to form during tempering (Chapter 4, section 4.3). The sequence of precipitation for a particular composition can be approximated to by drawing a line from the origin of the diagram, e.g. Fig. 4.10, to the composition of interest. The phase fields passed through would normally be those encountered in tempering, but the exact conditions cannot be forecast from such data.

Certain strong carbide formers, notably niobium, titanium and vanadium, have effects on tempering out of proportion to their concentration. In concentrations of 0.1 wt% or less, provided the tempering temperature is high enough, i.e. 550–650°C, they combine preferentially with part of the carbon and, in addition to the major carbide phase, e.g. Cr_7C_3 , Mo_2C , they form a separate, very much finer dispersion, more resistant to over-ageing (Fig. 9.20). This secondary dispersion can greatly augment the secondary-hardening reaction, illustrating the importance of these strong carbide-forming elements in achieving high strength levels, not only at room temperature but also at elevated temperatures, where creep resistance is often an essential requirement.

9.4.8 Mechanical properties of tempered alloy steels

A wide range of mechanical properties is obtainable by tempering alloy steels between 200°C and 700°C. A typical example is shown in Fig. 9.21 for a steel containing 1.5Ni-1Cr-0.25Mo-0.4C wt%, the tensile strength of which can be varied from 1800 down to 900 MPa by tempering at progressively high temperatures. The ductility of the steel improves as the tensile

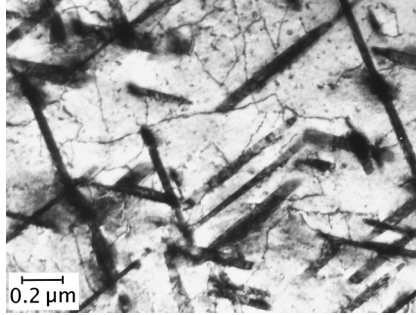


Figure 9.20 Fe-4Mo-0.1Nb-0.2C wt% steel tempered 6 h at 700°C. Coarse needles of Mo₂C in ferrite and fine particles of NbC on dislocations (courtesy of Irani).

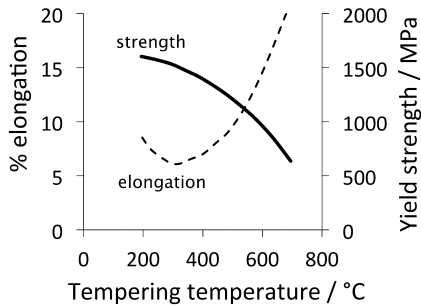


Figure 9.21 Change in mechanical properties of quenched Fe-1.5Ni-1Cr-0.25Mo-0.4C wt% steel as a function of tempering for 1 h at the temperature indicated. Selected data from Thelning [33].

strength falls. However, there is a ductility minimum around 275–300°C, which is often observed in plain carbon and lower-alloy steels. This is due to the formation of thin cementite films, as a result of the transformation of austenite at the interlath boundaries, a phenomenon known as tempered martensite embrittlement, as discussed in more detail in Chapter 11. At higher temperatures, these films spheroidise and the toughness improves.

To obtain really high strength levels in tempered steels ($\sim 1500 \text{ MN m}^{-2}$), it is usual to temper at low temperatures, i.e. 200–300°C, when the martensite is still heavily dislocated and the main strengthening dispersion is cementite or ϵ -iron carbide. Alloy steels, when tempered in this range, not only provide very high tensile strengths with some ductility but are also superior to plain carbon steels, as shown in Fig. 9.22. It is clear from Fig. 9.22a that the carbon content has a large influence on the strength. The alloying elements refine the iron carbide dispersion and, as the car-

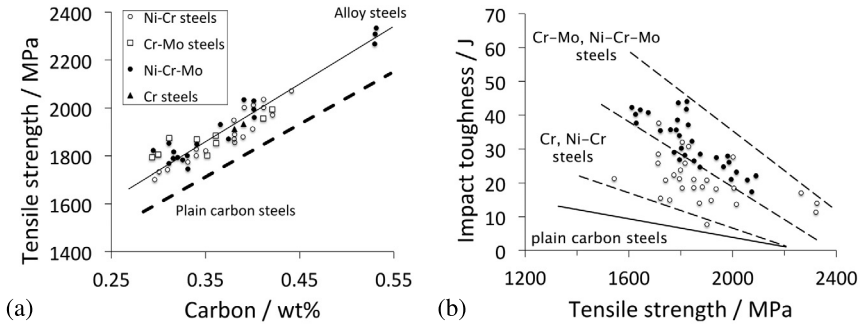


Figure 9.22 Comparison of mechanical properties of plain carbon and alloy steels that are quenched into a martensitic microstructure and then tempered at 200°C. (a) Effect of carbon on tensile strength; (b) relation between tensile strength and impact value. Note the beneficial effect of Mo. After Irvine and Pickering [29].

bon content is raised, the dispersion becomes more dense and, therefore, more effective. The toughness decreases with increasing strength, as shown in Fig. 9.22b. However, alloying elements very substantially improve the toughness, when compared with plain carbon steels of similar strength levels. When molybdenum is present in the steel, the toughness is increased further as the scatter bands indicate. This effect of alloying elements is again attributed to the breakdown of carbide films at grain and martensite lath boundaries. These films are particularly less noticeable in steels containing molybdenum.

Alloy steels which exhibit secondary hardening can provide high strength levels on tempering between 500°C and 700°C, with better ductility than that obtained at lower tempering temperatures. However, one of their main advantages is that, once a high strength level is reached by means of an alloy carbide dispersion formed between 550°C and 650°C, this structure will be relatively stable at temperatures up to 500°C. Therefore, the steels are suitable for use under stress at elevated temperatures. A typical example is given in Fig. 9.23 of a 12Cr-1Ni-0.2C wt% stainless steel, which can be quenched to martensite and then tempered to give a fine dispersion of chromium carbides in a ferritic matrix. The strength is well-maintained up to the secondary-hardening peak at 500°C, and is combined with a reasonable level of ductility. This type of steel is tempered to between 700 and 1000 MPa yield stress and is frequently used in steam and gas turbines, but can also be used for constructional purposes where lower temperatures are involved. Further improvements in mechanical properties

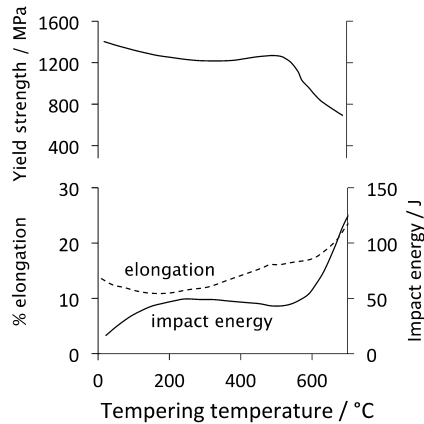


Figure 9.23 Effect of tempering for 1 h on the mechanical properties of a martensitic 12Cr-1Ni-0.2C wt% stainless steel. Selected data from Thelning [33].

at elevated temperatures can be obtained by addition of small concentrations of stronger carbide formers, e.g. molybdenum (2 wt%) and vanadium (0.25 wt%).

9.4.9 Mechanical properties: hydrogen trapping

It is very well established that small concentrations (1 ppm) of atomic, diffusible hydrogen can embrittle strong steel [34]. Any method that renders the hydrogen immobile should mitigate its detrimental effects. The strain fields of coherent or usually, semi-coherent carbide particles introduced by tempering reactions can attract hydrogen and trap it. The carbide particles that precipitate at temperatures where substitutional solutes such as molybdenum, vanadium, niobium and titanium become mobile over length scales of a few nanometres are particularly interesting from the point of view of hydrogen trapping. With appropriate tempering at temperatures in the range 500–600°C, fine dispersions of alloy carbides can be introduced in the microstructures of strong steel. The nature of the carbide dispersion can be carefully controlled while at the same time selecting tempering conditions that are suitable for the other properties required of the steel [35].

Some typical binding energies of hydrogen with carbides are given in Table 9.3; the higher the binding energy, the more effective the carbide is in preventing the hydrogen from diffusing. Fig. 9.24 shows that the mobility of hydrogen is dramatically reduced in the presence of vanadium carbides, and so is the propensity of hydrogen to embrittle the steel. Such steels are now

Table 9.3 Data on trapping (binding) energies E_b for hydrogen or deuterium atoms in ferritic steels. A more comprehensive list is available in [36]

Trap site	$-E_b/\text{kJ mol}^{-1}$	Reference
Cementite/ α interfaces	11–18	[37,38]
TiC	46–116	[39–41]
V_4C_3	33–35	[42]
Coherent M_2C (Mo-rich needles)	11–12	[43]

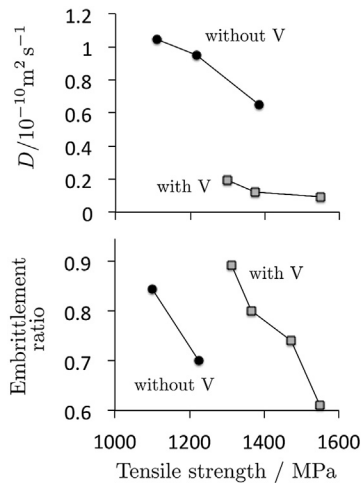


Figure 9.24 Comparison of the susceptibility to delayed fracture, of two bolting steels whose detailed chemical compositions are given in Table 9.4. The steel with vanadium contains vanadium carbides that serve to trap otherwise diffusible hydrogen, thus dramatically reducing its apparent diffusivity D . Therefore, the embrittlement ratio is much larger with the vanadium-containing steel, a higher ratio implying that the static fracture strength is less affected by hydrogen. Data from [46].

successfully implemented as extremely strong bolts used in the construction of bridges.

Vanadium based carbides have long been known to be effective in mitigating hydrogen-induced delayed fracture in strong bolting steels. The binding energy determined using thermal desorption analysis is found to be 33–35 kJ mol⁻¹. It has been argued [44] that the key trap in V_4C_3 is at carbon vacancies in the lattice, but the binding energy calculated for this is not consistent with that measured; furthermore, it has been demonstrated that the state of coherency with the ferrite influences the hydrogen trapping capacity [45], emphasising the role of the strain fields around the carbides.

Table 9.4 Compositions (wt%) of some of the steels containing substitutional solutes to form alloy carbides on tempering, that trap diffusible hydrogen and hence increase the resistance to embrittlement

Alloy	C	Si	Mn	Ni	Mo	Cr	V	Nb	Others	Reference
Bolt steel, quenched, tempered 550–650°C for 90 min	0.5		0.3	0.7	1.0	0.3	0.03			[46]
Bolt steel, without vanadium, quenched and tempered at 500–550°C for 90 min	0.39		0.82	0.16	1.11	–	0.03			[46]
Bolt steel with molybdenum carbides (NIMS17), quenched, tempered at 570°C, 90 min	0.59	1.98	0.20		0.94	0.99				[47–49]
Enamelling steel	0.048	0.05	0.47						0.3Ti, 0.0046 N	[50]

9.5 MARAGING STEELS

It has been shown that precipitation of alloy carbides in tempered martensite gives rise to age hardening, usually referred to as secondary hardening. There is no reason why other finely divided phases cannot be used for a similar purpose and, in fact, an important group of high-alloy steels, the maraging steels [51], reach high strength levels by the precipitation of various intermetallic compounds.

Carbide precipitation is practically eliminated by the use of low carbon compositions, and the steels contain between 18 and 25 wt% nickel so that, on quenching from the austenitic condition, they form a soft but heavily dislocated martensite. The high nickel content lowers the M_s to around 150°C, but on reheating the martensite there is considerable hysteresis, so that austenite is not reformed until the steel is held between 500°C and 600°C. At somewhat lower temperatures, i.e. 400–500°C, precipitation of intermetallic phases takes place, accelerated by the influence of the high dislocation density on the diffusion of substitutional solute atoms. Elements such as molybdenum and titanium are necessary additions, which result in the precipitation of Ni_3Mo , Ni_3Ti and the Laves phase, Fe_2Mo (Fig. 9.25). Cobalt is also a useful alloying element as it reduces the solu-

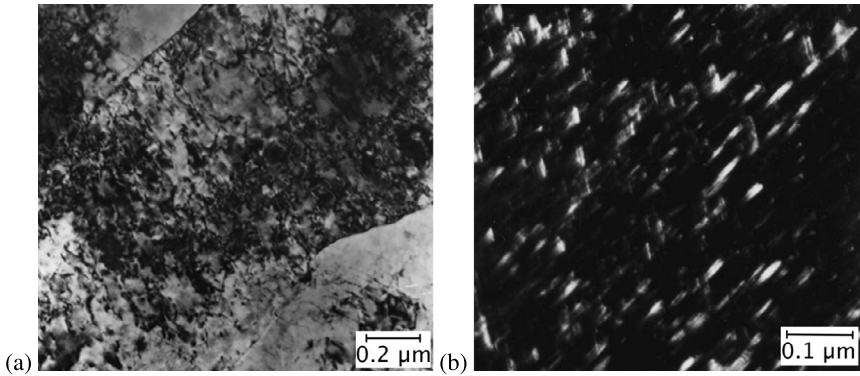


Figure 9.25 Maraging steel of composition Fe-18Ni-4.2Mo-12.5Co-1.7Ti-0.1Al wt%. (a) Martensitic state following air-cooling from 820°C. (b) Dark-field image showing precipitates of $\text{Ni}_3(\text{Ti},\text{Mo})$ intermetallic compound following tempering at 510°C for 30 min. After Tewari et al. [52], reproduced with the permission of Elsevier.

bility of molybdenum in the matrix and this increases the volume fraction of molybdenum-rich precipitate.

The precipitate reactions can lead to very high-volume fractions of precipitate, and thus to the achievement of high strength levels. For example, a steel with 18–19 Ni, 8.5–9.5 Co, 4.5–5 Mo and 0.5–0.8 Ti wt% can be heat treated to give a yield stress around 2000 MPa. However, the important point is that these high strength levels are accompanied by good ductility and toughness.

9.6 SUMMARY

The contents of this chapter are not dissimilar to discussions on precipitation in aluminium or nickel alloys, where allotropic transitions are absent. The tempering of martensite is carried out in a temperature range where austenite does not form – the goal is simply to optimise properties through low-temperature heat treatment, or to introduce precipitate dispersions at temperatures where substitutional solutes are mobile, in a matrix that is toughened by tempering so that strength and toughness can both be accessed. The phenomenon of secondary hardening, either by alloy carbides or intermetallic compounds, accounts for steels that are used in critical scenarios, such as aerospace bearings and rocket motor casings. Secondary hardened steels are the backbone of steam turbines that are responsible for the generation of most of the electricity that the world consumes.

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BACKNOTES

1. The temperatures quoted for the different stages of tempering can depend on the steel composition. For example, a large concentration of silicon retards tempering reactions [3,4].
2. There are three sub-lattices of interstitial sites for carbon in martensite. When the carbon atoms are ordered in just one of the sub-lattices, the martensite is tetragonal, but if the atoms are distributed at random on the three sub-lattices then the lattice has cubic symmetry. The ordering of carbon atoms is like any ordering reaction, i.e., the enthalpy change favours but the entropy change opposes ordering. The order-disorder transition occurs at the Zener ordering temperature [21–23]. The critical ordering temperature is carbon concentration dependent.
3. The amount of austenite retained can be calculated using Equation (5.18) to estimate the M_S temperature, which then is substituted into the Koistinen and Marburger Equation (5.2) to obtain the fraction of austenite retained.

CHAPTER 10

Thermomechanical Treatment of Steels

Abstract

The mass production of quality steel by deforming austenite in the presence of small quantities of microalloying additions such as niobium, has revolutionised the properties of structural steels. This is because the size of the austenite grains is limited by the compounds of these microalloying additions. The process can be adapted to ensure that the austenite grains are left in a deformed, pancaked shape prior to the onset of transformation because this again reduces the scale of the structure. The cooling rate during transformation can be controlled precisely using water spray technologies. These factors combine to give a final microstructure that is sufficiently refined to give an excellent combination of strength and toughness in steels that can be welded and fabricated into giant infrastructure projects. Such steels have proven to be so reliable that most people are oblivious of the underlying technologies, and yet, the quality of their lives has been dramatically improved by implementing about 40 billion tonnes of microalloyed steels. Dual phase, TRIP, TWIP and ausformed steels are also introduced.

10.1 INTRODUCTION

Thermomechanical treatment involves the simultaneous application to a steel of heating and cooling cycles combined with some sort of a deformation, in order to change its shape and ultimately to refine its microstructure for the sake of better properties. The deformation that is most common is hot rolling because the process is capable of handling vast quantities of steel and yet can be subjected to precise control and automation, Fig. 10.1. Continuously cast segments of steel, ranging from 1 to 50 tonnes in weight from a holding furnace, are introduced into the rolling sequence at a temperature typically in the range 1200–1300°C. They are then progressively rolled into a variety of shapes depending on application.

The use of energy can be optimised by introducing a continuous process in which the hot, solid-steel that emerges from continuous casting is processed immediately by rolling. This eliminates the stage where segments cut from the continuous casting process are held in a holding furnace, or reheated to the hot-rolling temperature.¹

The deformation leads to a breaking down of the original coarse microstructure that exists in the cast state, by repeated recrystallisation of the

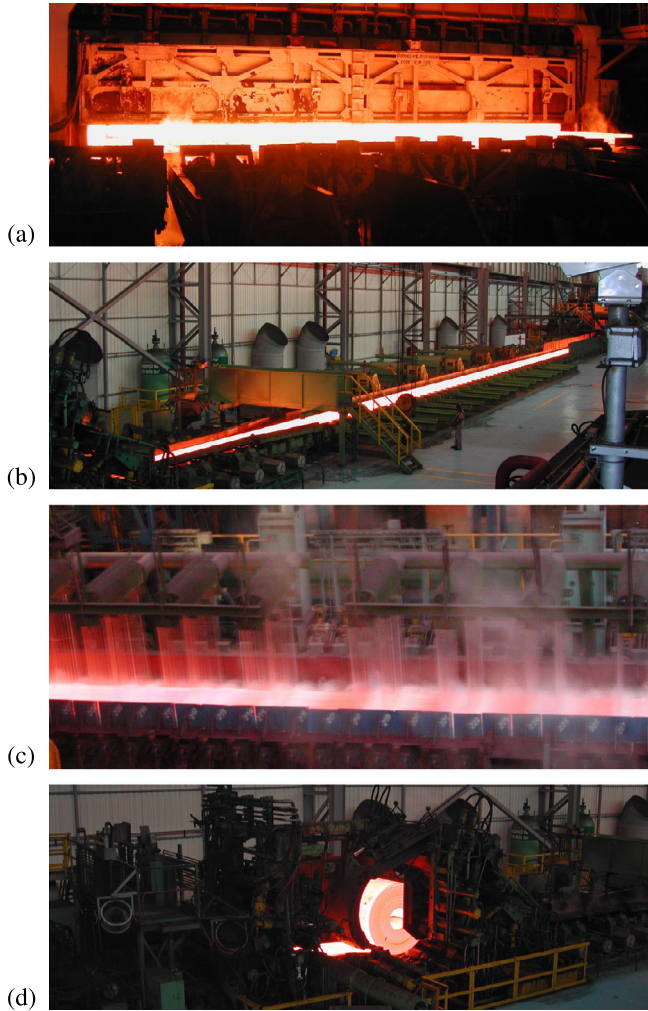


Figure 10.1 Thermomechanical processing of steel. (a) A 30 tonne slab emerges from the reheating furnace for hot-rolling. (b) The slab is elongated and thinned by multiple hot-rolling operations, although the width is maintained (plane-strain deformation). (c) Controlled water-cooling. (d) Coiling the long product. The final microstructure may be generated by transformation as the coil cools, or the hot-rolled product may be processed further by cold-rolling and heat-treatment.

steel while in the austenitic condition, at the same time gradually reducing the length-scale and magnitude of any chemical segregation. Any non-metallic inclusions, i.e. oxides, sulphides and silicates, are broken up, some

deformed and distributed throughout the steel in a more refined and uniform manner.

Hot rolling is not confined to the production of regular plates or sheet. With appropriate roll and rolling sequence design, it can be applied to make rods, rails, beams for infrastructure construction etc. There is no machining required following the rolling of rail and beam sections so these processes are superior to those classified as ‘near net-shape’ [1] or ‘additive manufacturing’ [2] where significant finishing operations are needed following manufacture. Additive manufacturing is modern jargon for an old process that refers to the layer-by-layer building up of a three-dimensional component using a variety of techniques.

Essentially the same concepts are applied in the production of specialised objects, for example the rotors for steam turbines where large ingots of steel are hot forged into shape and then machined. The nature of chemical segregation is different in ingot castings [3,4] so the forging process must be adjusted to ensure that any detrimental segregate does not occur in a critical region of the final component.

The hot rolling process is now a finely tuned operation in which more than a billion tonnes of steel is produced annually using automated arrays of equipment, resulting in impressive levels of productivity and reproducibility. The compositions of the low-alloy steels are chosen carefully to provide optimum mechanical properties when the hot deformation and subsequent cooling is complete. This process, in which the rolling parameters (temperature, strain, strain rate, number of rolling passes, finishing temperature, etc.) are predetermined and accurately defined for each steel grade, is called *controlled rolling*. It is now of the greatest importance in obtaining reliable mechanical properties in steels for pipelines, bridges, buildings and a huge variety of other products.

10.2 CONTROLLED ROLLING OF LOW-ALLOY STEELS

10.2.1 General

Before the Second World War, strength in hot-rolled low-alloy steels was achieved by the addition of carbon up to 0.4 wt% and manganese up to 1.5 wt%, giving yield stresses of 350–400 MPa. However, such steels are essentially ferrite-pearlite aggregates, which do not possess adequate toughness for many modern applications. Indeed, the toughness, as measured by the ductile/brittle transition, decreases dramatically with carbon content, i.e. with increasing volume of pearlite in the steel (Fig. 10.2). Furthermore,

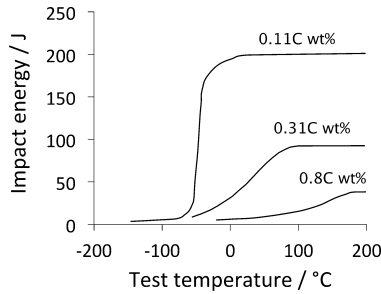


Figure 10.2 Effect of carbon content on the impact transition temperature curves of ferrite / pearlite steels.

with the introduction of welding as the main fabrication technique, the high carbon contents led to serious cracking problems, which could only be eliminated by the use of lower-carbon steels. The great advantage of producing in these steels a fine ferrite grain size soon became apparent (Section 2.5), so controlled rolling in the austenitic condition was gradually introduced to achieve this. Fine ferrite grain sizes in the finished steel were found to be greatly expedited by the addition of small concentrations (<0.1 wt%) of grain refining elements such as niobium, titanium and vanadium, and also aluminium [5]. On adding such elements to steels with 0.03–0.08 wt% C and up to 1.5 wt% Mn, it became possible to produce fine-grained material with yield strengths between 450 and 550 MPa, and with ductile/brittle transition temperatures as low as -70°C . Such steels are now referred to as high-strength low-alloy (HSLA) steels, or microalloyed steels. This progress, from the relatively low strength of ordinary mild steel (220–250 MPa) in a period of 20 years represents a major metallurgical development, the importance of which, in engineering applications, cannot be overstated.

In the majority of cases, the thermomechanical processing aims to refine the austenite grain size so that the ferrite that forms by transformation after hot-rolling is also fine. During hot deformation, the stress required to deform the steel is a function of the plastic strain (ϵ), strain rate ($\dot{\epsilon}$) and temperature. That stress is a function $f\{\epsilon\}$ of plastic strain, is of course well understood from any tensile test of a steel. However, Zener and Hollomon proposed [6,7] that the effects of strain rate and temperature can be combined by writing $\sigma = f\{\epsilon, Z\}$ where Z , now known as the Zener-Hollomon parameter, is defined as:

$$Z = \dot{\epsilon} \exp\left(\frac{Q}{RT}\right) \text{ s}^{-1} \quad (10.1)$$

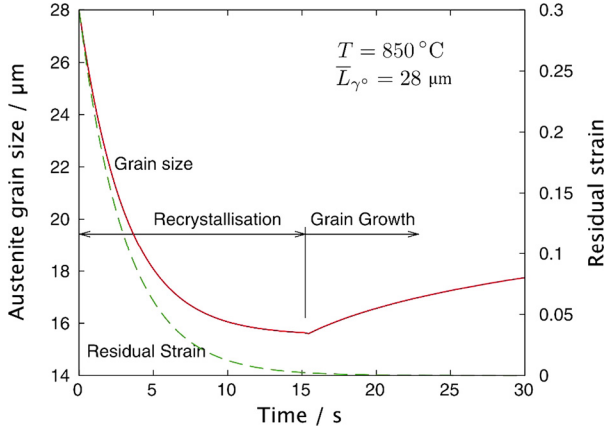


Figure 10.3 The calculated [8] influence of a single pass of rolling deformation to a strain of 0.3, on the evolution of the austenite grain size and residual strain (0.3 multiplied by the fraction of unrecrystallised austenite), as a function of time after the rolling deformation was applied (courtesy David Bombac).

where Q is an unspecified heat of activation since most rates are associated with an activated event. The material work hardens during hot-rolling but softens as a critical strain ϵ_c is reached inducing the austenite to recrystallise, with

$$\epsilon_c \propto \bar{L}_{\gamma^\circ}^{C_4} Z^{C_5} \quad (10.2)$$

where $\bar{L}_{\gamma^\circ}$ is the austenite grain size prior to deformation and C_i are empirical constants.

If the strain ϵ_c is reached while the steel is still being rolled, then the process is known as *dynamic recrystallisation*. On the other hand, *metadynamic recrystallisation* is said to occur when recrystallisation occurs immediately after a rolling pass when the strain retained in the austenite exceeds that needed to induce recrystallisation. The recrystallised austenite grain size will in general be smaller than the initial size, and grain growth may follow, as illustrated in Fig. 10.3 and Fig. 10.4 [8]. The full theory for recrystallisation and grain growth is not presented here because it tends to be alloy specific, but can be accessed from extensive literature on the subject [9,10].

The general features of controlled rolling are summarised in Fig. 10.5. Really quite sophisticated process models now exist to treat the entire sequence of rolling [12–14], microstructure [15] and properties [16,17], so much so that some of these are now used in the on-line control [18] of

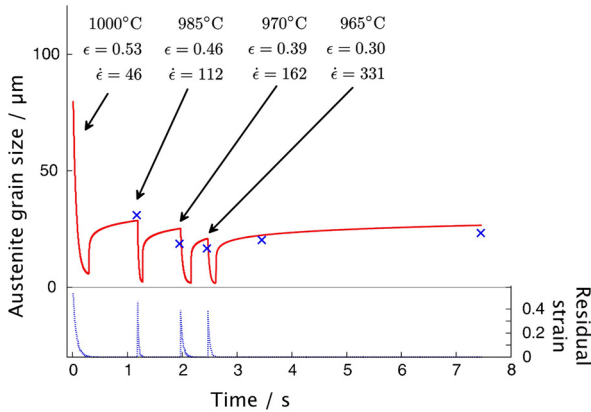


Figure 10.4 The calculated [8] influence of four passes of rolling deformation to a strain of 0.3, on the evolution of the austenite grain size and residual strain. Note that recrystallisation is completed when the residual strain becomes zero, with subsequent grain growth contributing to the increase in grain size. The position where the deformation is applied is indicated by the arrows (courtesy of David Bombac). The units of $\dot{\epsilon}$ are in s^{-1} . The points are actual data from Senuma et al. [11].

rolling mills using artificial intelligence methods [19] to ensure product uniformity.

10.2.2 Grain size control during controlled rolling

The primary grain refinement mechanism in controlled rolling is the recrystallisation of austenite during hot deformation, referred to earlier as dynamic recrystallisation. This process is influenced by the temperature and the degree of deformation which takes place during each pass through the rolls. However, in austenite devoid of second-phase particles, the high temperatures involved in hot rolling lead to marked grain growth, with the result that grain refinement during subsequent working is limited.

The situation is improved substantially if fine particles are introduced into the austenitic matrix. The particles usually are found on grain boundaries, because an interaction takes place between the particles and the boundary. A short length of grain boundary is replaced by the particle and the interfacial energy ensures a stable configuration. When the grain boundary attempts to migrate away from the particles, the local energy increases and thus a drag is exerted on the boundary by the particles.

The theory of boundary pinning by particles already has been referred to in Chapter 9. Equation (9.5) defines the critical size of particle be-

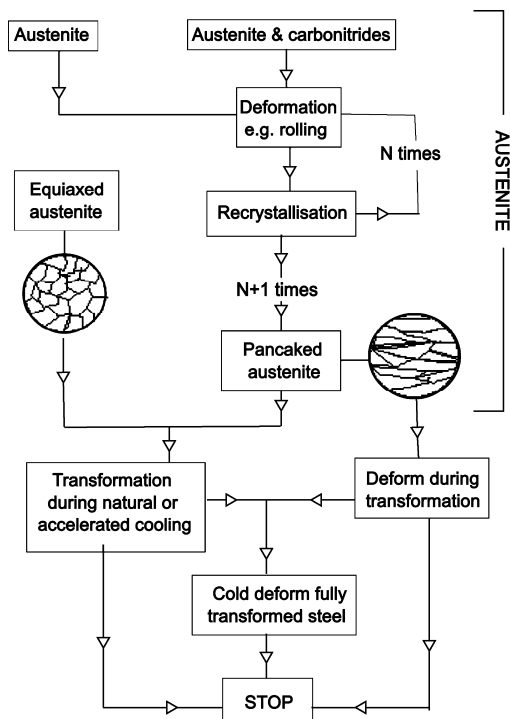


Figure 10.5 The variety of thermomechanical processing routes. Controlled rolling, followed by accelerated cooling is often designated *thermomechanical controlled processing* or TMCP.

low which pinning is effective. Clearly, the control of grain size at high austenitising temperatures requires as fine a grain boundary precipitate as possible, and one which will not dissolve completely in the austenite, even at the highest working temperatures (1200–1300°C). The best grain refining elements are very strong carbide and nitride formers, such as niobium, titanium and vanadium, also aluminium which forms only a nitride. As both carbon and nitrogen are present in control-rolled steels, and as the nitrides can be even more stable than the carbides (Fig. 4.9), it is likely that the most effective grain refining compounds are the respective carbo-nitrides, except in the case of aluminium nitride.

Equally important is the degree of solubility that such stable compounds have in austenite. It is essential that there is sufficient solid solubility at the highest austenitising temperatures to allow fine precipitation to occur during controlled rolling at temperatures which decrease as rolling proceeds.

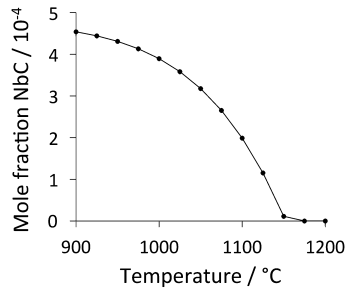


Figure 10.6 Equilibrium solubility curve for NbC in a steel with 0.15C-1.14Mn-0.04Nb wt%. Calculated using MTDATA [21] and the SGTE database.

The solubility products (in atomic per cent) of several relevant carbides and nitrides have been shown in Fig. 4.21 as a function of the reciprocal of the temperature. All of these compounds have a small but increasing solubility in the critical temperature range $\approx 900\text{--}1300^\circ\text{C}$ (Fig. 10.6). In contrast, the carbides of chromium and molybdenum have much higher solubilities, which ensure that they will normally go completely into solution in the austenite, if the temperature is high enough, and will not precipitate until the temperature is well below the critical range for grain growth. Data from another source [20] have provided the following equations for solubilities expressed in weight per cent as a function of absolute temperature:

$$\begin{aligned}\log_{10}[\text{Al}][\text{N}] &= -6770/T + 1.03, \\ \log_{10}[\text{V}][\text{N}] &= -8330/T + 3.46, \\ \log_{10}[\text{Nb}][\text{C}] &= -6770/T + 2.26, \\ \log_{10}[\text{Ti}][\text{C}] &= -7000/T + 2.75.\end{aligned}$$

The compositional changes possible are many, so discussion will be limited to general principles which apply equally, whichever compound is the effective grain refiner in a given steel. While grain growth at the highest austenitising temperatures may be restricted to some extent by a residual dispersion, the main refinement is achieved during rolling as the temperature progressively falls, and fine carbo-nitrides are precipitated from the austenite. These new precipitates will:

1. Increase the strain, for a given temperature, at which recrystallisation will commence, Fig. 10.7a.
2. Restrict the movement of recrystallisation fronts, Fig. 10.7b.

It should be borne in mind that the austenite may recrystallise several times during a controlled-rolling schedule and the total effect of this will be a marked austenite grain refinement by the time the steel reaches the γ/α

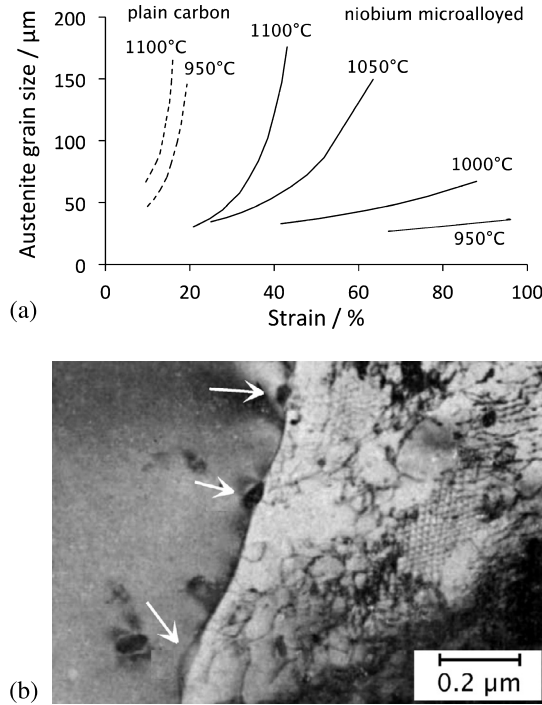


Figure 10.7 (a) Critical strain needed to complete recrystallisation of austenite as a function of deformation temperature and grain size. Comparison of Nb steel with plain carbon steel (adapted from Tanaka et al. [24]). (b) The pinning by niobium carbide precipitates (arrowed) of a recrystallisation front separating deformed austenite on the right from recrystallised austenite on the left. After Jones and Ralph [25], reproduced with permission of Elsevier.

transformation temperature (Fig. 10.7). In the later stages of austenite deformation, at the lower temperatures, recrystallisation may not occur, with the result that deformed austenite grains elongated and flattened by rolling may transform directly to ferrite (Fig. 10.8). Such flattened grains are often described as being ‘pancaked’. The austenite grain surface to volume ratio increases when an equiaxed grain is flattened [22,23] so that the number density of ferrite nucleation sites increases, and the deformation structures within the flattened austenite grains themselves contribute as nucleation sites. All this leads to a further refinement of the final microstructure. The effect of the finish-rolling temperature on the ferrite grain size obtained is illustrated in Fig. 10.9a.

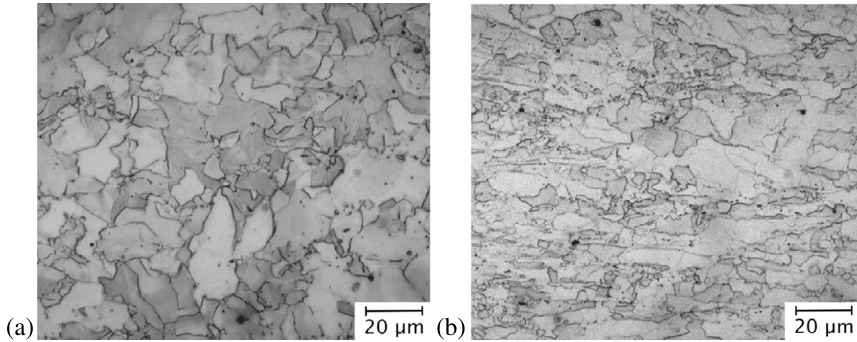


Figure 10.8 Austenite grain structure obtained during the thermomechanical processing of a steel that is microalloyed with small concentrations of titanium and molybdenum. (a) Finish-rolling temperature of 1050°C, showing equiaxed austenite grains. (b) Finish-rolling temperature of 800°C, showing austenite grains that are flattened, i.e. in a deformed state prior to transformation into ferrite. After Kim et al. [26], reproduced with permission of Elsevier.

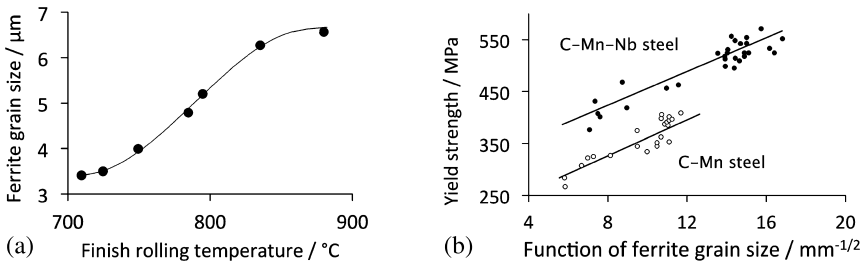


Figure 10.9 (a) Effect of finish rolling temperature on final ferrite grain size of a microalloyed steel (after McKenzie [27]). (b) Effect of grain size expressed as $(\bar{L}_\alpha)^{-1/2}$, on yield stress of a carbon-manganese-niobium steel (after Le Bon and Saint Martin [28]).

In the final stages of controlled rolling, austenite grain growth can be further suppressed by rapid cooling from the finishing temperature, which allows the γ/α transformation to take place sub-critically, i.e. below A_{r1} , in austenite which is still deformed. It is sometimes the practice to continue rolling through the γ/α transformation and even into the fully ferritic region. Such treatments lead to finer grain sizes, and higher yield stresses in the finished product, but impose much higher loads on the rolling mills.

As a result of the combined use of controlled rolling and fine dispersions of carbo-nitrides in low-alloy steels, it has been possible to obtain routinely, ferrite grain sizes between 5 and 10 µm, in commercial practice. Laboratory tests have achieved grain sizes approaching 1 µm, which would appear

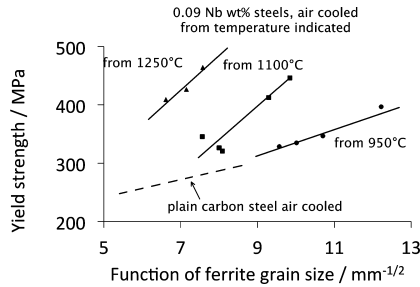


Figure 10.10 Effect of austenitising temperature on the yield strength of a 0.1C-0.6Mn-0.09Nb wt% steel (adapted from Gladman et al. [29]). The ferrite grain size is expressed as $(\bar{L}_\alpha)^{-1/2}$.

to be a practical limit using this approach. The Hall-Petch relationship between grain size and yield strength, which was discussed in Chapter 2, is very relevant to microalloyed steels and, in fact, linear plots are obtained for the yield stress against $(\bar{L}_\alpha)^{-1/2}$, Fig. 10.9b. Addition of 0.05–0.09 wt% Nb to a plain carbon steel refines the ferrite grain size, allowing it to be reduced to below $5\ \mu\text{m}$ ($\bar{L}_\alpha)^{-1/2} = 14\ \text{mm}^{-1/2}$, with a consequent substantial increase in yield strength. The displacement of $\sim 100\ \text{MPa}$ between the C-Mn and C-Mn-Nb curves arises from dispersion strengthening due to NbC. This is further illustrated in the two lower curves of Fig. 10.10, which were obtained from specimens austenitised at 950°C prior to air cooling. If, however, progressively higher austenitising temperatures are used, e.g. 1100°C and 1250°C followed by air cooling, the resulting curves, although still linear, have much steeper slopes, indicating a marked increase in yield strength for a particular grain size. This large increment in strength is due to the precipitation of NbC during cooling, following its solution at the higher austenitising temperatures.

10.2.3 Niobium atom clusters

Much of the discussion of the role of microalloying additions naturally focuses on precipitation, but high-resolution techniques have revealed that niobium atoms in particular can cluster within the austenite prior to precipitation proper [30]. The density and size of clusters increases as the temperature is reduced (Fig. 10.11a). The composition of the clusters is not constant but evolves as a function of temperature. They are said not to significantly affect the recrystallisation of deformed austenite except when the deformation is conducted at a low temperature.

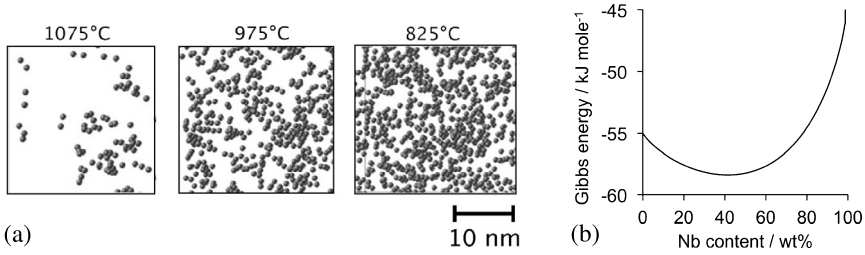


Figure 10.11 (a) Niobium clusters observed using atom-probe tomography. The temperature indicates that at which the austenite was deformed. The atoms illustrated are only those of niobium. After Kostryzhev et al. [30], reproduced with the permission of Elsevier. (b) Calculated austenite free energy curve for mixtures of iron and niobium at 900°C. The data are generated using MatCalc Version 5.62 with the mc_fe_v2.021.tdb database, courtesy of Arunim Ray.

The mechanism by which such clusters form is not clear because the iron-niobium solution is of a kind where clustering is not favoured, as shown in Fig. 10.11b, and evident from the fact that the activity coefficient of niobium in austenite is less than unity [31]. It is possible, therefore, that the clusters represent nuclei of NbC; the fact that they enrich in composition as they grow may simply be a reflection of the capillarity effect [32] whence the interfacial energy changes the equilibrium between the precipitate and matrix due to the very large surface to volume ratio due to the small particle size.

10.2.4 Minimum achievable grain size

It is interesting to consider what might be the smallest grain size achievable using large-scale thermomechanical processing [33]. A reduction in ferrite grain size (mean linear intercept $\bar{L}$) is equivalent to an increase in the amount of grain boundary surface per unit volume (S_V) since $\bar{L} = 2/S_V$. Grain boundaries have an energy $\sigma_{\alpha\alpha}$ per unit area, so that the interfacial energy stored per unit volume of steel is:

$$\sigma_{\alpha\alpha} \times S_V \equiv 2\sigma_{\alpha\alpha}/\bar{L}.$$

This stored energy cannot exceed the magnitude of the free energy change when austenite transforms to ferrite, i.e. $|\Delta G_V^{\gamma\alpha}|$:

$$|\Delta G_V^{\gamma\alpha}| \geq \frac{2\sigma_{\alpha\alpha}}{\bar{L}_\alpha}.$$

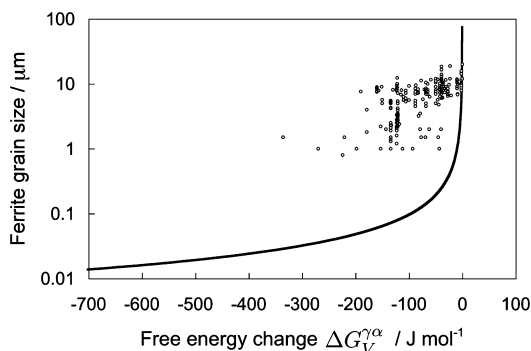


Figure 10.12 Plot of the logarithm of ferrite grain size versus the free energy change available to generate grain boundaries. The curve represents the values of $\bar{L}_\alpha^{\min}$. The points are experimental data.

It follows that the smallest ferrite grain size that can be achieved is when all of $\Delta G_V^{\gamma/\alpha}$ is used up in creating α/α grain boundaries, so that:

$$\bar{L}_\alpha^{\min} = \frac{2\sigma_{\alpha\alpha}}{|\Delta G_V^{\gamma/\alpha}|}.$$

Fig. 10.12 shows the variation in this limiting ferrite grain size as a function of $\Delta G_V^{\gamma/\alpha}$, together with a compilation of experimental data on the smallest grain size achieved commercially, using thermomechanical processing [33]. The curve indicates that at large grain sizes, $\bar{L}_\alpha^{\min}$ is sensitive to $\Delta G_V^{\gamma/\alpha}$ and hence to the undercooling below the equilibrium transformation temperature. However, reductions in grain size in the sub-micrometre range require huge values of $|\Delta G_V^{\gamma/\alpha}|$, meaning that the transformations would have to be suppressed to large undercoolings to achieve fine grain size.

Comparison of the industrial data against the calculated curve indicates that in spite of tremendous efforts in developing processing routes, the smallest ferrite grain size obtained commercially using thermomechanical processing is stuck at values greater than $1\ \mu\text{m}$. The reason is *recalescence*, which is the rise in temperature of the steel caused by release of the latent heat of transformation at a rate which is so high that it cannot easily be dissipated by diffusion. It causes the temperature of the steel to rise, thus reducing $\Delta G_V^{\gamma/\alpha}$ and preventing the achievement of ultrafine grain structures. Large-scale thermomechanical processing is therefore limited by recalescence and is unlikely to lead to grain sizes which are uniformly less than about $1\ \mu\text{m}$.

10.2.5 Dispersion strengthening during controlled rolling

The solubility data imply that, in a microalloyed steel, carbides and carbonitrides of Nb, Ti and V will precipitate progressively during controlled rolling as the temperature falls. While the primary effect of these fine dispersions is to control grain size, dispersion strengthening will take place. The strengthening arising from this cause will depend both on the particle size r , and the interparticle spacing L_p which is determined by the volume fraction of precipitate (Equation (2.12)). These parameters will depend primarily on the type of compound which is precipitating, and that is determined by the microalloying content of the steel. However the maximum solution temperature reached and the detailed schedule of the controlling rolling operation are also important variables.

It is now known, not only that precipitation takes place in the austenite, but that further precipitation occurs during the transformation to ferrite. The precipitation of niobium, titanium and vanadium carbides has been shown to take place progressively as the interphase boundaries move through the steel. This is the interphase precipitation discussed in section 4.5.3. As this precipitation is normally on an extremely fine scale occurring between 850°C and 650°C, it is likely to be the major contribution to the dispersion strengthening. In view of the higher solubility of vanadium carbide in austenite, the effect will be most pronounced in the presence of this element, with titanium and niobium in decreasing order of effectiveness. If the rate of cooling through the transformation is high, leading to the formation of supersaturated plates of ferrite, the carbides will tend to precipitate within the grains, usually on the dislocations which are numerous in this type of ferrite.

In arriving at optimum compositions of microalloyed steels, it should be borne in mind that the maximum volume fraction of precipitate which can be put into solid solution in austenite at high temperatures is achieved by use of stoichiometric compositions. For example, if titanium (atomic weight 47.9) is used, it will combine with approximately one quarter its weight of carbon (atomic weight 12), so that for a 0.025 wt% C steel, 0.10 wt% of Ti will provide carbide of the stoichiometric composition. In Fig. 10.13 the stoichiometric line for TiC is shown superimposed on the solubility curves for titanium carbide at 1100°C, 1200°C and 1300°C. If the precipitation in steels with 0.10 wt% titanium cooled from 1200°C is considered, at low carbon contents, i.e. to the left of the stoichiometric line, the carbide fraction is limited by the carbon content, i.e. zone A, lower

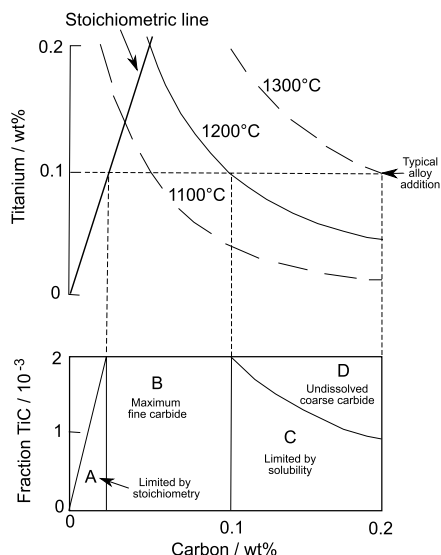


Figure 10.13 Effect of stoichiometry on the precipitation of TiC in a microalloyed steel (after Gladman et al. [29]).

diagram. For carbon contents between the stoichiometric line and the solubility line at 1200°C, the full potential volume fraction of fine TiC will form on cooling (zone B). When the carbon content exceeds the solubility limit (>0.10 wt%), the titanium is progressively precipitated at 1200°C as coarse carbide, thus reducing the amount of titanium available to combine with carbon to form fine TiC during cooling. As coarse carbide particles are ineffective in controlling grain growth, it is highly desirable to have steel compositions which avoid their formations. It also follows from Fig. 10.13 that high austenitising temperatures are essential to obtain full benefit from the precipitation of finely divided carbide phases.

10.2.6 Strength of microalloyed steels: an overall view

In modern control-rolled microalloyed steels, there are at least three strengthening mechanisms which contribute to the final strength achieved. The relative contribution from each is determined by the composition of the steel and, equally important, the details of the thermomechanical treatment to which the steel is subjected. The several strengthening contributions for steels with 0.2 wt% carbon, 0.2 wt% silicon, 0.15 wt% vanadium and 0.015 wt% nitrogen as a function of increasing manganese content

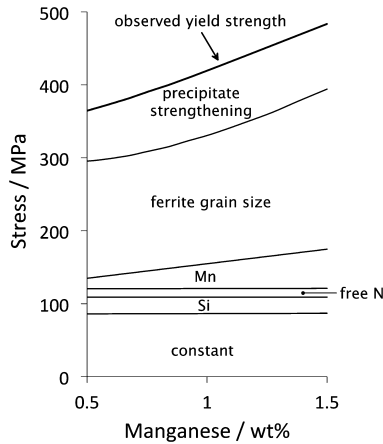


Figure 10.14 The contributions to strength in a 0.2C-0.15V steel as a function of Mn content (after Gladman et al. [29]).

are shown schematically in Fig. 10.14. Firstly, there are the solid solution strengthening increments from manganese, silicon and uncombined nitrogen. Secondly, the grain size contribution to the yield stress is shown as a very substantial component, the magnitude of which is very sensitive to the detailed thermomechanical history. Finally, a typical increment for dispersion strengthening is shown. The total result is a range of yield strengths between about 350 and 500 MPa. In this particular example, the steel was normalised (air cooled) from 900°C, but had it been control rolled down to 800°C or even lower, the strength levels would have been substantially raised.

The effect of the finishing temperature for rolling is important in determining the grain size and, therefore, strength level reached for a particular steel. It is now becoming possible to roll through the transformation into the completely ferritic condition, and so obtain fine subgrain structures in the ferrite, which provide an additional contribution to strength. Alternatively, the rolling is finished above the γ/α transformation, and the nature of the transformation is altered by increasing the cooling rate. Slow rates of cooling obtained by coiling at a particular temperature will give lower strengths than rapid rates imposed by water spray cooling following rolling. The latter route can change the ferrite from equiaxed to Widmanstätten with a much higher dislocation density. The result is a steel with improved mechanical properties and, in many cases, the sharp yield point can be sup-

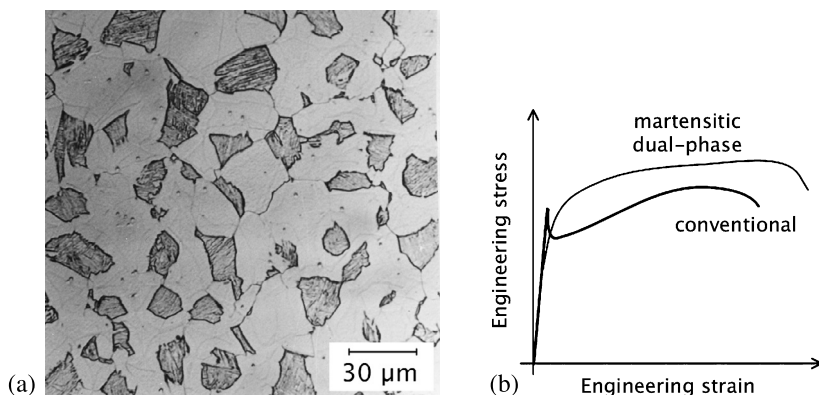


Figure 10.15 (a) Typical microstructure of dual-phase steel, consisting of a mixture of martensite (dark) and ferrite. (b) Schematic stress-strain curves comparing the behaviour of a conventional automobile steel with that of a dual-phase steel.

pressed. This has practical advantages in fabrication of sheet steel, e.g. pipe manufacture, where a continuous stress-strain curve is preferred.

10.3 DUAL-PHASE STEELS

The HSLA steels described in Section 10.2 give improved strength to weight ratios over ordinary steels. However, they are not readily formed, e.g. by cold pressing and related techniques. The worldwide demand for safety and fuel economy in transportation has led to the development of a number of steel types which are not only strong, but at the same time have the formability required for mass production of car bodies and components. A measure of formability is the product of strength and uniform elongation.

The *dual-phase* steels are low-alloy steels which satisfy these requirements by exploiting microstructures in which there are two major phases (Fig. 10.15), one of which is soft and the other significantly harder. The ferrite-martensite dual-phase steels typically contain manganese and silicon, and are strong and yet are formable. They exhibit continuous yielding, i.e. no sharp yield point, and a relatively low proof strength (300–350 MPa). The simplest steels in this category contain 0.08–0.2C, 0.5–1.5Mn wt%, but steels microalloyed with vanadium are also suitable, while small additions of Cr (0.5 wt%) and Mo (0.2–0.4 wt%) are frequently used to control the development of microstructure.

The simplest way of achieving a duplex structure is to use intercritical annealing in which the steel is heated into the ($\alpha + \gamma$) region between the A_{e1} and A_{e3} and held, typically at 790°C for several minutes to allow small regions of austenite to form in the ferrite. As it is essential to transform these regions of austenite into martensite, cooling to ambient temperature must be sufficiently rapid to avoid other intervening transformations. Alternatively, the hardenability of the austenite must be enhanced by adding between 0.2 and 0.4 wt% Mo to a steel already containing 1.5 wt% manganese. The required microstructure can then be obtained by air cooling after intercritical annealing.

To eliminate an extra heat treatment step, dual-phase steels have now been developed which can be given the required structure during cooling after controlled rolling. Typically, these steels have additions of 0.5Cr and 0.4Mo wt%. After completion of hot rolling around 870°C, the steel forms approximately 80% ferrite on the water cooled run-out table from the mill. The material is then coiled in the metastable region (510–620°C) below the pearlite/ferrite transformation and, on subsequent cooling, the austenite regions transform to martensite.

10.4 TRIP-ASSISTED STEELS

The steels developed to exploit the properties obtained when the martensite reaction occurs during plastic deformation are known as *transformation-induced plasticity* (TRIP) steels. They are strong and exhibit considerable uniform elongation before failure. There are several varieties of such steels. Those which are made fully austenitic by using large quantities of austenite-stabilising solutes, but transform to martensite when stressed, are simply called the TRIP steels (discussed in Chapter 12). When the austenite is a minor phase in the overall microstructure, but undergoes martensitic transformation during straining, the steels are said to be TRIP assisted and are usually low alloy steels.

Martensitic transformation induced by local stress has the effect of relieving stress concentrations, increasing the work-hardening rate, and promoting homogeneous deformation, with consequent improvements in the strength, ductility and toughness of steels. TRIP-assisted steels are mass produced, made using a complex heat treatment which is often completed within a short time during the processing of steel strip. Their microstructure consists of allotriomorphic ferrite as the major phase together with a total of 30–40% of harder regions. The latter consist of mixtures of bainite,

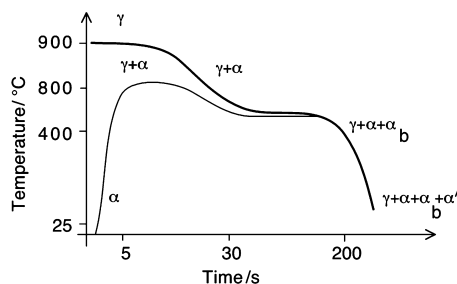


Figure 10.16 The two kinds of heat treatment used to generate the microstructures of TRIP-assisted steels. The terms γ , α , α_b and α' represent austenite, allotriomorphic ferrite, bainite and martensite, respectively.

martensite and carbon-enriched retained austenite. The chemical composition is typically Fe-0.12C-1.5Si-1.5Mn wt%. Some austenite is retained in spite of the low overall solute content because when the bainite forms, the silicon prevents cementite precipitation, thereby enriching the residual austenite with carbon (Chapter 6). The major application of TRIP-assisted steels is in the automobile industries, both for painted surfaces and for enhancing the safety of the passenger compartment in the event of a crash.

There are two kinds of TRIP-assisted steels. In the first case a cold-rolled strip is heated rapidly from ambient temperature for intercritical treatment in the $\alpha + \gamma$ phase field between the A_{c1} and A_{c3} temperatures (Fig. 10.16). The intercritical annealing induces partial transformation to austenite and at the same time recrystallises the residual ferrite. The strip is then cooled at a controlled rate during which some of the austenite transforms into allotriomorphic ferrite and at lower temperatures into bainitic ferrite. This latter reaction causes the austenite to become enriched in carbon, allowing it to be retained to ambient temperature (Fig. 10.17).

The details of the microstructure and mechanical properties can be altered by manipulating the cooling condition. For example, it is common practice to allow more time in the bainite transformation temperature range than at the higher temperatures where allotriomorphic ferrite grows. Fig. 10.18 shows the effect of holding in the bainite transformation temperature range on the final microstructure. An inadequate amount of bainite leaves the austenite susceptible to martensitic transformation. Similarly, because the carbon concentration in the austenite is limited by the T_0 curve (Chapter 6), transformation to bainite at too high a temperature also renders the austenite unstable.

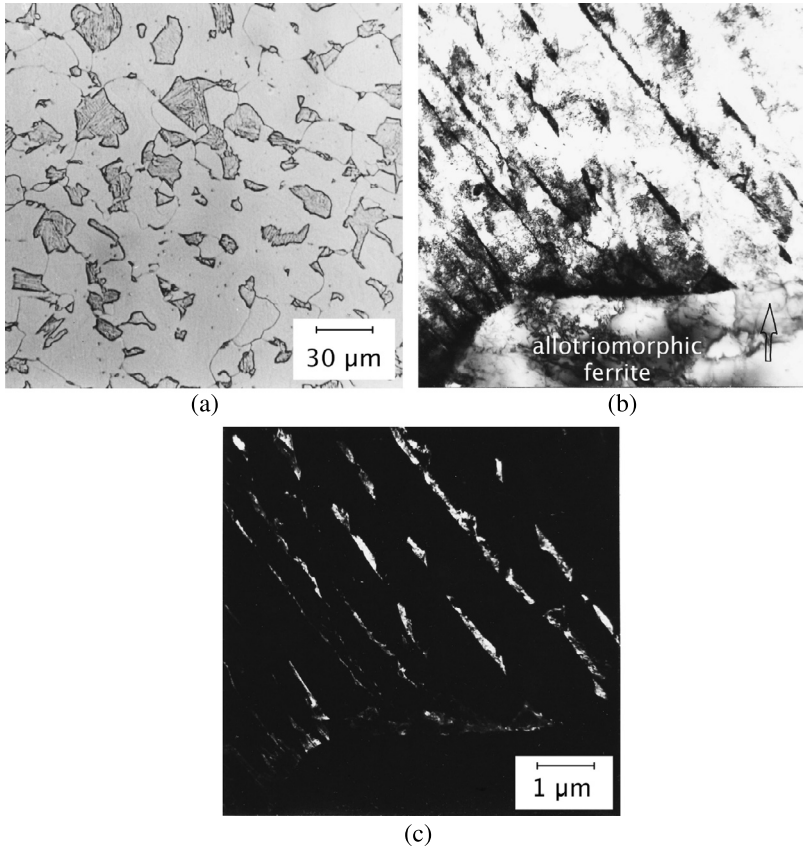


Figure 10.17 TRIP-assisted steel showing a mixed microstructure of allotriomorphic ferrite, bainitic ferrite and retained austenite films. (a) Optical micrograph. (b) Bright field transmission electron micrograph. (c) Dark field image of retained austenite.

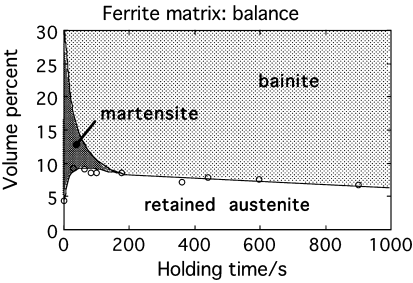


Figure 10.18 Evolution of room temperature microstructure as a function of the time during isothermal transformation to bainite. After Girault et al. [34], reproduced with permission of Elsevier.

The second kind of heat treatment starts from a hot-rolled strip which is fully austenitic (Fig. 10.16) and forms both allotriomorphic ferrite and bainite during the cooling part of the thermal cycle. This has the advantage that the microstructure can be produced directly from the hot strip which has been rolled to its final dimensions. The process is cheap since the strip does not have to be heated to the intercritical annealing temperature. However, hot-rolling mills are restricted by rolling loads to strips thicker than about 3 mm, although there are modern mills which can cope with 1.4 mm thickness. Cold-rolled strips can, on the other hand, be made routinely into thinner gauges. Hot-rolled strips are preferred for automobile applications where cost is a prime factor in the choice of materials.

The transformation strain due to the formation of martensite does not account for the observed uniform tensile elongation of some 15–30%. The shape deformation due to martensite (Chapter 5) is at most equivalent to a 2% tensile strain because the amount of austenite available for transformation is quite small in TRIP-assisted steels. The major contributions to uniform elongation arise partly from the enhanced work-hardening coefficient of the material due to the progressive formation of hard martensite during deformation. There is a further significant contribution from dislocations induced into the ferrite by the strains associated with martensitic transformation [35]. These dislocations strengthen the ferrite and are visible in Fig. 10.17b.

The austenite also delays the necking process during a tensile test by transforming to martensite at stress concentrations. It is important therefore to delay the transformation of retained austenite to the late stages of deformation when significant damage accumulates in the steel. It is at this point that the TRIP effect can be most beneficial. It is useful therefore to examine further the transformation of austenite as a function of plastic strain.

It is reasonable to assume that the change in the fraction of martensite ($dV_V^{\alpha'}$) obtained for a given increment of plastic strain ($d\epsilon$) should be proportional to the fraction of remaining austenite:

$$\frac{dV_V^{\alpha'}}{d\epsilon} = k_\gamma V_V^\gamma, \quad (10.3)$$

where k_γ is a function of the steel composition and test temperature and V_V^γ is the fraction of austenite remaining untransformed. If the fraction of austenite at zero strain is $V_V^{\gamma_0}$, then $V^{\alpha'} = V_V^{\gamma_0} - V_V^\gamma$, and integration of Equation (10.3) gives:

$$\ln\{V_V^{\gamma_0}\} - \ln\{V_V^\gamma\} = k_\gamma \epsilon.$$

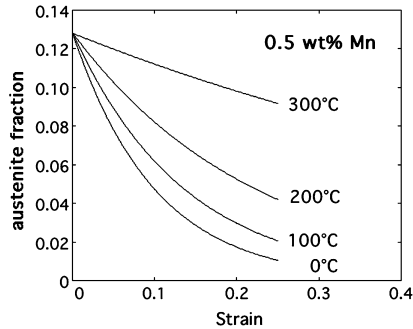


Figure 10.19 Martensitic transformation of retained austenite in a TRIP-assisted steel as a function of deformation temperature and plastic strain. After Sherif et al. [36].

The form of this equation is illustrated in Fig. 10.19.

10.4.1 Low- or zero-silicon TRIP-assisted steels

The substantial silicon addition to TRIP-assisted steels leads to the formation of hard, adherent oxide (fayalite, Fe_2SiO_4) which is difficult to remove prior to hot rolling. This leads in turn to a blemish on the surface known as *red oxide* [37–40], which is FeO that has been sequentially oxidised into Fe_3O_4 and Fe_2O_3 , with the latter being the coloured oxide from which the name derives, resulting in a poor surface finish [37–39]. Routine descaling operations fail to remove the oxide because the fayalite forms a eutectic with FeO , and its liquid phase penetrates both the steel and any prior oxide [39,41]. The resulting convoluted interface with the steel provides a mechanical key which prevents the uniform removal of the oxide. This is not acceptable when the surface finish of the steel is paramount.

Since silicon is the culprit, it is natural to seek low-silicon TRIP steels as illustrated in Fig. 10.20. The austenite in such alloys is more difficult to retain because of the tendency to precipitate cementite, but this can be minimised with careful heat treatment. When this is done, strengths in excess of 600 MPa with a uniform ductility of 15% have been achieved.

10.4.2 Galvanising of TRIP-assisted steels

There are two basic methods of galvanising, by dipping the steel in liquid zinc or by electrolytically depositing the zinc. The typical concentrations of silicon and manganese in TRIP-assisted steels lead to a stable Mn_2SiO_4 oxide film on the surface during the heat treatment that leads to the desired

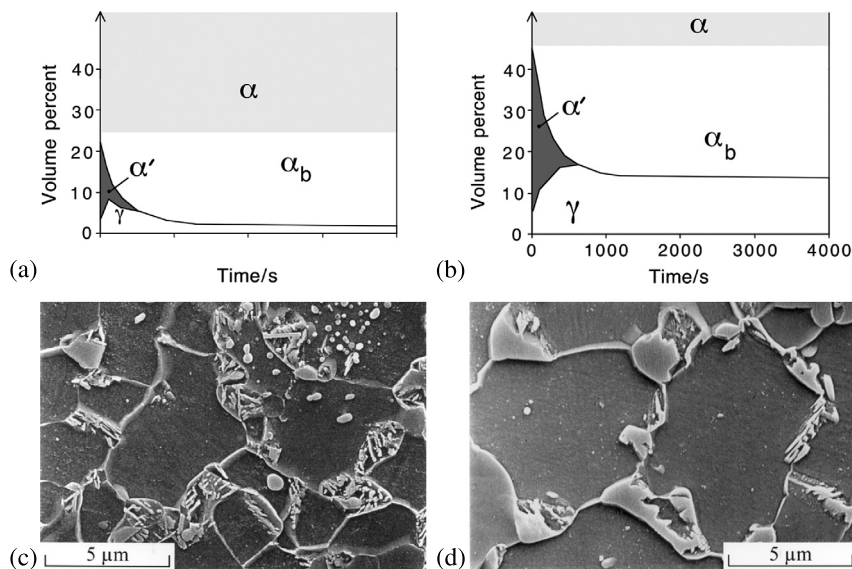


Figure 10.20 Evolution of room-temperature microstructure as a function of time during isothermal transformation to bainite. (a) Low-silicon steel Fe-0.16C-0.38Si-1.3Mn wt%. (b) High-silicon steel Fe-0.29C-1.41Si-1.42Mn wt%. (c) Scanning electron micrograph of low-silicon alloy isothermally transformed to bainite for 1800 s. Much of the austenite has decomposed to bainitic ferrite and cementite. (d) Corresponding micrograph for high-silicon steel transformed to bainite for 900 s with plenty of austenite evident (courtesy of Pascal Jacques).

microstructure. This makes it difficult for the zinc to wet the steel surface, making it necessary to electrolytically galvanise such alloys.

The problem can be alleviated by increasing the humidity in the annealing furnace. The oxide coverage of the surface is then reduced, giving better wetting by zinc. The higher humidity causes the internal oxidation of Mn and Si below the steel surface, thus reducing their availability to form Mn_2SiO_4 at the surface.

An alternative approach is to eliminate the silicon and add aluminium to retain the cementite-free microstructure. Aluminium oxidises easily to form alumina by internal oxidation near the surface, again limiting the amount of FeAl_2O_4 that can form at the free surface when the humidity in the annealing furnace is low. Such a steel can easily be hot-dip galvanised. At high humidity, MnO begins to cover the surface leading to a deterioration in the ability of the liquid zinc to wet the surface. The aluminium-containing steels are therefore better suited to continuous galvanising lines.

It is clear that silicon and manganese must diffuse to the surface to form oxides. Some of the diffusion flux is via grain boundaries. When phosphorus is present, its segregation to the grain boundaries reduces the boundary diffusion-flux, thereby reducing the extent to which oxides form. Such steels are more amenable to wetting by molten zinc (in contrast, the same effect makes it more difficult to form iron-zinc compounds during the galvannealing process).

10.5 TWIP STEELS

There are three essential modes by which steels can be permanently deformed at ambient temperature, without recourse to diffusion. Individual dislocations whose Burgers vectors correspond to lattice vectors can glide, leading to a change in shape without altering the crystal structure or volume. In contrast, a displacive transformation (e.g. martensite or bainite) results not only in a plastic strain, but also a change of crystal structure and density; this is the phenomenon exploited in the TRIP steels.

The third mode of deformation is mechanical twinning, in which the crystal structure of the steel is preserved but the twinned region is reoriented in the process. Mechanical twinning results in a much larger shear strain $s = 1/\sqrt{2}$, compared with displacive transformations where s is typically 0.26. There is a particular class of extraordinarily ductile alloys of iron, known as the TWIP steels, which exploit mechanical twinning to achieve their properties.

TWIP stands for twinning-induced plasticity. The alloys are austenitic and remain so during mechanical deformation, but the material is able to accommodate strain via both the glide of individual dislocations and through mechanical twinning on the $\{1\ 1\ 1\}_\gamma$ $\langle 1\ 1\ \bar{2} \rangle_\gamma$ system. The alloys typically contain a large amount of manganese, some aluminium and silicon (e.g. Fe-25Mn-3Si-3Al wt%) with carbon and nitrogen in some versions present essentially as impurities. Larger concentrations of carbon may be added to enhance strength. At high manganese concentrations, there is a tendency for the austenite to transform into ϵ -martensite (hexagonal close packed) during deformation. ϵ -martensite can form by the dissociation of a perfect $a/2\langle 0\ 1\ 1 \rangle_\gamma$ dislocation into Shockley partials on a close packed $\{1\ 1\ \bar{1}\}_\gamma$ plane, with a fault between the partials. This faulted region represents a three layer thick plate of ϵ -martensite [42,43]. A reduction in the fault energy therefore favours the formation of this kind of martensite. The

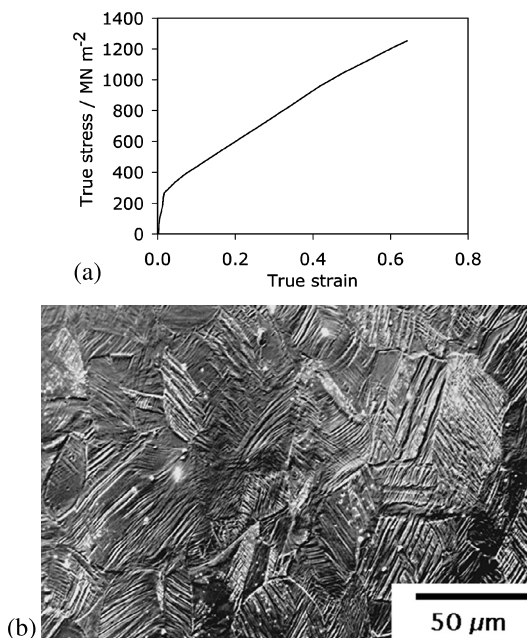


Figure 10.21 (a) Typical stress-strain curve for a TWIP steel. (b) Optical microstructure of a TWIP steel following deformation, showing profuse twinning (image and data courtesy of Frommeyer G., Brück U. and Neumann P.).

addition of aluminium counters this because it raises the stacking fault energy of the austenite. Silicon has the opposite effect of reducing the stacking fault energy, but like aluminium, it leads to a reduction in the density of the steel; the combination of Al and Si at the concentrations used typically reduces the overall density from some 7.8 g cm^{-3} to about 7.3 g cm^{-3} .

The alloys have a rather low yield strength at 200–300 MPa but the ultimate tensile strength can be much higher, in excess of 1100 MPa. This is because the strain-hardening coefficient is large, resulting in a great deal of uniform elongation, and a total elongation of some 60–95%. The effect of mechanical twinning is two-fold. The twins add to plasticity, but they also have a powerful effect in increasing the work-hardening rate by subdividing the untwinned austenite into finer regions (Fig. 10.21).

One major advantage of TWIP steels is that they are austenitic and they maintain attractive properties at cryogenic temperatures (-150°C) and high strain rates, e.g., 10^3 s^{-1} . They therefore have great potential in wider applications than just transportation.

10.6 INDUSTRIAL STEELS SUBJECTED TO THERMOMECHANICAL TREATMENTS

Microalloyed steels produced by controlled rolling are a most attractive proposition in many engineering applications because of their relatively low cost, moderate strength, and very good toughness and fatigue strength, together with their ability to be readily welded. They have, to a considerable degree, eliminated quenched and tempered steels in many applications.

These steels are most frequently available in control-rolled sheet, which is then coiled over a range of temperatures between 750°C and 550°C. The coiling temperature has an important influence as it represents the final transformation temperature, and this influences the microstructure. The lower this temperature, under the same conditions, the higher the strength achieved. The normal range of yield strength obtained in these steels varies from about 350 to 550 MPa. The strength is controlled both by the detailed thermomechanical treatment, by varying the manganese content from 0.5 to 1.5 wt%, and by using the micro-alloying additions in the range 0.03 to above 0.1 wt%. Niobium is used alone, or with vanadium, while titanium can be used in combination with the other two carbide-forming elements. The interactions between these elements are complex, but in general terms niobium precipitates more readily in austenite than does vanadium as carbide or carbo-nitride, so it is relatively more effective as a grain refiner. The greater solubility of vanadium carbide in austenite underlines the superior dispersion strengthening potential of this element shared to a lesser degree with titanium. Titanium also interacts with sulphur and can have a beneficial effect on the shape of sulphide inclusions. Bearing in mind that the total effect of these elements used in conjunction is not a simple sum of their individual influence, the detailed metallurgy of these steels becomes extremely complex.

One of the most extensive applications is in pipelines for the conveyance of natural gas and oil, where the improved weldability due to the overall lower alloying content (lower hardenability) and, particularly, the lower carbon levels is a great advantage. Furthermore, as the need for larger diameter pipes has grown, steels of higher yield stress have to be used to avoid excessive wall thicknesses. In practice, wall thicknesses of 10–12.5 mm have been found to be the most convenient. Typical compositions (wt%) to achieve a yield stress of around 410 MPa:

C 0.12	S 0.012	Mn 1.35	Nb 0.03	
C 0.12	S 0.006	Mn 1.33	Nb 0.02	V 0.04

Table 10.1 Typical compositions in wt%, of microalloyed vanadium steels in two classes of yield strength (σ_Y)

Alloying element	Steels with $\sigma_Y = 345 \text{ MPa}$	Steels with $\sigma_Y = 550 \text{ MPa}$
Carbon	0.08–0.12	0.12–0.17
Manganese	0.75–1.10	1.20–1.55
Phosphorus	0.008–0.013	0.008–0.013
Sulphur	0.007–0.020	0.007–0.020
Silicon	0.05–0.15	0.30–0.55
Aluminium	0.03–0.06	0.03–0.06
Vanadium	0.03–0.07	0.10–0.14
Nitrogen	0.006–0.012	0.015–0.022
Cerium	0.02–0.06	0.02–0.06

for higher yield strengths (450 MPa):

C 0.06 S 0.006 Mn 1.55 Nb 0.05 V 0.10

However, it should be emphasised that often higher yield stresses are achieved by control of the fabrication variables such as the temperature at which rolling is finished and the temperature used for coiling the sheet. Nitrogen is often deliberately used as an alloying element. One successful range of steels relies on vanadium to form carbo-nitride precipitates for grain size control and dispersion strengthening. In some steels, rare earth additions are made to control the inclusion shape. Typical compositions at lower and higher strength levels are given in [Table 10.1](#).

At the higher strength levels, microalloyed steels are used for heavy duty truck frames, tractor components, crane booms and lighting standards, etc. The control of sulphide inclusions gives the steels a high degree of formability in cold fabrication processes. This recent development has allowed the use of HSLA steels for many applications involving substantial cold forming which previously led to cracking in the absence of rare earth additions.

10.7 AUSFORMING

A steel is said to have been ausformed when martensite is produced from plastically deformed austenite. Ausforming has provided some of the strongest, toughest steels so far produced, with the added advantage of very good fatigue resistance. However, they usually have high concentrations of expensive alloying elements and must be subjected to large deformations which impose heavy work loads on rolling mills. Nevertheless, these steels

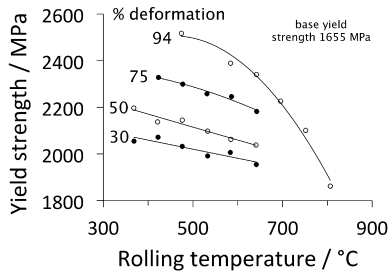


Figure 10.22 Effect of amount and temperature of deformation on the yield strength of 0.4C-5.0Cr-1.3Mo-1.0Si-0.5V wt% steel quenched after ausforming and tempered at 510°C (after Schmatz et al. [44]).

are particularly useful where a high strength to weight ratio is required and where cost is a secondary factor. Typical applications have included parts for undercarriages of aircraft, special springs and bolts.

The 12 wt% Cr transformable steels respond readily to ausforming to the extent that tensile strengths of over 3000 MPa can be obtained in appropriate compositions. A 0.4C-6Mn-3Cr-1.5Si steel has been ausformed to a tensile strength of 3400 MPa, with an improvement in ductility over the conventional heat treatment. Similar high strength levels with good ductility have been reported for 0.4C-5Cr-1.3Mo-1.0Si-0.5V wt% steel (Fig. 10.22). All of these steels are sufficiently highly alloyed to allow adequate time for substantial deformation in the austenitic bay of the time-temperature-transformation curve prior to transformation.

10.8 SUMMARY

There is no need to wax lyrical about the success of high-strength low-alloy steels. The steels pervade so many aspects of everyday life that we are numbed to their presence. One reason is that the reliability of these steels far exceeds the annoying quality of the software that we are also exposed to in our everyday interactions with technology. It is not necessary, therefore, for the ordinary person to think about the technology behind this wonder material.

The notion that minute quantities of solutes can so dramatically influence the properties of steels is now well-established. When combined with thermomechanical processing, one vision is for the variety of steels that exist now to be reduced fiercely in order to make it easier to recycle steels.

There will, of course, remain a demand for specialist steels which are made in relatively small quantities, for example the TWIP alloys, where the imagination can run wild on what might be possible in the future in terms of applications.

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BACKNOTES

1. In another variant, the steel is continuously cast in the form of thin slab or strip, thereby reducing the effort of rolling, although this may not always lead to the best properties since deformation has a role in modifying the cast structure.

CHAPTER 11

The Embrittlement and Fracture of Steels

Abstract

A brittle material is usually hard so less able to accommodate work; thus, it can easily be broken. To embrittle means to make something brittle. This is undesirable in most cases. In particular, the nicely engineered properties of steel can be ruined by a number of mechanisms that cause the steel to split or splinter along particular crystallographic planes instead of behaving in a malleable manner. Tiny atoms like hydrogen can permeate into the steel when the latter is exposed to the elements and cause a dramatic drop in ductility. Others that are not well accommodated in the lattice tend to segregate at the interfaces between crystals and cause havoc there. This chapter has a description of the ductile to brittle transition in steels with a focus on mechanisms and methods of preventing the unexpected deterioration in properties that is commonly referred to as “embrittlement”. The role of inclusions and phases that liquify at a temperature well below that at which iron melts is also described.

11.1 INTRODUCTION

Most groups of alloys can exhibit failure by cracking in circumstances where the apparent applied stress is well below that at which failure would normally be expected. Steels are no exception to this, and probably exhibit a wider variety of failure mechanisms than any other category of material. While ultimate failure under excessive stress must occur and can reasonably be predicted by appropriate mechanical tests, premature failure is always dangerous, involving a considerable element of unpredictability. However, a detailed knowledge of structure and of the distribution of impurities in steels is gradually leading to a much better understanding of the origins and mechanisms of the various types of cracks encountered. Furthermore, the now well-established science of fracture mechanics allows the quantitative assessment of growth of cracks in various stress situations, to an extent that it is now frequently possible to estimate the tolerance of engineering structures to avoid the risk of sudden failure.

There are essentially three fracture modes in steels at ambient temperature. Ductile failure is accompanied by gross plastic deformation so that the work done in fracture is orders of magnitude greater than purely attributable to the creation of new surfaces as the steel is parted. Cleavage

fracture, and the failure of the material by the separation of grain surfaces, involve minimal absorption of energy and hence are regarded as brittle fracture mechanisms. For pure metals, the transition from ductile to brittle fracture is described by the ratio of the modulus μ which is a measure of the resistance to shear, and the bulk modulus K because the stress field at a brittle crack tip is similar to pure dilatation [1]. A small value of the ratio μ/K favours ductile failure because plastic deformation by shear is relatively easy. For pure α -iron made using electron beam zone-melting under high vacuum, the ratio is 0.33 which is less than the critical value associated with brittle failure. Indeed, high-purity iron is found to be ductile at temperatures as low as 4.2 K [2]. Such behaviour is not expected in commercial steels because they cannot be made as pure and because they are designed to be strong, i.e., more resistant to plastic deformation.

11.2 CLEAVAGE FRACTURE IN IRON AND STEEL

Cleavage fracture is familiar in many minerals and inorganic crystalline solids as a mechanism involving little plastic deformation and occurring in a crystallographic fashion along planes of low indices, i.e. relatively high atom density. At low temperatures, zinc cleaves along the basal plane, but in contrast, body-centred cubic iron cleaves on $\{100\}$ which is not the most densely packed plane (Fig. 11.1). It is all the more surprising then, that the surface energy per unit area increases in the order $\{110\}_\alpha$, $\{100\}_\alpha$ and $\{111\}_\alpha$ [3]; on these grounds alone it should be easier to cleave on the $\{110\}_\alpha$ in contradiction to experimental evidence. However, cleavage does not simply involve the parting of atoms under the influence of a stress normal to the plane of interest. Crack growth phenomena even during cleavage involve features such as dislocation emission and twinning. Atomistic simulations indicate that these processes are more complex when propagation is on the $\{110\}_\alpha$ and $\{111\}_\alpha$ planes [4], which may account for the more brittle behaviour of the $\{100\}_\alpha$ planes. Mechanical twinning as illustrated in Fig. 11.1 is sometimes observed in association with cleavage but is predicted by the simulations to occur at a relatively late stage in the growth of cleavage cracks, as a mechanism that relieves stress.

Fig. 11.1 also illustrates that not all the grains at the fracture surface have clear facets consistent with cleavage; the macroscopic fracture of a polycrystalline material must involve a mixture of fracture mechanisms dependent on the distribution of grain orientations relative to the applied stresses. If a greater fraction of cleavage planes from different grains are aligned along

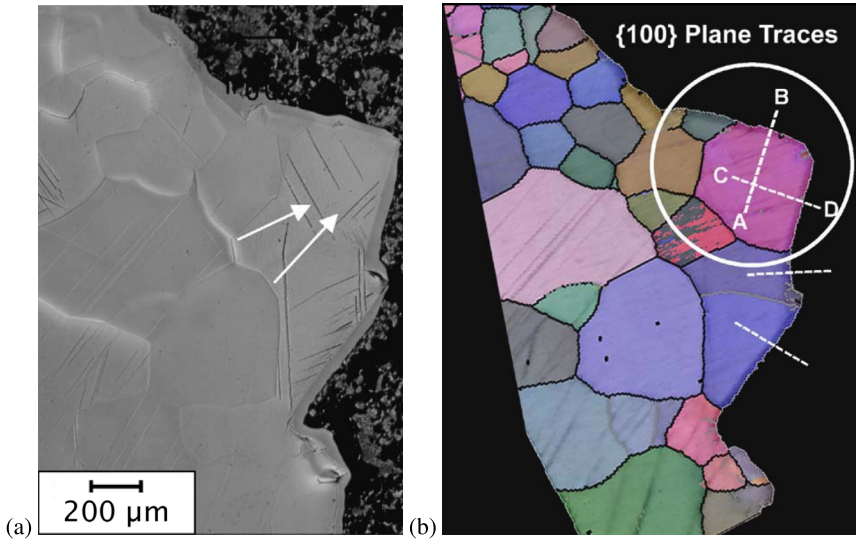


Figure 11.1 Cleavage fracture in commercially pure iron. (a) Cross-section of fracture surface; the arrows point to mechanical twins on $\{112\}_{\alpha}$ planes. (b) Electron backscatter diffraction crystallographic-orientation image, with dashed lines parallel to the traces of $\{100\}_{\alpha}$ planes. After Ayer et al. [5], reproduced with permission of Elsevier.

the fracture surface then the toughness is expected to be reduced. Fig. 11.2 illustrates how the toughness drops dramatically in the heat-affected zone of a weld, as large blocks of similarly oriented grains increase the tendency for the cleavage planes of ferrite to align along the macroscopic fracture plane [6]. This effect can be labelled as *texture embrittlement* and manifests particularly in steels that are thermomechanically processed and hence do not consist of random arrangements of polycrystals, but exist in a state best described as between a single crystal and random array of crystals; i.e. the steel is crystallographically textured. In such steels, the texture is a principal reason for the observed anisotropy of toughness [7–9].

This fact that body-centred cubic iron cleaves when tested in regimes that reduce plasticity would appear to be an intrinsic characteristic of iron, but it has been shown that iron, highly purified by zone refining and containing minimal concentrations of carbon, oxygen and nitrogen, is very ductile even at extremely low temperatures. For example, at 4.2 K reductions in area in tensile tests of up to 90% have been observed with iron specimens of the highest available purity [2]. The temperature and strain-rate sensitivity of the flow stress is an intrinsic function of the lattice [10],

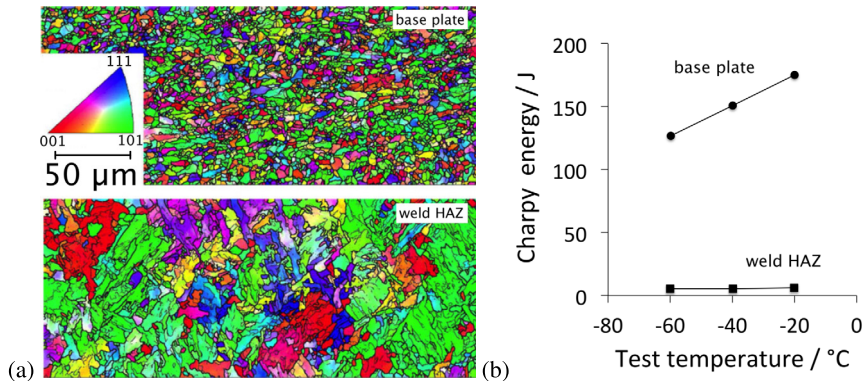


Figure 11.2 (a) Orientation images of the base plate, and of the heat-affected zone of a weld in the same material. (b) Charpy toughness data for the two regions illustrated in (a). A Charpy test is an empirical measure of the ability of a material to absorb energy during fracture. After Yan et al. [6], reproduced with the permission of Elsevier.

a Peierls-Nabarro force, due to the non-planar decomposition of dislocations parallel to $[111]_{\alpha}$ into stacking faults intersecting on the $\{11\bar{2}\}_{\alpha}$ planes [11]. Since pure iron behaves in a ductile manner at cryogenic temperatures, cleavage is induced in the same circumstances when attempts are made to increase the resistance to dislocation motion, in which case the cleavage stress can exceed that required for plastic flow.

As the carbon and nitrogen content of the iron is increased, the transition from ductile to brittle cleavage behaviour takes place at increasing temperatures, until in some steels this can occur at ambient and above-ambient temperatures. Clearly, the significant variables in such a transition are of great basic and practical importance.

Even if there is a tiny bit of plasticity involved with the emission of dislocations during the propagation of a cleavage crack in iron, the work done in extending such a crack is far less than associated with the growth of a macroscopically ductile crack. This is easily shown by carrying out impact tests in a pendulum apparatus where a notched sample is broken and the energy absorbed measured over a range of temperature. The presence of the notch provides a particular triaxial state of stress which makes brittle failure more likely; the Charpy test involves a square sectioned (10 mm × 10 mm) piece 55 mm long with a central 2 mm deep notch with a tip radius of 0.25 mm machined on one face.

The energy absorbed by the specimen from the pendulum when plotted as a function of temperature usually exhibits a substantial change in slope

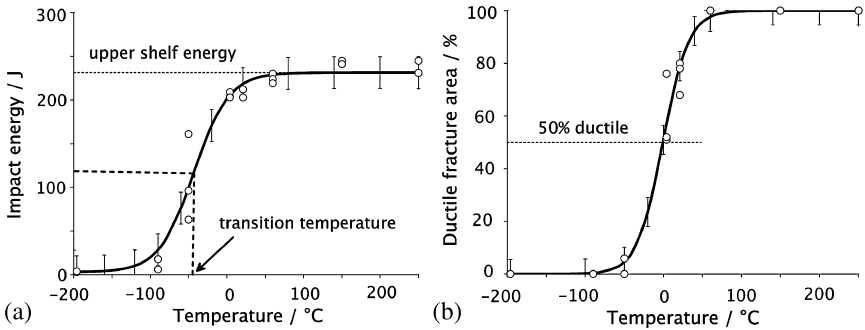


Figure 11.3 Charpy impact toughness data for a nuclear pressure vessel steel. The points represent experimental data and the curves are fitted with error bars indicating the local level of uncertainty. (a) Impact energy absorbed during the test versus test-temperature. (b) The portion of the resulting fracture surface that is ductile, versus test-temperature. Courtesy of Hector Pous Romero [12].

(Fig. 11.3a) as the mode of fracture changes from ductile to brittle with the lowering of the test temperature. Since the test is essentially empirical, parameters such as the energy absorbed and the transition temperature cannot be used in design, but nevertheless serve in quality control and in the ranking of different steels and heat treatment processes. Completely ductile fracture begins usually with the nucleation, growth and linking of voids and defines the upper shelf region of the impact transition curve. At a sufficiently low temperature, the steel fails by cleavage, and in between the two failure modes is the so-called transition temperature T_c . The ductile-brittle transition can be dramatic as illustrated in Fig. 11.3a, but the difference between the upper and lower shelf energies diminishes as the strength of the steel increases, and it becomes difficult to identify a clear transition temperature. An alternative strategy is to define a temperature at which 50% of the fracture surface exhibits the ductile mode of failure (Fig. 11.3b).

The impact transition curve has a shape that is well represented by a hyperbolic tangent function [12]¹:

$$\text{energy absorbed} = C_7 + C_8 \left[1 + \tanh \left(\frac{T - C_9}{C_{10}} \right) \right] \quad (11.1)$$

where C_i are fitting constants and T is the test temperature. One advantage in fitting such an equation is to estimate the uncertainties in the experimental data; real materials or test samples are not homogeneous and hence scatter must be expressed quantitatively.

Tests in which the toughness measured is a material parameter rather than a function of samples size and geometry are useful in the design of engineering components and structures. One such test measures the critical value of the stress intensity beyond which a sharp crack propagates rapidly and leads to failure. The stress intensity² when a sample is loaded in a direction normal to the crack face is defined as:

$$K_I = \sigma (\pi c)^{1/2} \quad (11.2)$$

for a body of infinite extent containing a through-thickness crack of length $2c$ normal to the applied stress σ . Fracture propagates rapidly when the stress intensity reaches the critical value K_{IC} , so that the tolerable defect size for a given applied stress can be readily calculated.

11.3 FACTORS INFLUENCING THE ONSET OF CLEAVAGE FRACTURE

There are several factors, some interrelated, which play an important part in the initiation of cleavage fracture:

1. The temperature dependence of the yield stress.
2. The development of a sharp yield point.
3. Nucleation of cracks at twins.
4. Nucleation of cracks at carbide particles.
5. Grain size.

All bcc metals including iron shown a marked temperature dependence of the yield stress, even when the interstitial impurity content is very low, i.e. the stress necessary to move dislocations, the Peierls-Nabarro stress, is strongly temperature dependent. This means that as the temperature is lowered the first dislocations to move will do so more rapidly as the velocity is proportional to the stress, and so the chances of forming a crack nucleus, e.g. by dislocation coalescence, will increase. [Fig. 11.4](#) shows schematically two ways in which dislocation pile-ups could nucleate cracks.

The interstitial atoms, carbon and nitrogen, will cause the steel to exhibit a sharp yield point (Chapter 2) either by the catastrophic break-away of dislocations from their interstitial atom atmospheres, or by the rapid movement of freshly generated dislocations. In either case, the conditions are suitable for the localised rapid movement of dislocations as a result of high stresses which provides a favourable situation for the nucleation of cracks by dislocation coalescence.

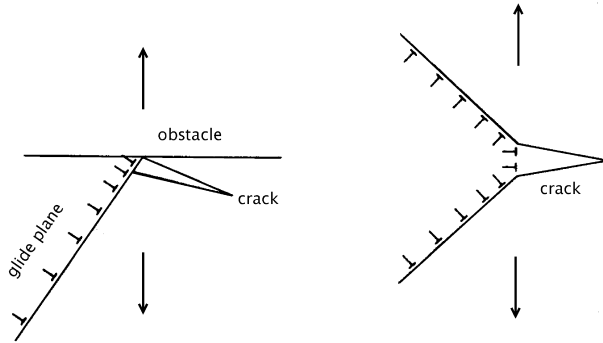


Figure 11.4 Schematic diagram of dislocation mechanisms for crack nucleation.

The flow stress of iron increases rapidly with decreasing temperature (Fig. 2.3) to a point where deformation twinning is stimulated, which then becomes a significant deformation mechanism. It has been shown that cracks are preferentially nucleated at various twin configurations, e.g. at twin intersections [14] and at points where twins contact grain boundaries, so that, under the same conditions, crack propagation is more likely in twinned iron. It should also be noted that the temperature dependence of the flow stress makes plastic deformation more difficult at the tip of a moving crack, so less plastic blunting of the crack tip will take place at low temperatures, thus aiding propagation.

So far, we have discussed crack nucleation mechanisms which can take place in a single phase material, e.g. relatively pure iron, but in the presence of a second phase such as cementite it is still easier to nucleate cracks. Plastic deformation can crack grain boundary cementite particles or cementite lamellae in pearlite so as to produce micro-cracks (Fig. 11.5a) which, in certain circumstances, propagate to cause catastrophic cleavage failure (Fig. 11.5b). Recent work supports the view that this microstructural parameter is extremely important in determining the fracture characteristics of a steel. Brittle inclusions such as alumina particles or various silicates found in steels can also be a source of crack nuclei.

Grain size is a particularly important variable for, as the ferrite grain size is reduced, the transition temperature T_c is lowered, despite the fact that the yield strength increases. This is, therefore, an important strengthening mechanism which actually improves the ductility of the steel. It has been shown by Petch that T_c is linearly related to $(\bar{L})^{-1/2}$ [15], and an appropriate relationship of this type can be derived from a dislocation model involving

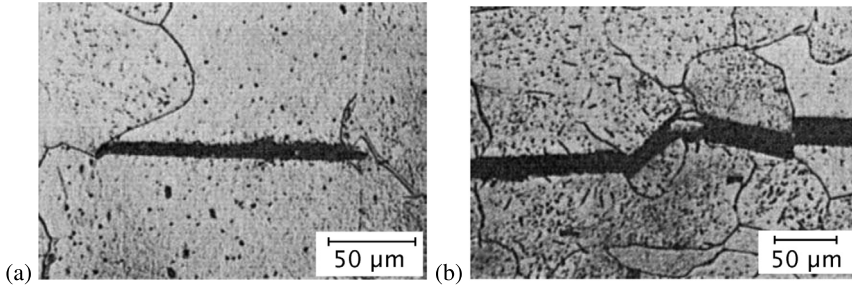


Figure 11.5 (a) Nucleation of a cleavage crack at a carbide particle in a low-carbon steel (courtesy of Knott). (b) Transgranular propagation of a crack in a low-carbon steel (courtesy of Knott).

the formation of crack nuclei at dislocation pile-ups at grain boundaries. The smaller the grain size, the smaller the number of dislocations piling-up where a slip band arrives at a boundary. Bearing in mind that the shear stress at the head of such a pile-up is $n\tau$, where n is the number of dislocations and τ is the shear stress in the slip direction, it follows that as the grain size is reduced, n will be smaller and the local stress concentrations at grain boundaries will be correspondingly less for a given value of applied stress. This situation will lead to less crack nuclei regardless of whether they are formed by dislocation coalescence or by dislocation pile-ups causing carbides to crack or by twinning interactions.

11.4 CRITERIA FOR THE DUCTILE-BRITTLE TRANSITION

The starting point of all theories on brittle fracture is the work of Griffith [16], who considered the condition needed for propagation of a pre-existing crack, of length $2c$, in a brittle solid. When the applied stress σ is high enough, the crack will propagate and release elastic energy. This energy U_e in the case of remotely loaded thin plates (plane stress) is:

$$U_e = \frac{\pi c^2 \sigma^2}{E} \text{ per unit plate thickness,} \quad (11.3)$$

where E is Young's modulus.³ The term is negative because this energy is released. However, as the crack creates two new surfaces, each with energy $= 2c\gamma_s$, there is a positive surface energy term U_s :

$$U_s = 4c\gamma_s, \quad \text{where } \gamma_s = \text{surface energy per unit area.}$$

Griffith showed that the crack would propagate if the increase in surface energy, U_s , was less than the decrease in elastic energy U_e . The equilibrium position is defined as that in which the change in energy with crack length is zero:

$$\frac{dU}{dc} = \frac{d(U_e + U_s)}{dc} = 0. \quad (11.4)$$

This is the elastic energy release 'rate', usually referred to as G :

$$\therefore \left(-\frac{2\pi c\sigma^2}{E} + 4\gamma_s \right) = 0,$$

and

$$\sigma_f = \sqrt{\frac{2\gamma_s E}{\pi c}}, \quad (11.5)$$

where σ_f is the fracture stress, which is defined as that just above which energy is released and the crack propagates. This equation shows that the stress σ is inversely related to crack length, so that as the crack propagates the stress needed drops and the crack thus accelerates. Orowan pointed out that in crystalline solids plastic deformation will occur both during nucleation of the crack, and then at the root of the crack during propagation. This root deformation blunts the crack and, in practice, means that more energy is needed to continue the crack propagation. Thus, the Griffith equation is modified to include a plastic work term γ_p :

$$\sigma_f = \sqrt{\frac{E(2\gamma_s + \gamma_p)}{\pi c}}. \quad (11.6)$$

It has been found that $\gamma_p \gg \gamma$, hence the condition for crack spreading in a crystalline solid such as iron is:

$$\sigma_f = \sqrt{\frac{E\gamma_p}{\pi c}}. \quad (11.7)$$

The local stress field at the crack tip is usually characterised by a parameter K , the stress intensity factor, which reaches a critical value K_c when propagation takes place. This critical value is given by:

$$K_c = \sigma_f \sqrt{\pi c}. \quad (11.8)$$

In plane stress conditions:

$$K_c = \sqrt{EG_c},$$

where G_c is the critical release rate of strain energy.

In plane strain conditions, the critical value of strain energy release rate is $G_{IC} = \gamma_p$, where:

$$\sigma_f = \sqrt{\frac{EG_{IC}}{\pi(1-\nu^2)c}}, \quad (11.9)$$

and where ν is the Poisson's ratio.

The critical value of stress intensity, K_{IC} , is then related to G_{IC} :

$$K_{IC} = \sqrt{\frac{EG_{IC}}{\pi(1-\nu^2)}}. \quad (11.10)$$

The fracture toughness of a steel is often expressed as a K_{IC} value obtained from tests on notched specimens which are pre-cracked by fatigue, and are stressed to fracture in bending or tension.

The nucleation and the propagation of a cleavage crack must be distinguished clearly. Nucleation occurs when a critical value of the *effective shear stress* is reached, corresponding to a critical grouping, ideally a pile-up, of dislocations which can create a crack nucleus, e.g. by fracturing a carbide particle. In contrast, propagation of a crack depends on the magnitude of the local *tensile stress* which must reach a critical level σ_f . Simple models of slip-nucleated fracture assume either interaction of dislocations or cracks formed in grain boundary carbides. However, recently it has been realised that both these structural features must be taken into account in deriving an expression for the critical fracture stress σ_f . The critical stress does not appear to be temperature dependent. At low temperatures the yield stress is higher, so the crack propagates when the plastic zone ahead of the crack is small, whereas at higher temperatures, the yield stress being smaller, a larger plastic zone is required to achieve the critical local tensile stress σ_f .

This tensile stress σ_f has been determined for a wide variety of mild steels, and has been shown to vary roughly linearly with $(\bar{L})^{-1/2}$, Fig. 11.6. The scatter probably arises from differences in test temperature and carbide dimensions. This is conclusive evidence for the role of finer grain sizes in increasing the resistance to crack propagation. Regarding grain boundary carbide size, effective crack nuclei will occur in particles above a certain critical size so that, if the size distribution of carbide particles in a particular steel is known, it should be possible to predict its critical fracture stress. Therefore, in mild steels in which the structure is essentially ferrite grains containing carbide particles, the particle size distribution of carbides is the most important factor. In contrast, in bainitic and martensitic steels the austenite grains transform to lath structures where the lath width is usually

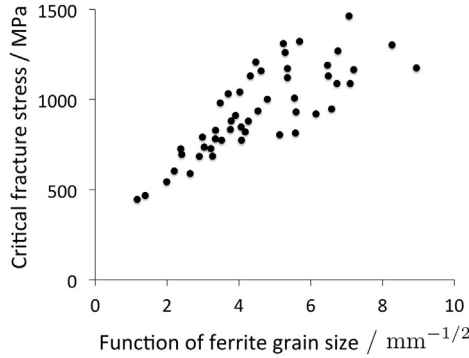


Figure 11.6 Dependence of local fracture stress σ_f on the grain size of mild steel. Data compiled from many sources (courtesy of Knott).

between 0.2 and 2 μm , the laths occur in bundles or packets (Chapter 5) with low angle boundaries between the laths. Larger misorientations occur across packet boundaries. In such structures, the packet width is the main microstructural feature controlling cleavage crack propagation.

The critical local fracture stress σ_f has been related to the two types of structure, as follows:

1. For ferritic steels with spheroidal carbide particles:

$$\sigma_f = \sqrt{\frac{\pi E \gamma_p}{2c_0}}, \quad (11.11)$$

where c_0 is carbide diameter.

2. For bainitic and martensitic steels with packets of laths:

$$\sigma_f = \sqrt{\frac{4E\gamma_p}{(1-\nu^2)d_p}}, \quad (11.12)$$

where d_p is packet width and ν is Poisson's ratio.

11.5 PRACTICAL ASPECTS OF BRITTLE FRACTURE

At the onset of fracture, elastic energy stored in the stressed steel is only partly used for creation of the new surfaces and the associated plastic deformation and the remainder provides kinetic energy to the system. Using a Griffith-type model, the crack velocity $\dot{c}$ can be shown to be [17]:

$$\dot{c} = \dot{c}_{\max} \left(1 - \frac{c_0}{c}\right) \quad \text{where} \quad \dot{c}_{\max} = \sqrt{\frac{2\pi E}{C_{11} \rho}} \quad (11.13)$$

where in a sheet of unit thickness $2c_0$ is the critical crack size, c is the crack size at a given instant, ρ is density and C_{11} is the constant and $\dot{c}_{\max}$ is the maximum crack growth velocity. This relation shows that the velocity increases with increasing crack size and reaches a limiting value $\dot{c}_{\max}$ at large values of c . In practice, $\dot{c}_{\max}$ is between 0.4 and 0.5 of the speed of sound in the metal, so brittle fracture occurs with catastrophic rapidity, as many disasters testify.

The phenomenon of brittle fracture became particularly prevalent with the introduction of welding as the major steel fabrication technique. Previously, brittle cracks often stopped at the joints of riveted plates but the steel structures resulting from welding provided continuous paths for crack propagation. Added to this, incorrect welding procedures can give rise to high stress concentrations and also to the formation of weld-zone cracks which may initiate brittle fracture. While brittle failures of steels have been experienced since the latter half of the nineteenth century when steel began to be used widely for structural work, the most serious failures have occurred in more recent years as the demand for integral large steel structures has greatly increased, e.g. in ships, pipelines, bridges and pressure vessels. Spectacular failures took place in many of the all-welded Liberty ships produced during the Second World War, when nearly 1500 incidents involving serious brittle failure were recognised and 19 ships broke completely in two without warning. Despite our increasing understanding of the phenomenon and the great improvements in steel making and in welding since then, serious brittle failures still occur (Fig. 11.7), a constant reminder that human error and lack of scientific control can be disastrous.

Bearing in mind the temperature dependence of the failure behaviour, and the widening use of steels at low temperatures, e.g. in Arctic pipelines, for storage of liquid gases, etc., it is increasingly necessary to have steels with very low transition temperatures and high fracture toughness. While there are many variables to consider in achieving this end, including the detailed steel-making practice, the composition including trace elements and the fabrication processes involved, the most important is probably grain size refinement. The development of high strength low alloy steels or microalloyed steels (Chapter 9), in the manufacture of which controlled rolling plays a vital part, has led to the production of structural steels with grain sizes often less than $10\ \mu\text{m}$ combined with yield strengths between 400 and 600 MPa and low transition temperatures. In these steels, to which small concentrations ($<0.1\ \text{wt}\%$) of niobium, vanadium or titanium are added, the carbon level is usually less than 0.15 wt% and often below 0.10 wt%,

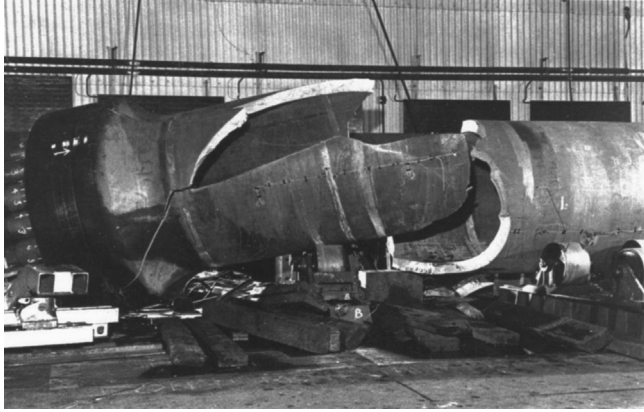


Figure 11.7 Brittle fracture of a thick-walled steel pressure vessel (the Welding Institute).

so that the carbide phase occupies a small volume fraction. In any case, cementite, which forms relatively coarse particles or lamellae in pearlite, is partly replaced by much finer dispersions of alloy carbides, NbC, etc. Addition of certain other alloying elements to steel, notably manganese and nickel, results in a lowering of the transition temperature. For example, alloy steels with 9 wt% nickel and less than 0.1 wt% carbon have a sufficiently low transition temperature to be able to be used for large containers of liquid gases, where the temperature can be as low as 77 K. Below this temperature, austenitic steels have to be used. Of the elements unavoidably present in steels, phosphorus, which is substantially soluble in α -iron, raises the transition temperature and thus must be kept to as low a concentration as possible. On the other hand, sulphur has a very low solubility, and is usually present as manganese sulphide with little effect on the transition temperature but with an important role in ductile fracture. Oxygen is an embrittling element even when present in very small concentrations. However, it is easily removed by deoxidation practice involving elements such as manganese, silicon and aluminium.

Finally, the fabrication process is often of crucial importance. In welding it is essential to have a steel with a low carbon equivalent, i.e. a factor incorporating the effects on hardenability of the common alloying elements. A simple empirical relationship, as a rough guide, is:

$$\text{CE} = w_{\text{C}} + \frac{w_{\text{Mn}} + w_{\text{Si}}}{6} + \frac{w_{\text{Ni}} + w_{\text{Cu}}}{15} + \frac{w_{\text{Cr}} + w_{\text{Mo}} + w_{\text{V}}}{5} \text{ wt\%}, \quad (11.14)$$

where w is the wt% of the element identified in the subscript. A steel with an equivalent of less than 0.45 should be weldable with modern techniques. The main hazard in welding is the formation of martensite in the heat-affected zone (HAZ), near the weld, which can lead to microcracks. This can be avoided, not only by control of hardenability but also by preheating the weld area to lead to slower cooling after welding or by post-heat treatment of the weld region. However, in some high-strength steels, slower cooling may result in the formation of upper bainite in the HAZ which encourages cleavage fracture. More detailed discussion is reserved for Chapter 13.

11.6 HYDROGEN EMBRITTLEMENT

It has been known for a long time that minute concentrations of hydrogen embrittle steel; Johnson's 1875 paper [18] reached the following conclusions which remain valid to this day:

1. The hydrogen that embrittles steel is atomic, not molecular;
2. It is *diffusible* hydrogen that embrittles. This is why incredibly small concentrations (<1 parts per million) of hydrogen in steel have a large effect on toughness. The atoms of hydrogen are attracted towards stress fields of the type associated with a crack tip. They therefore diffuse there, concentrate and thereby alter the fracture mechanism to the detriment of steel. Hence the need for diffusible hydrogen for embrittlement. Since a supply of hydrogen must be delivered to the crack tip during the time scale of the fracture process, deformation at large strain rates exhibit less embrittlement than when the loading is applied slowly.
3. It follows that the phenomenon is reversible; if the hydrogen is given the opportunity to diffuse out of the steel then the metal recovers its properties.
4. Stronger steel is more susceptible to embrittlement than softer versions.

There are several explanations for the deleterious effect of hydrogen on the mechanical properties of steel. Hydrogen may encourage the decohesion of the body-centred cubic iron lattice [19,20], although atomistic calculations show that this may be a minor effect at the concentrations involved [21]. A mechanism that seems counter-intuitive to brittle failure relies on an enhancement of plasticity by hydrogen [22]. When concentrated at a crack tip, the hydrogen is postulated to enhance localised crack tip plasticity by dislocation emission so the fracture surface looks macroscopically brittle but is ductile on a fine scale.

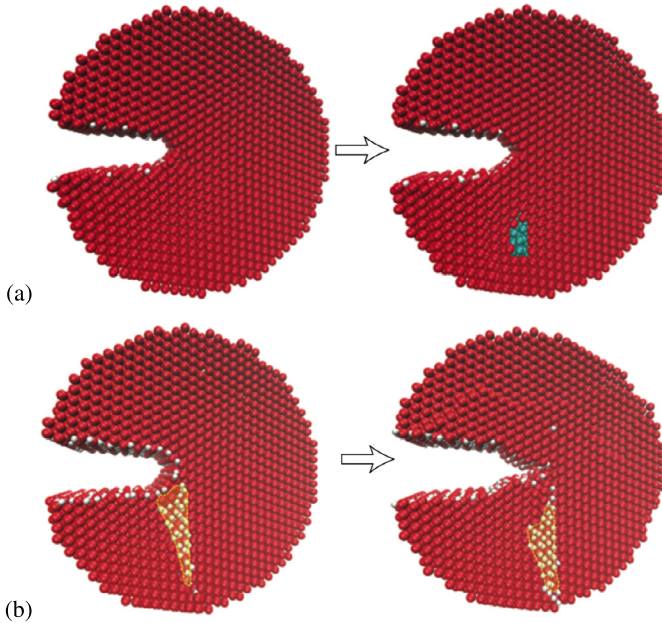


Figure 11.8 Simulated atomic configurations during mode I loading of a crack tip. Hydrogen atoms are coloured white, iron atoms red except those at dislocation cores which are cyan. (a) At a low hydrogen concentration, the atoms simply segregate to the crack surfaces and do not contribute to embrittlement, so the crack is blunted by dislocation emission. (b) At greater hydrogen concentration the hydrogen accumulates in a wedge shaped region which undergoes a phase transformation that blocks dislocation emission and hence brittle cleavage follows. Reprinted by permission from Macmillan Publishers Ltd: Nature Materials [23], copyright 2013.

These mechanisms are essentially qualitative and hence lack the ability to predict properties. An alternative view due to Song and Curtin [23] also involves the attraction and accumulation of hydrogen at the crack tip stress-field, but the consequence this time is the *suppression* of dislocation activity, confirmed using molecular dynamics simulations. The mechanism of dislocation suppression revealed by the simulations is that local regions at the crack tip adopt alternative crystal structures, Fig. 11.8. As a result, the crack tip is not blunted by plasticity and cleavage initiates.

The continued growth of the initial cleavage event requires a corresponding continuing supply of hydrogen to the crack tip. The crack growth rate ($\dot{c}$) therefore depends on a number of thermodynamic and kinetic pa-

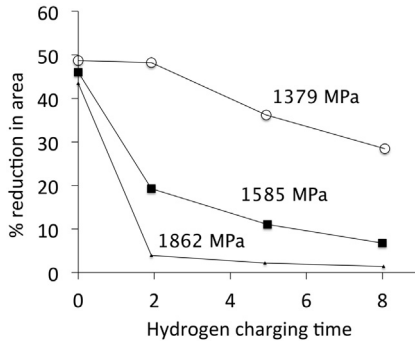


Figure 11.9 Effect of hydrogen charging time (a reflection of the quantity of hydrogen introduced into the steel), on the fracture strength in tension. Data from Frohberg et al. [25].

rameters:

$$\dot{c} \propto \frac{D\bar{V}_p}{T} K_I (\bar{c}_H)^{5/4} \quad (11.15)$$

where D is the hydrogen diffusion coefficient, $\bar{V}_p$ is the partial volume of a hydrogen interstitial in iron and determines the magnitude of the interaction of hydrogen with the pressure field at the tip of the crack. This pressure is related to the stress intensity K_I which defines the loading of the crack, and $\bar{c}_H$ is related to the concentration of hydrogen in the material. The relationship defines nicely the dependence of the crack growth rate on parameters related to concentration, diffusivity and loading during brittle fracture due to hydrogen. It becomes possible using these concepts to predict quantitatively the onset of hydrogen embrittlement in a large variety of steels without fitting parameters.⁴

Hydrogen embrittlement is not in general sensitive to composition *per se*, but to the microstructure and strength of the steel, the problem being most pronounced in high strength alloy steels. Fig. 11.9 shows that in steels that have almost identical ductility in the absence of hydrogen, behave quite differently when hydrogen is introduced. The decrease in ductility is greatest for the strongest steels for a constant hydrogen content. A stronger steel presents greater barriers to dislocation emission at the crack tip, and hence is more susceptible to embrittlement. On the other hand, macroscopic ductility as measured in a tensile test in the absence of dissolved hydrogen depends to a large extent on the ability of the material to work harden and avoid plastic instabilities.

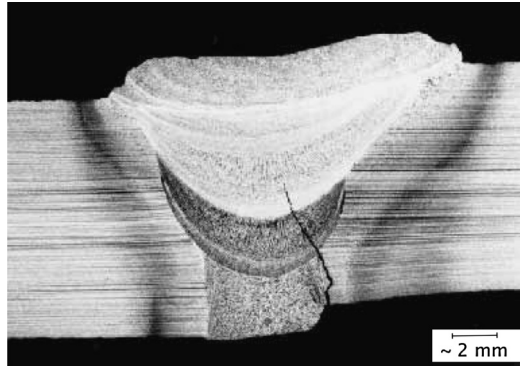


Figure 11.10 Cleavage crack due to hydrogen embrittlement, beginning in the heat-affected zone and then extending into the weld. Reproduced from [26], with permission of P. Woolin of TWI.

There are many ways in which hydrogen can enter into steel, both during the manufacturing process and during service. It is encountered frequently after welding (Fig. 11.10), where it can be introduced by use of damp welding electrodes, leading to cracking which is variously referred to as *underbead* cracking, cold cracking and *delayed cracking*. This phenomenon can be minimised by the use of welding electrodes with very low hydrogen contents, which are oven-dried prior to use.

11.6.1 Prevention of hydrogen embrittlement

It is diffusible hydrogen that causes embrittlement, so anything that traps the hydrogen inside the steel, or prevents its ingress into the steel, will be effective in ameliorating the embrittlement [27]. Fig. 11.11 summarises the large range of methods available to do so.

A trap provides a favourable environment for hydrogen to reside in, for example at the coherency strain fields surrounding small carbide particles, at weak interfaces between non-metallic inclusions and ferrite, or by dissolving in particles where the hydrogen has a much greater solubility than the matrix. The potency of trapping is defined as the reduction in free energy when a hydrogen atom is transferred from the matrix to the trap site. An irreversible trap has a large binding energy and hence immobilises the hydrogen over the life time of the component and its specific service conditions. Examples of the latter include vanadium and titanium carbides. A reversible trap is one that is able to easily release the hydrogen in similar circumstances, if the concentration in the matrix drops for whatever reason,

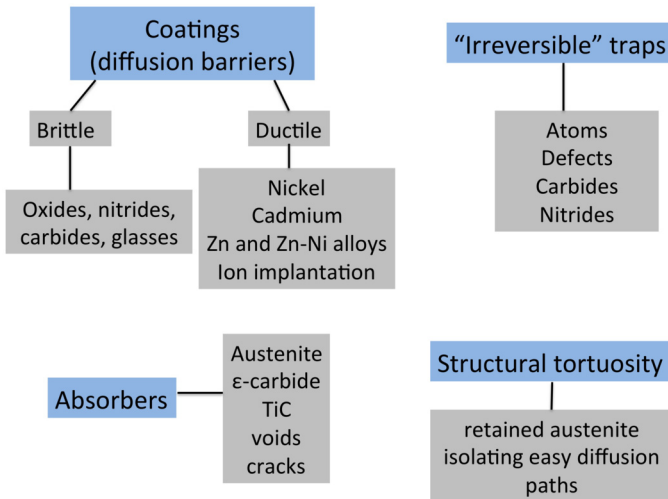


Figure 11.11 Mechanisms available for the modification of steel and its surface to better resist hydrogen [27].

and hence is not a particularly effective means for avoiding embrittlement. Nevertheless, both kinds of traps interfere with the transport of hydrogen and dramatically reduce the effective diffusivity of hydrogen through the steel [28]. This is useful in limiting the ingress of hydrogen into the steel, for example that which is generated through corrosion reactions at the steel surface.

In steels, the diffusivity of hydrogen in austenite is orders of magnitude smaller than in ferrite (Fig. 11.12), although its solubility is much greater in austenite. Retained austenite in the microstructure can therefore act as a strong trap for hydrogen. And if the austenite is present in the form of percolating films between the ferritic phase, then it will greatly retard the passage of hydrogen through the microstructure [29,30], while at the same time acting as a sink that absorbs hydrogen into itself rather than via strain fields as is the case for carbides and nitrides.

Many kinds of coatings exist including alumina, titanium carbide, silicon nitride, titanium oxide, ‘black’ oxide etc. [27], that have been demonstrated to reduce either the outgassing of hydrogen in vacuum systems, or as diffusion barriers to the ingress of hydrogen. However, the choice of coatings available decreases when they have to perform multiple functions, for example to resist abrasion and impact. Coatings may also contain defects that locally expose the steel in which case a sacrificial layer is helpful; Zn-Ni

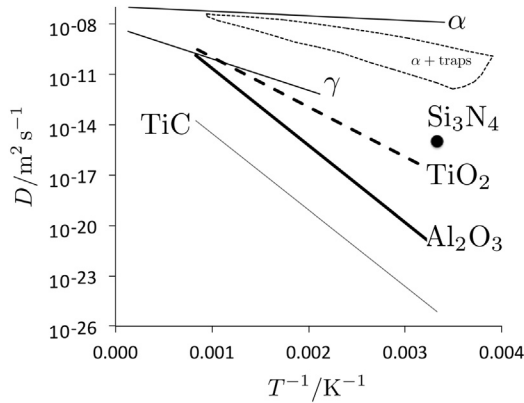


Figure 11.12 Hydrogen diffusion data for TiC [31], TiO₂ parallel to the c-axis [32], Al₂O₃ [33] and Si₃N₄ [34], compared against corresponding diffusivities in steels from Fig. 1.10. γ and α refer to austenite and ferrite respectively. After Bhadeshia [27].

coatings act in this manner. The thickness and integrity of the coating will vary with the manufacturing process and has to be compatible with the service conditions of the protected component. The quality of the coating can depend on the chemical composition and structure of the substrate. Ion implantation can be used to favourably alter the surface of the steel.

11.7 INTERGRANULAR EMBRITTLEMENT

There are many cases where embrittlement involves the parting of grains at their boundaries, leading to *intragranular failure*, Fig. 11.13a. It is intriguing that in steels, the failure can occur along the *prior* austenite grain boundaries, i.e., between austenite grains that no longer exist. This is because displacive transformations (Widmanstätten ferrite, bainite, acicular ferrite, martensite) involve the coordinated motion of atoms, which cannot be sustained across the austenite grain boundaries during transformation, Fig. 11.13b. Hence, in a fully transformed microstructure, a vestige of the austenite grain boundary remains when the transformation is displacive. In contrast, diffusional transformations products are not limited by the austenite grain boundaries so that no trace is left of those boundaries in the final microstructure [35].

This behaviour is encountered in quenched steels, on tempering (*temper embrittlement*), after heating at very high austenitising temperatures (*overheating* and *burning*), and in the *rock candy fracture* in cast steels. These forms

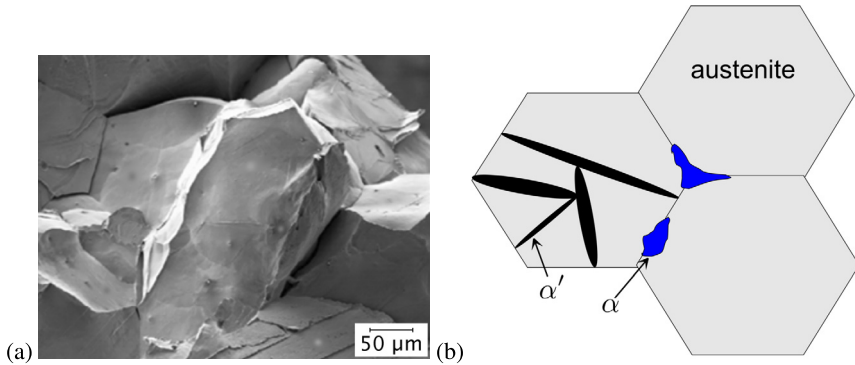


Figure 11.13 (a) Intergranular embrittlement of ferrite grain boundaries in a Fe-0.17P wt% alloy (courtesy of Jeong In Kim). (b) Displacive transformation products such as martensite (α') do not cross austenite grain boundaries whereas allotriomorphic ferrite is not limited in this way and hence consumes portions of the γ boundaries across which it grows.

of embrittlement are exhibited at or around room temperature. There are, however, other phenomena involving failure along grain boundaries which are essentially high temperature events, e.g. hot shortness during the hot working of steels and high temperature creep failure. It is clear that no one mechanism will explain the various types of embrittlement, but the processes leading to intergranular grain fracture all lead to reduced cohesion along the grain boundaries. This can arise in different ways but the most relevant appear to be:

1. Segregation of solute atoms preferentially to grain boundaries.
2. Distribution of second-phase particles at grain boundaries.
3. Penetration of low melting-temperature liquid metal at grain boundaries (liquid metal embrittlement).

These phenomena reduce the work of fracture, i.e. the $(2\gamma + \gamma_p)$ term in Equation (11.6) either by lowering the grain boundary energy by segregation, or by reducing the plastic work term γ_p by having particles which more easily provide crack nuclei.

11.7.1 Temper embrittlement

Many alloy steels when tempered in the range 500–650°C following quenching to form martensite become progressively embrittled in an intergranular manner. A similar phenomenon can occur when the steels are continuously cooled through the critical range. It is revealed by the ef-

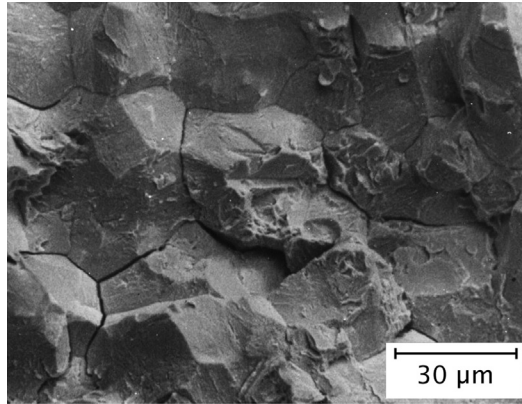


Figure 11.14 Temper embrittlement due to phosphorus, of a low-alloy steel that was heat treated at 550°C for 5 h and then cooled to ambient temperature (courtesy of Liou-Chun Chang).

fect on the notched bar impact test, where the transition temperature is raised and the shelf energy lowered, the transgranular fracture mode being replaced by an intergranular mode below the transition temperature (Fig. 11.14).

This phenomenon is now known to be associated with the segregation of certain elements to the grain boundaries, which reduce the intergranular cohesion of iron. Elements that do not fit well in the substitutional or interstitial sites within the lattice tend to segregate to grain boundaries where there is a greater free volume. This includes solutes such as C, Si, Ge, Sn (Group IVB), N, P, As, Sb, Bi (Group VB), O, S, Se and Te (Group VIB).⁵ With the exception of carbon and silicon, most of these would be present as impurity elements in common steels. The segregation of many of these atoms to the boundaries has been demonstrated by Auger electron spectroscopy on specimens fractured intergranularly within the vacuum system of the apparatus. This technique has allowed the precise determination of the concentrations of segregating species at the boundaries, usually expressed in terms of fractions of a monolayer of atoms. These fractions vary between about 0.3 and 1.0 for steels containing the above elements, usually in bulk concentrations well below ≈ 0.1 wt%.

A useful concept is that if a solute in iron has a greater reduction in energy (Δg_s) when transferred from solid solution to a free surface, than when it is similarly transferred to a grain boundary (Δg_b), then it embrittles the boundary because it becomes favourable to separate the grains [36].

Table 11.1 Selected segregation free energies for solutes in iron, from a compilation by Anderson et al. [36]

Segregant	$-\Delta g_b/\text{kJ mol}^{-1}$	$-\Delta g_s/\text{kJ mol}^{-1}$
Carbon	50–75	73–85
Tin	30–35	61–87
Antimony	8–25	83–130
Sulphur	50–58	165–190
Phosphorus	32–41	76–80
Hydrogen	65–68	71–109

Noting that both these energies would be negative for any solute that tends spontaneously to segregate, the potency to embrittle scales with the positive $\Delta g_b - \Delta g_s$. For example, Table 11.1 shows that phosphorus has a strong tendency to embrittle grain boundaries, and first principles calculations confirm this expectation for special low- Σ boundaries⁶ [38].

Some aspects of the mechanism by which impurities embrittle boundaries are known. Krasko and Olson first demonstrated using first principles calculations that atoms including P and S on segregating tend to enhance the bonding of atoms along the plane of the boundary to the detriment of bonding across the boundary plane [39].

Whether or not embrittlement actually occurs depends on a number of factors other than just $\Delta g_b - \Delta g_s$ [40]. Plastic deformation by slip, and separation at grain boundaries are competing mechanisms. Anything which makes slip more difficult will in general tend to make grain boundary failure more likely [41], depending on the ability of the material within the grains to accommodate strain. Factors that should *enhance* grain boundary failure can be listed as follows:

- (i) as already stated, a strong matrix effectively focuses deformation on the boundaries which become the weak links;
- (ii) low testing temperatures because the matrix then becomes stronger, thus reducing the mobility of dislocations;
- (iii) large grain size [42] since a fixed impurity content is then distributed over a smaller boundary area per unit volume resulting in a greater concentration of the segregant at the boundaries.
- (iv) A large fraction of high energy boundaries where impurity segregation is favoured [43,44]. Low-energy boundaries have greater coherency and hence are better able to resist separation, but also have less free volume for impurities to segregate [45].

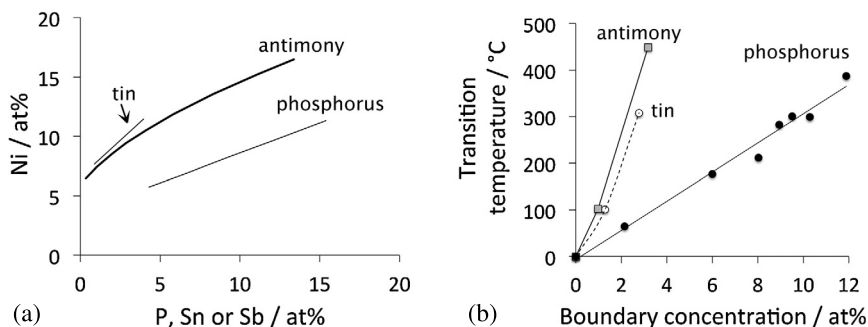


Figure 11.15 (a) Interrelation between concentrations of Sn, Sb and P and of Ni at grain boundaries in Ni-Cr steels of constant hardness and grain size. (b) Effect of grain boundary concentrations of P, Sb and Sn on the ductility of Ni-Cr steels of constant hardness and grain size. After McMahon [46].

With the individual elements, the tendency to embrittle appears to increase both with Group and Period number, i.e. S, Se and Te in increasing order are the most surface active elements in iron. However, it is doubtful whether they contribute greatly to temper embrittlement because they combine strongly with elements such as Mn and Cr which effectively reduce their solubility in iron to very low levels. While the elements in Groups IVB and VB are less surface active, they play a greater role in embrittlement because they interact with certain metallic elements, e.g. Ni and Mn, which are common alloying elements in steels. These interactions lead to co-segregation of alloy element and impurity elements at the grain boundaries, and to resultant lowering of cohesion by the impurity element. Analysis of the composition of grain boundaries by Auger spectroscopy has confirmed strong interactions between Ni-Sb, Ni-P, Ni-Sn and Mn-Sb. Fig. 11.15a shows the grain boundary concentrations for three of these interactions in Ni-Cr steels, while the relative effects of Sb, Sn and P on the transition temperature of Ni-Cr steels are shown in Fig. 11.15b.

Therefore, the driving force for co-segregation to boundaries is a stronger interaction between the alloying element and the impurity element than between either of these and iron. If the interaction is too strong, segregation does not take place. Instead a scavenging effect is obtained, as exemplified by Ti-P and Mo-P interactions in Ni-Cr steels. In this connection it is well known that molybdenum additions to Ni-Cr steels can eliminate temper embrittlement. A third inter-alloy effect is that one alloying element, e.g. Cr, promotes the segregation of Ni and P, also Ni and Sb.

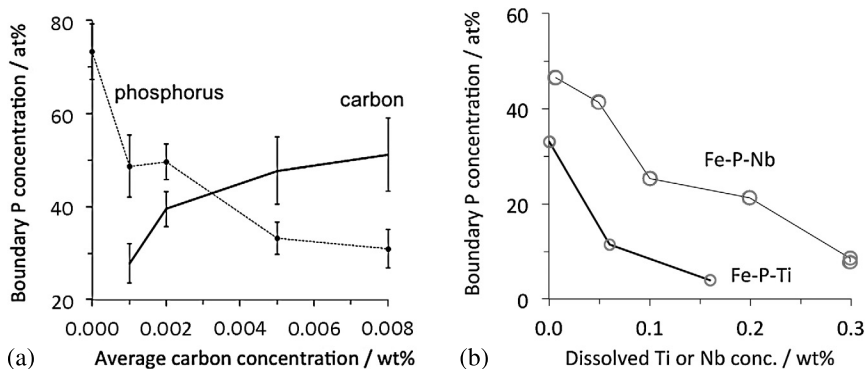


Figure 11.16 (a) Intergranular concentrations of phosphorus and carbon, as a function of the average carbon concentration in a Fe-0.17P wt% steels annealed at 600°C. Adapted from [47]. (b) Reduction in phosphorus segregation to grain boundaries at 550°C, due to the presence of niobium (Fe-Nb-0.068P wt%) or titanium (Fe-Nb-0.04P wt%) in solid solution. Adapted from [48].

There can be site competition when more than one solute has a tendency to segregate to boundaries. Fig. 11.16a shows how carbon segregation reduces the concentration of phosphorus at the boundaries, an effect beneficial to toughness because phosphorus is more pernicious in embrittling boundaries. Niobium and titanium lead to dramatic reductions in the amount of phosphorus at grain boundaries (Fig. 11.16b).

In addition to solute atom segregation to boundaries, there are microstructural factors which influence the intensity of temper embrittlement. In most alloy steels in which this phenomenon is encountered the grain boundaries are the sites for carbide precipitation, either cementite or alloy carbides. It is likely that these provide the sites for intergranular grain crack nuclei. As in the nucleation of cleavage fracture, dislocations impinge on a grain boundary carbide particle and as it is not deformable the carbide will either crack or the ferrite/carbide interface will part. The latter separation is more likely if the interfacial energy has been reduced by segregation of impurity atoms to it. This can occur by rejection of these impurity atoms during the growth of the carbide or by equilibrium segregation. Interfacial separation has been observed in iron containing coarse grain boundary iron carbide, the interfaces of which contained Sb, As, Sn or P. The effectiveness of this nucleating stage of intergranular grain crack formation will be influenced by the extent of grain boundary carbide and the concentration of surface active impurities in the steel, in particular at carbide/matrix interfaces.

The propagation of the grain boundary crack will depend not only on the cohesion of the boundary but also on the relative toughness of the grain interior. For example, if the grain interior has a tough microstructure, the intergranular grain crack nucleus is more likely to propagate along the boundary. Further, as the yield stress of a steel rises sharply with decreasing temperature intergranular grain failure will, like cleavage fracture, be encouraged by reducing the testing temperature. Increasing the austenite grain size, by use of high austenitising temperatures, under the same conditions, should increase the embrittlement because the size of the dislocation arrays impinging on the grain boundary carbides will be larger and thus more effective in forming crack nuclei.

The optimum temperature range for temper embrittlement is between 500°C and 575°C. However, in some steels embrittlement occurs in the range 250–400°C [49–51]. This phenomenon is called 350°C embrittlement, and occurs at too low a temperature to attribute it to the diffusion of metalloids such as Sb to the austenite grain boundaries. It seems more likely that it could arise from smaller and more mobile atoms, e.g. P, which would be rejected during grain boundary growth of iron carbide which takes place in this temperature range. However, the morphology of the grain boundary Fe_3C , if predominantly sheet-like, could be a prime cause of low ductility in this temperature range.

Stress corrosion cracking involves failure by cracking in the presence of both a stress and of a corrosive medium. It can occur in either a transgranular or an intergranular grain mode. The latter mode appears to be encouraged in some alloy steels by heat treatments which produce temper embrittlement. For example, a temper embrittled Cr-Mo steel cracks along the grain boundaries when stressed in a boiling NaOH solution. Use of a heat treatment to remove the temper embrittlement also removes the sensitivity to stress corrosion.

11.8 DUCTILE OR FIBROUS FRACTURE

11.8.1 General

The higher temperature side of the ductile/brittle transition is associated with a much tougher mode of failure, which absorbs much more energy in the impact test. While the failure mode is often referred to as ductile fracture, it could be described as rupture, a slow separation process which, although transgranular, is not markedly crystallographic in nature. Scanning electron micrographs of the ductile fracture surface (Fig. 11.17), in striking

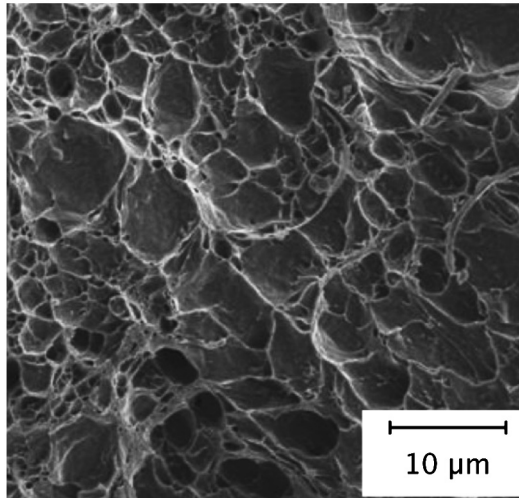


Figure 11.17 Ductile fracture surface of a low alloy steel showing a combination of large and small voids that link up to lead eventually to the parting of the sample. In commercial steels, the voids are nucleated inevitably at non-metallic inclusions (courtesy of Minsung Joo).

contrast to those from the smooth faceted cleavage surface, reveal a heavily dimpled surface, each depression being associated with a hard particle, either a carbide or non-metallic inclusion.

It is now established that ductile failure is initiated by the nucleation of voids at second-phase particles. In steels these particles are either carbides, sulphide or silicate inclusions. The voids form either by cracking of the particles, or by decohesion at the particle/matrix interfaces, so it is clear that the volume fractions, distribution and morphology of both carbides and of inclusions are important in determining the ductile behaviour, not only in the simple tensile test, but in complex working operations. Therefore, significant variables, which determine ductility of steels, are to be found in the steel-making process, where the nature and distribution of inclusions is partly determined, and in subsequent solidification and working processes. Likewise, the carbide distribution will depend on composition and on steel-making practice, and particularly on the final heat treatment involving the transformation from austenite, which largely determines the carbide size, shape and distribution.

The formation of voids begins very early in a tensile test, as a result of high stresses imposed by dislocation arrays on individual hard particles.

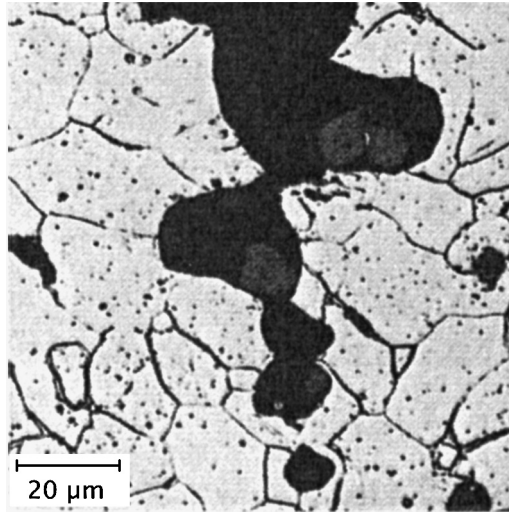


Figure 11.18 Growth of a ductile crack in a free-cutting mild steel containing sulphides (courtesy of R. F. Smith).

Depending on the strength of the particle/matrix bond, the voids occur at varying strains, but for inclusions in steels the bonding is usually weak so voids are observed at low plastic strains. These elongate under the influence of the tensile stress but, additionally, a lateral stress is needed for them to grow sideways and link up with adjacent voids forming *micronecks*. These necks progressively part (Fig. 11.18) leading to the ductile fracture surfaces with a highly dimpled appearance. The second-phase particles (MnS) can be clearly seen in Fig. 11.18.

Many higher-strength steels exhibit lower work-hardening capacity as shown by relatively flat stress-strain curves in tension. As a result, at high strains the flow localises in shear bands, where intense deformation leads to decohesion, a type of shear fracture. While the detailed mechanism of this process is not yet clear, it involves the localised interaction of high dislocation densities with carbide particles.

11.8.2 Role of inclusions in ductility

It is now generally recognised that the deformability of inclusions is a crucial factor which plays a major role, not only in service where risk of fracture exists, but also during hot and cold working operations such as

rolling, forging, machining. Kiessling has divided the inclusions found in steels into five categories relating to their deformation behaviour:

1. Al_2O_3 and calcium aluminates: these arise during deoxidation of molten steels. They are brittle solids, which are in practical terms undeformable at all temperatures.
2. Spinel-type oxides $\text{AO-B}_2\text{O}_3$: these are undeformable in the range room temperature to 1200°C , but may be deformed above this temperature.
3. Silicates of calcium, manganese, iron and aluminium in various proportions: these inclusions are brittle at room temperature, but increasingly deformable at higher temperatures. The formability increases with decreasing melting point of the silicate, e.g. from aluminium silicate to iron and manganese silicates.
4. FeO , MnO and $(\text{FeMn})\text{O}$: these are plastic at room temperature, but appear gradually to become less plastic above 400°C .
5. Manganese sulphide MnS : this common inclusion type is deformable. There are three main types of MnS inclusion dependent on their mode of formation, which markedly influences their morphology:
 - Type I: Globular, formed only when oxygen is present in the melt, e.g. in rimming steels (Fig. 11.19a).
 - Type II: Interdendritic eutectic form, familiar in killed steels (Fig. 11.19b).
 - Type III: Random angular particles, found in fully deoxidised steels (Fig. 11.19c).

It is now known that ductile failure can be associated with any of the types of inclusion listed above, from the brittle alumina type to the much more ductile sulphide inclusions. However, the inclusions are more effective in initiating ductile cracks above a critical size range. The coarser particles lead to higher local stress concentrations, which cause localised rupture and microcrack formation. Some quantitative work has now been done on model systems, e.g. iron-alumina where the progressive effect on ductility of increasing volume fraction of alumina is readily shown. The reduction in yield stress, also observed, arises from stress concentrations around the inclusions and is already evident at relatively low volume fractions.

The presence of particles in the size range $1\text{--}35\text{ }\mu\text{m}$ broadens substantially the temperature range of the ductile/brittle transition in impact tests and also lowers the energy absorbed during ductile failure, the *shelf energy*.

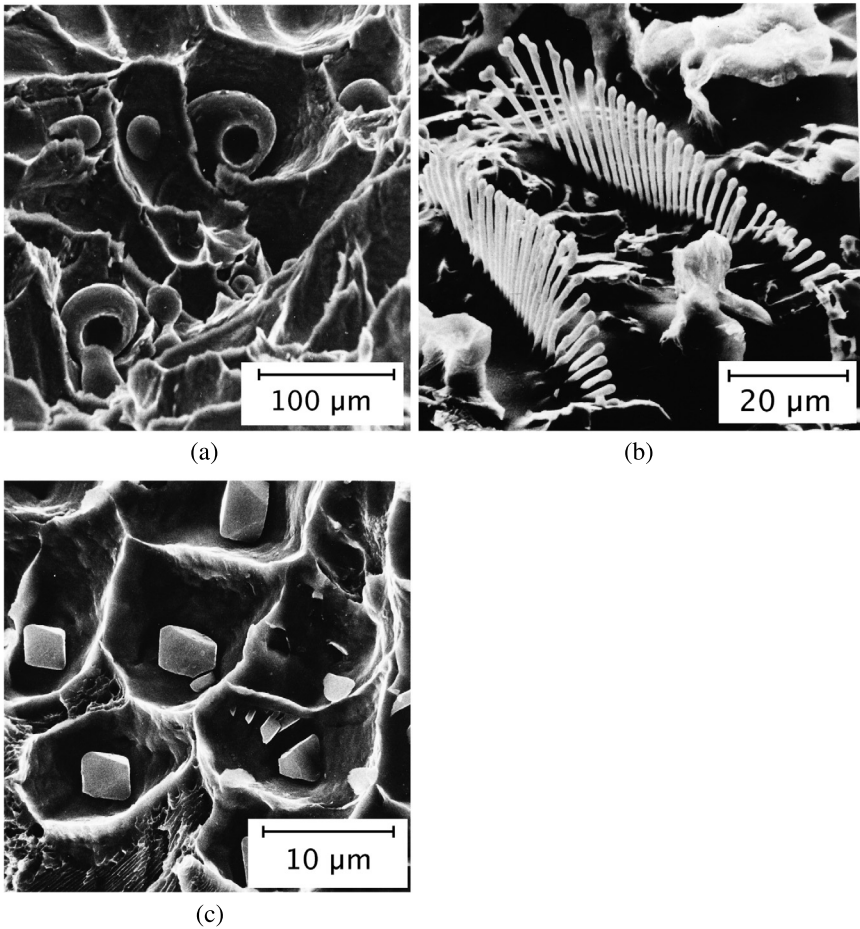


Figure 11.19 Manganese sulphide inclusions in steels: (a) type I; (b) type II; (c) type III (courtesy of T. J. Baker).

A fine dispersion of non-brittle type inclusions can delay cleavage fracture by localised relaxation of stresses with a concomitant increase in yield stress.

Regarding cyclic stressing, it appears that inclusions must reach a critical size before they can nucleate a fatigue crack but the size effect depends also very much on the particular shape, e.g. whether spherical or angular. It has been found in some steels, e.g. ball bearing steels, that fatigue cracks originate only at brittle oxide inclusions, and not at manganese sulphide particles or oxides coated with manganese sulphide. In such circumstances the stresses which develop at particle interfaces with the steel matrix, as

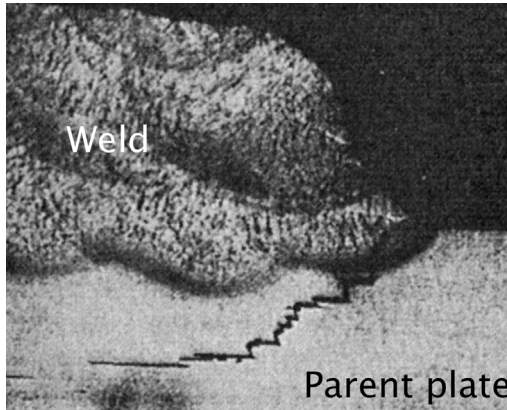


Figure 11.20 Lamellar tearing near a weld (the Welding Institute).

a result of differences in thermal expansion, appear to play an important part. It has been found that the highest stresses arise in calcium aluminates, alumina and spinel inclusions, which have substantially smaller thermal expansion coefficients than steel. These inclusions have the most deleterious effects on fatigue life.

The behaviour of ductile inclusions such as MnS during fabrication processes involving deformation has a marked effect on the ductility of the final product. Types I and III manganese sulphide will be deformed to ellipsoidal shapes, while type II colonies will rotate during rolling into the rolling plane, giving rise to very much reduced toughness and ductility in the transverse direction. This type of sulphide precipitate is the most harmful so efforts are now made to eliminate it by addition of strong sulphide forming elements such as Ti, Zr and Ca. The lack of ductility is undoubtedly encouraged by the formation at the inclusion interfaces of voids because the MnS contracts more than the iron matrix on cooling, and the interfacial bond is probably insufficiently strong to suppress void formation. The variation in ductility with direction in rolled steels can be extreme because of the directionality of the strings of sulphide inclusions, and this in turn can adversely affect ductility during many working operations.

Cracking can also occur during welding of steel sheet with low transverse ductility. This takes place particularly in the parent plate under butt welds, the cracks following the line of the sulphide inclusion stringers. The phenomenon is referred to as *lamellar tearing* (Fig. 11.20).

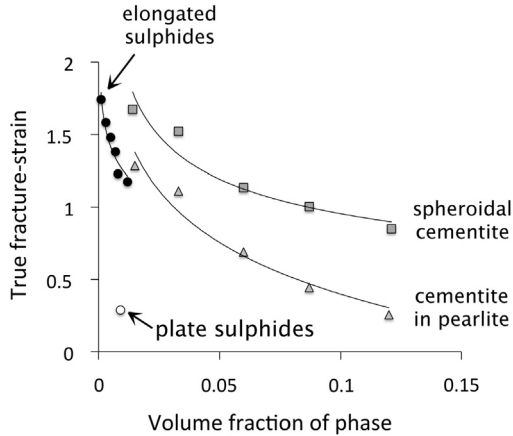


Figure 11.21 Effect of second-phase particles on the ductility of steel. Adapted from Gladman et al. [52].

11.8.3 Role of carbides in ductility

The ductility of steel is influenced by the carbide distribution which can vary from spheroidal particles to lamellar pearlitic cementite. Comparing spheroidal cementite with sulphides of similar morphology, the carbide particles are stronger and do not crack or exhibit decohesion at small strains, with the result that a spheroidised steel can withstand substantial deformation before voids are nucleated and so exhibits good ductility. The strain needed for void nucleation decreases with increasing volume fraction of carbide and so can be linked to the carbon content of the steel.

Pearlitic cementite does not crack at small strains, but the critical strain for void nucleation is lower than for spheroidised carbides. Another factor which reduces the overall ductility of pearlitic steels is the fact that once a single lamella cracks, the crack is transmitted over much of a pearlite colony leading to well-defined cracks in the pearlite regions. The result is that the normal ductile dimpled fractures are obtained with fractured pearlite at the base of the dimples.

The effects of second phases on the ductility of steel are summarised in Fig. 11.21, where the sulphides are shown to have a more pronounced effect than either carbide distribution. This arises because, in the case of the sulphide inclusions, voids nucleate at a very early stage of the deformation process. The secondary effect of the particle shape both for carbides and sulphides is also indicated.

11.8.4 Overheating, burning and liquid metal embrittlement

Many alloy steels when held in the range 1200–1400°C and subsequently heat treated by quenching and tempering, fail intergranularly along the original austenitic boundaries. There is strong evidence to suggest that this phenomenon is associated with the segregation of sulphur to the austenite grain boundaries at the high temperature, and indeed the phenomenon is not obtained when the sulphur content of a steel is less than 0.002 wt%. Sulphur has been shown to be one of the most surface active elements in iron. Work by Goux and colleagues on pure iron–sulphur alloys has shown that an increase in sulphur content from 5 to 25 ppm raises the ductile/brittle transition temperature by over 200°C. Further, Auger spectroscopy on the intergranular grain fracture surfaces has given direct evidence of sulphur segregation. However, this embrittling effect of sulphur as a result of equilibrium segregation is seen only in pure iron and not in steels where there are other impurity elements, and also where interaction of sulphur occurs with alloying elements, notably manganese and chromium.

The presence of manganese substantially lowers the solubility of sulphur in both γ - and α -iron, with the result that when sulphur segregates to high-temperature austenite boundaries, manganese sulphide is either formed there or during subsequent cooling. In either case, the manganese sulphide particles lying on the austenite boundaries are revealed by electron microscopy of the intergranular grain fracture surfaces where they are associated with small dimples. Typically the MnS particles are about 0.5 μm while the dimples are approximately 2–5 μm in diameter. Thus, the grain boundary fracture process is nucleated by the sulphide particles, and the mode of fracture will clearly be determined by the size distribution, which will in turn be controlled by the rate of cooling from the austenite temperature, assuming that MnS forms during cooling. With very slow cooling rates, the intergranular grain fracture is replaced by cleavage or transgranular fibrous fracture as the grain boundary sulphide distribution is too coarse. Oil quenching from the austenitising temperature does not eliminate the phenomenon which is accentuated on tempering in the range 600–650°C. This arises from the redistribution of carbides which will strengthen the grain interiors, and by precipitation at the grain boundaries which may further reduce grain boundary ductility.

When very high austenitising temperatures are used (1400–1450°C) extensive MnS precipitate is formed, often in impressive dendritic forms (Fig. 11.22). In extreme cases, partial formation of liquid phase occurs (liquidation) which, on subsequent heat treatment, greatly accentuates the

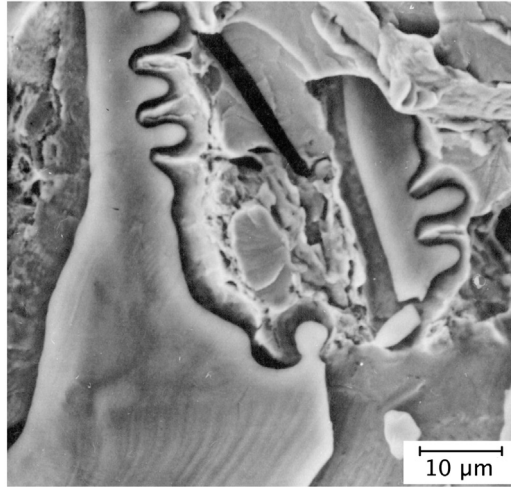


Figure 11.22 Dendrites of sulphide, which melt at a lower temperature than the steel and lead to hot shortness (courtesy of Martin Moeser).

intergranular grain embrittlement. In the absence of manganese, e.g. in wrought iron, liquid films of the iron-iron sulphide eutectic cause embrittlement during hot working processes down to 1000°C (*hot shortness*). The fact that in normal steels burning occurs only at very high temperatures should not be allowed to detract from its significance. The phenomenon may well intrude in high temperature working processes such as forging if temperature control is not exact, but in any case it can certainly be significant in steels which are cast, and by definition pass through the burning and overheating temperature range. In many cases intergranular grain fracture is encountered in cast alloy steels where the as-cast grain structure is clearly involved. Examination of the fractures reveals extensive grain boundary sheets of manganese sulphide, often only 0.2–0.5 μm thick but covering large areas. Marked embrittlement can occur in the as-cast state or after subsequent heat treatment in the range 500–600°C, and is often referred to as as-cast brittleness or rock candy fracture. Precipitation of aluminium nitride may also play an important role in this type of fracture.

Liquid metal embrittlement refers to a phenomenon in which a material that is otherwise well-behaved, suffers from failure when in contact with another which is liquid at a temperature below the melting point of the material.

A liquid (*l*) is said to wet a grain boundary when the grain boundary energy per unit area (say $\sigma_{\gamma\gamma}$) exceeds that of the two new interfaces that

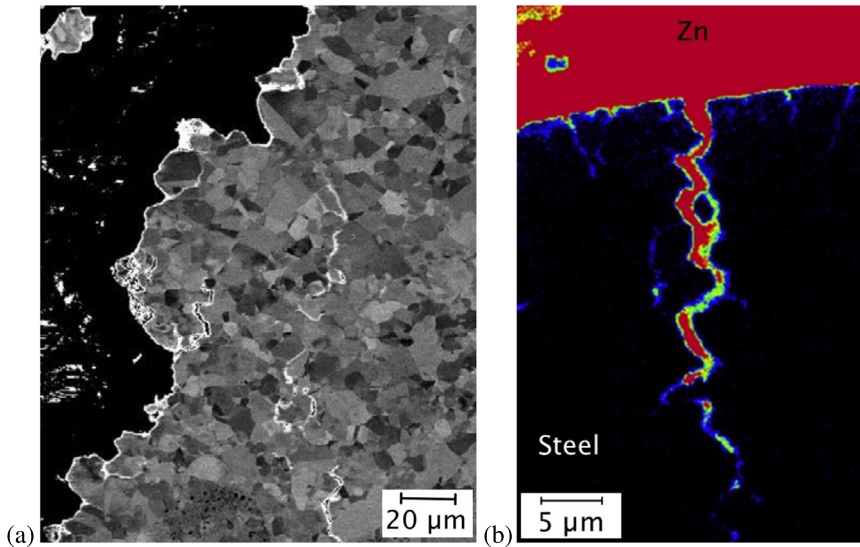


Figure 11.23 (a) Intergranular fracture of TWIP steel due to liquid-metal embrittlement by zinc (after Beal et al. [58]). (b) Microanalysis image showing the penetration of zinc into a spot-welded TWIP steel, showing a meandering of the crack along the austenite grain boundaries (after Ashiri et al. [59]). Images reproduced with the permission of Elsevier.

replace the boundary, i.e. $\sigma_{\gamma\gamma} > 2\sigma_{ly}$. Such wetting would lead to embrittlement even without the application of an external stress because there is then a reduction in free energy when the liquid penetrates the boundary. However, wetting of this kind is rare and other mechanisms need to be considered, although all mechanisms imply the supply of the liquid or associated vapour to the crack tip [53]; this requirement sets the limits to the temperature range over which the embrittlement can be induced [54]. A second requirement is that the material must be stressed sufficiently to produce plastic deformation, whether this is at a stress concentration or in general yielding [55].

Austenitic steels have long been known to be susceptible to liquid metal embrittlement by zinc [56]. The invention of TWIP steels (Chapter 10) has once again brought the phenomenon to the fore, because the galvanised versions suffer from this phenomenon when resistance spot welded. The process of embrittlement in the case of tensile tests conducted on TWIP steel in contact with liquid zinc appears to be sequential. There is first the penetration of liquid zinc along the austenite grain boundaries (Fig. 11.23)

while the sample is stressed, leading to cracking, followed by the further penetration along intact boundaries and more cracking [57].

The type of liquid induced embrittlement described above is but one of a class of liquid metal phenomena, including corrosive attack that is localised at microstructural features in the vicinity of the surface of the steel. The resulting crack-like features can then reduce the mechanical performance of the alloy. There may also exist chemical reactions between the liquid metal and the steel that increase brittle behaviour.

11.9 SUMMARY

Very major improvements have been achieved in the safe use of steels through an understanding of what happens when impurities wreak havoc with the toughness of steels. Given that steels are manufactured on a vast scale, it is not economical to rid them, during steel making, of elements such as the metalloids to concentrations that are small enough to be innocuous. Hydrogen is unique in that even if due care is exercised during steel production, it is able to penetrate the steel through surface reactions such as those typical in corrosion, or during fabrication and heat treatment.

It is remarkable nevertheless, that methods have been found to control the consequences of these impurities. Phosphorus-induced intergranular embrittlement can be controlled by alloying the steel with molybdenum. Nascent hydrogen that has entered the steel can be trapped at deliberately engineered sites within the steel; since hydrogen embrittlement requires the atom to be mobile in the lattice, the traps protect against its pernicious effects.

These, and many other embrittlement and fracture phenomena are well understood, but they are sometimes still overlooked through ignorance. Modern steels represent the most advanced of materials and hence have to be treated with due care and respect.

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BACKNOTES

1. Hyperbolic tangent functions in general are flexible and often form the basis of neural networks [13].
2. It is fine to talk of a stress when a uniform body is homogeneously loaded, but in the presence of a crack or sharp geometrical feature, applying a load leads to an intensification of the applied stress in the vicinity of the feature. Hence, the term *stress intensity*.

3. For a linear elastic solid without a crack, U_e would be half this value, given simply by the area under the elastic stress versus elastic strain curve. However, the stress around an elliptical crack is more complex and an exact solution due to Griffith [16] gives double the value expected from a simple application of Hooke's law.
4. There are other theories of the mechanism of hydrogen embrittlement, reviewed in a recent book by Nagumo [24], for example the internal pressure model where hydrogen accumulates at a suitable defect in the form of molecular hydrogen and the resulting pressure initiates cleavage.
5. The groups refer to the periodic table of elements.
6. Σ refers to the fraction of lattice points that are common to two crystals that share a common origin and are allowed to interpenetrate and fill all space (e.g. [37]). Thus, a low- Σ boundary would, in general, correspond to a low energy boundary. First principles calculations are often limited to low- Σ boundaries because computational limits mean that they can deal only with a few hundreds of atoms whereas a general grain boundary would require much greater 'supercells'.

CHAPTER 12

Stainless Steel

Abstract

A stainless steel is, in its raw form, resistant to stains, discolouration or loss of mass due to rusting. This is because it contains sufficient chromium to form a passive film of oxide on the surface, which isolates the substrate from the reactive environment. The film is able to reform in seconds in the event of damage. With an appropriate combination of alloying elements, stainless steels can be fully austenitic, a mixture of ferrite and austenite, fully ferritic or martensitic. They may or may not be precipitation hardened. The palette of alloys available permits considerable creativity in the application of stainless steel, from the facade of modern buildings, to artistic creations and in critical applications such as nuclear reactors.

12.1 INTRODUCTION

Some elements extend the γ -loop in the iron-carbon equilibrium diagram (Chapter 4), e.g. nickel and manganese. When sufficient alloying element is added, it is possible to preserve the face-centred cubic austenite at room temperature, either in a stable or metastable condition. Chromium added alone to a plain carbon steel tends to close the γ -loop and favour the formation of ferrite. However, when chromium is added to a steel-containing nickel it retards the kinetics of the $\gamma \rightarrow \alpha$ transformation, thus making it easier to retain austenite at room temperature.

The presence of chromium greatly improves the corrosion resistance of the steel by forming a very thin, stable, regenerative and passive chromium-rich oxide film on the surface. The term “passive” means that the reaction of the metal with its surroundings, for example with atmospheric oxygen, forms a protective surface layer that is uniform and stifles further reaction [1]. If the film is damaged, the chromium in the steel reacts again to reform the protective layer, a reaction that takes mere seconds. The actual composition of the oxide film is better represented as $\text{Cr}_{2-x}\text{Fe}_x\text{O}_3$ where x is nearly zero for chromium-rich alloys [2]. The oxide film often is able to adapt further to the environment in which the steel is placed [3], for example, Fig. 12.1. This is why chromium-nickel stainless steels are now the most used materials in a wide range of corrosive environments both at room and elevated temperatures, in engineering as well as artistic constructions (Fig. 12.2).

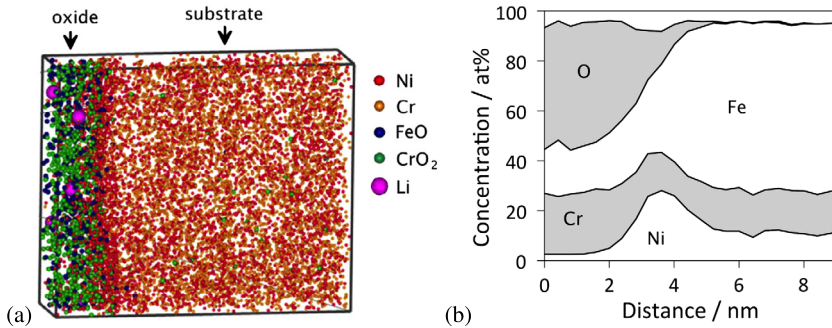


Figure 12.1 (a) Atom probe tomograph showing the atoms in the chromium-rich oxide covering a 316 stainless steel that has been exposed to pressurised-water nuclear reactor conditions. (b) Variation of chemical composition at the oxide-metal interface – not all species are plotted for the sake of clarity. After Lozano-Perez et al. [4], reproduced and adapted with permission of Elsevier.

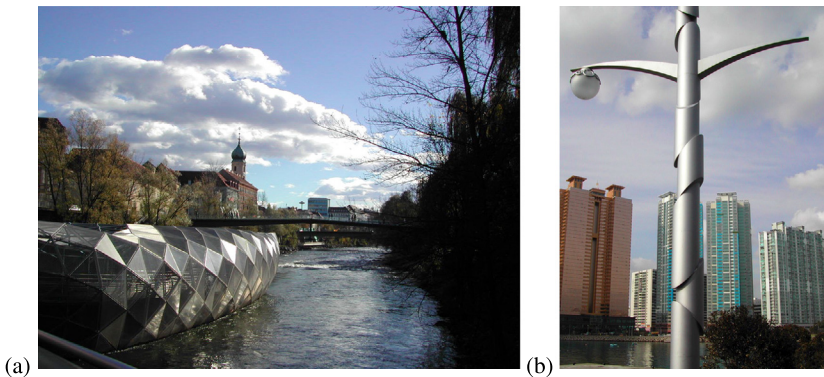


Figure 12.2 Corrosion-resistant artistic creations using stainless steel. (a) A fresh-water island on the river Mur, in Graz, Austria. (b) A street lamp on the sea-port Busan, Republic of Korea.

Added to the attributes that chromium confers to steel as described above, austenitic steels are readily fabricated and do not undergo a ductile/brittle transition which can cause problems in ferritic steels. This has ensured that they have become a most important group of construction steels, often in very demanding environments. Nevertheless, there also are some important ferritic stainless steels which will be discussed in this chapter. In terms of strength and ductility, stainless steels of all varieties follow the same general trend as the low-alloy steels, Fig. 12.3.

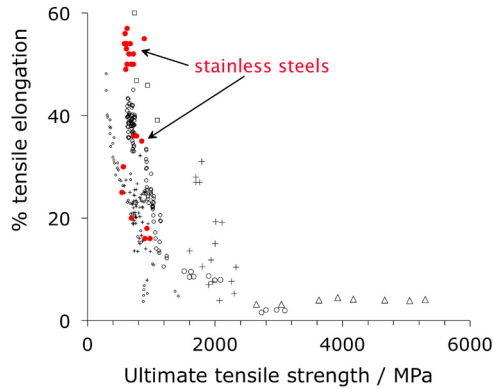


Figure 12.3 The typical combinations of ultimate tensile strength and elongation of commercially available stainless steels plotted on the same diagram as for the low-alloy steels described in Fig. 2.1.

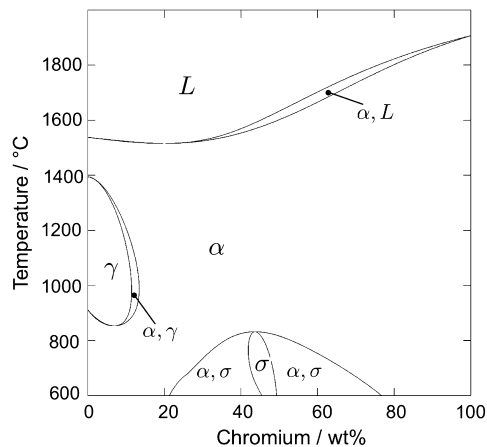


Figure 12.4 Calculated Fe-Cr equilibrium phase diagram. *L* stands for liquid and the iron-chromium intermetallic compound is sigma phase, labelled σ (courtesy of Mathew Peet).

12.2 THE IRON-CHROMIUM-NICKEL SYSTEM

The binary iron-chromium equilibrium diagram (Fig. 12.4) shows that chromium restricts the occurrence of the γ -loop such that the alloy is fully ferritic over the whole temperature range below melting, when the chromium content exceeds 13 wt%; the regime where $\alpha + \gamma$ coexist is also narrow, between 12 and 13 wt% Cr. The ferrite that is retained from the

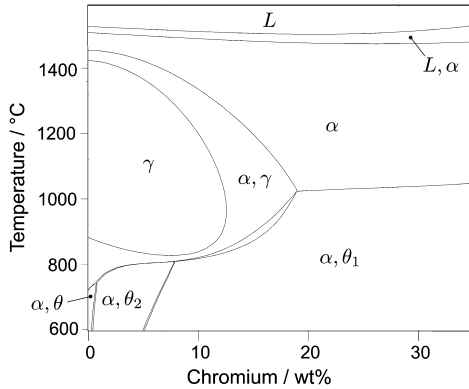


Figure 12.5 Calculated Fe-Cr-0.05C wt% equilibrium phase diagram. θ , θ_1 and θ_2 , stand for cementite, $M_{23}C_6$ and M_7C_3 respectively (courtesy of Mathew Peet).

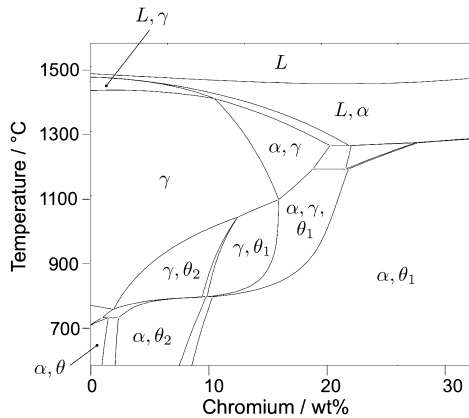


Figure 12.6 Calculated Fe-Cr-0.4C wt% equilibrium phase diagram. θ , θ_1 and θ_2 , stand for cementite, $M_{23}C_6$ and M_7C_3 respectively (courtesy of Mathew Peet).

solidification stage is normally referred to as δ -ferrite. Even though the extent of the γ and $\gamma + \alpha$ phase fields becomes greater with the addition of 0.05 wt% carbon, an alloy containing 19 wt% chromium alloy will not contain austenite at any temperature (Fig. 12.5). Between 0.08 and 0.22C wt%, partial transformation is possible leading to $\alpha + \gamma$ structures, while above 0.4C wt% the steel can be made fully austenitic (Fig. 12.6) if cooled sufficiently rapidly from the γ -loop region. The second effect of carbon is to introduce carbides to the structure as indicated in Figs 12.5 and 12.6:

$$\theta \equiv M_3C, \quad \theta_1 \equiv M_{23}C_6, \quad \theta_2 \equiv M_7C_3,$$

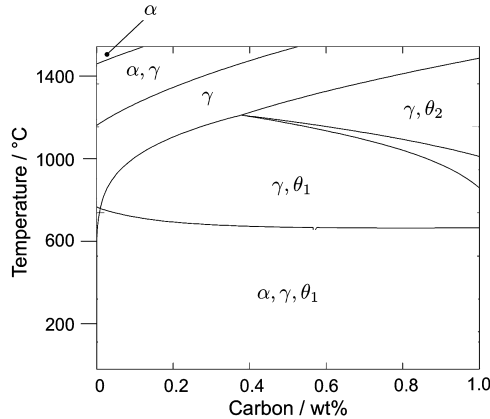


Figure 12.7 Calculated effect of carbon on the phase diagram for 18Cr-8Ni steel. θ_1 and θ_2 , stand for $M_{23}C_6$ and M_7C_3 respectively (courtesy of Mathew Peet).

where ‘M’ represents a mixture of metal atoms. In austenitic steels, $M_{23}C_6$ is the most significant carbide formed and it can have a substantial detrimental influence on corrosion resistance.

If nickel is added to a low carbon iron-18Cr wt% alloy, the γ -phase field is expanded until at about 8Ni wt% the γ -phase persists to room temperature (Fig. 12.7) leading to the familiar group of the so-called 18-8 (18Cr-8Ni) austenitic stainless steels. This particular composition arises because a minimum nickel content is required to retain γ at room temperature. With both lower and higher Cr contents more nickel is needed. For example, with more corrosion resistant, higher-Cr steels, e.g. 25 wt% Cr, about 15 wt% nickel is needed to retain the austenite at room temperature. Lack of complete retention is indicated by the formation of martensite. A stable austenite can be defined as one in which the M_S is lower than room temperature. The 18Cr-8Ni steel, in fact, has an M_S just below room temperature and, on cryogenic cooling, e.g. in liquid nitrogen, it will transform very substantially into martensite.

Fig. 12.7 also shows that the carbide $M_{23}C_6$ exists below about 900°C. However, it goes into solution when the steel is heated to 1100–1150°C and since it requires substitutional atom diffusion in order to form, quenching from the high temperatures results in a precipitate-free austenite at ambient temperature. However, on reheating in the range 550–750°C, $M_{23}C_6$ is re-precipitated preferentially at the grain boundaries.

Manganese expands the γ -loop and can, therefore, be used instead of nickel. However, it is not as strong a γ -former but about half as effective, so higher concentrations are required. In the absence of chromium, around 12 wt% Mn is required to stabilise even higher carbon (1–1.2 wt%) austenite, achieved in Hadfield's steel which approximates to this composition. Typically, Cr-Mn steels require 12–15 wt% Cr and 12–15 wt% Mn to remain austenitic at room temperature if the carbon content is low.

Like carbon, nitrogen is a very strong austenite former. Both elements, being interstitial solutes in austenite, are the most effective solid solution strengtheners available. Nitrogen is more useful in this respect as it has less tendency to cause intergranular corrosion due to the precipitation of chromium-rich compounds, largely because it has a greater solubility in austenite than does carbon. Concentrations of nitrogen up to 0.25 wt% are used, which can nearly double the proof stress of a Cr-Ni austenitic steel. Up to 0.4 wt% of nitrogen can be introduced in austenitic steel when melting and processing at ambient pressure. There are high-pressure melting and powder metallurgical techniques whereby greater concentrations of nitrogen can be introduced [5], but obviously, at greater cost.

One of the most convenient ways of representing the effect of various elements on the basic structure of chromium-nickel stainless steels is the Schaeffler diagram, often used in assessing the likely structure of welding alloys. It plots the compositional limits at room temperature of austenite, ferrite and martensite, in terms of nickel and chromium equivalents (Fig. 12.8). At its simplest level, the diagram shows the regions of existence of the three phases for iron-chromium-nickel alloys. However, the diagram becomes of much wider application when the equivalents of chromium and of nickel are used for the other alloying elements:

$$\begin{aligned}\text{Cr equivalent, castings} &= w_{\text{Cr}} + 2w_{\text{Si}} + 1.5w_{\text{Mo}} + 5w_{\text{V}} \\ \text{Ni equivalent, castings} &= w_{\text{Ni}} + w_{\text{Co}} + 0.5w_{\text{Mn}} + 30w_{\text{C}}\end{aligned}\quad (12.1)$$

$$\begin{aligned}\text{Cr equivalent, welds} &= w_{\text{Cr}} + 1.5w_{\text{Si}} + w_{\text{Mo}} + w_{\text{V}} + 3.5w_{\text{Ti}} \\ \text{Ni equivalent, welds} &= w_{\text{Ni}} + 0.5w_{\text{Mn}} + 30w_{\text{C}} + 30w_{\text{N}}\end{aligned}\quad (12.2)$$

The large influence of C and N relative to that of the metallic elements should be particularly noted. The diagram is very useful in determining whether a particular steel is likely to be fully austenitic at room temperature. This is relevant to bulk steels, but particularly to weld metal where it is frequently important to predict the structure in order to avoid weld defects and excessive localised corrosive attack.

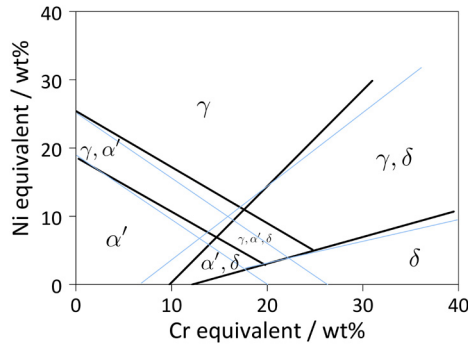


Figure 12.8 Domains plotting the expected microstructure at room temperature as a function of the chromium and nickel equivalents. The black lines are for castings and the blue for welds. For castings, the equivalent concentrations are given by Equation (12.1) whereas for welds by Equation (12.2). Adapted from Schneider [7] and Kakhovskii et al. [8]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this chapter.)

The differences apparent in Fig. 12.8 between the welded and cast steel forms of the Schaeffler diagram emphasise that thermal and size effects are not accounted for. Thus, the diagram developed originally for arc welding does not correctly estimate the structure for laser welds where the cooling rates can be much greater [6]. The diagrams should therefore be used as a rough guide rather than a rigorous tool.

12.3 CHROMIUM-RICH CARBIDE IN Cr-Ni AUSTENITIC STEELS

Simple austenitic steels usually contain between 18 and 30 wt% chromium, 8 to 20 wt% nickel and between 0.03 and 0.1 wt% carbon. The solubility limit of carbon is about 0.05 wt% at 800°C, rising to 0.5 wt% at 1100°C. Therefore, solution treatment between 1050°C and 1150°C will take all of the carbon into solution and rapid cooling from this temperature range will give a supersaturated austenite solid solution at room temperature. However, slow cooling or reheating within the range 550–800°C will lead to the rejection of carbon from solution, usually as the chromium-rich carbide, $M_{23}C_6$, even when the carbon content of the steel is very low (<0.05 wt%).

This carbide nucleates preferentially at the austenitic grain boundaries as faceted particles (Fig. 12.9) or often as complex dendritic arrays. While such precipitation can have an adverse effect on mechanical properties, in

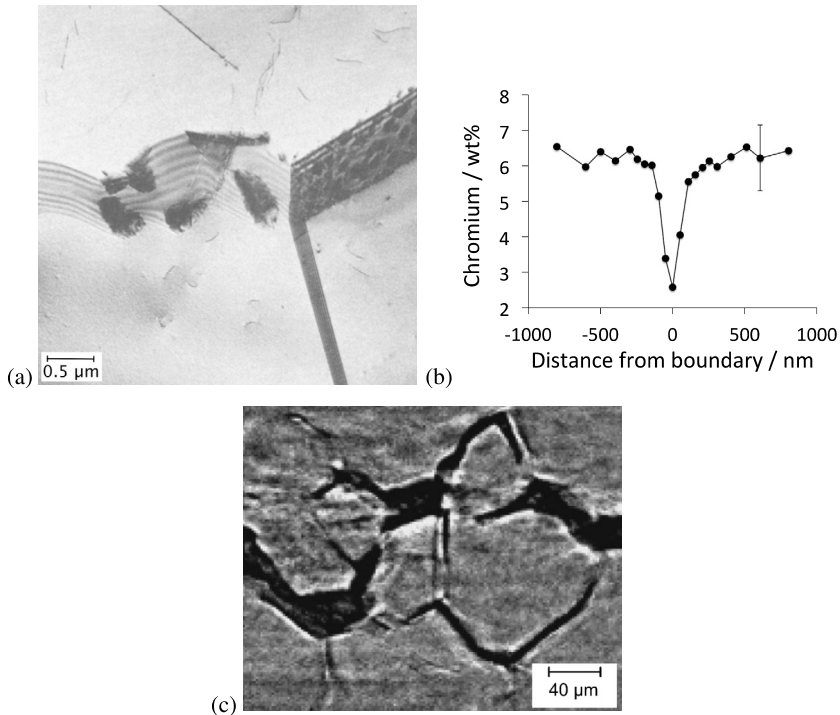


Figure 12.9 Grain boundary precipitation of $M_{23}C_6$ in 316L austenitic stainless steel heat treated at 700°C for 100 h. (a) The precipitation varies along all three of the boundaries shown. (b) A concentration profile across one of the boundaries with precipitates, showing the depletion of chromium in the vicinity of the boundary. Reproduced from Hall and Briant [13] with permission of Springer. (c) Intergranular stress-corrosion cracking in sensitised austenitic stainless steel. Reproduced from Jivkov et al. [12], with permission of Elsevier.

particular low-temperature ductility, the most significant result is the depletion of the regions adjacent to the grain boundaries with respect to chromium. This has been revealed directly by microprobe analysis. The surface oxide-film in these regions is thus depleted in chromium and as a result it becomes anodic with respect to its surroundings, so the steel is more prone to corrosive attack. Consequently, a classic form of intergranular corrosion is experienced which, in severe cases, can lead to disintegration of the steel, as illustrated in Fig. 12.9c. This type of corrosion is also experienced in martensitic chromium steels, e.g. 12 wt% Cr steel, in which grain boundary precipitation of $M_{23}C_6$ occurs as well. The corrosion-induced cracking is most potent at boundaries connecting grains that have a large

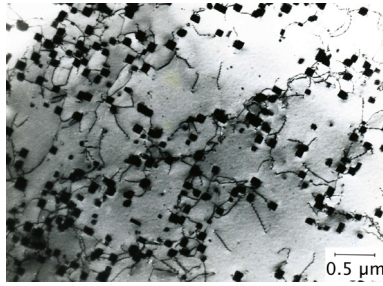


Figure 12.10 Precipitation of $M_{23}C_6$ on dislocations in a 18Cr-12Ni steel after 80 h at 700°C under stress (courtesy of Sully).

relative crystallographic-misorientation. Boundaries with good atomic fit between the grains have a lower energy per unit area and hence are not readily attacked. This has led to attempts at grain boundary engineering, in which specific crystallographic textures are introduced in order to increase the proportion of low-energy grain boundaries in the steel [9–11]. In the propagation of fracture, it is relevant to consider the connectivity of the most sensitive grain boundaries [12].

$M_{23}C_6$ can precipitate within the austenite grains, particularly at high supersaturations, on dislocations and on solute atom/vacancy clusters. Both the matrix and the carbide have cubic symmetry, and electron diffraction evidence from thin-foil specimens invariably gives the orientation relationship:

$$\{100\}_{M_{23}C_6} \parallel \{100\}_{\gamma} : \langle 010 \rangle_{M_{23}C_6} \parallel \langle 010 \rangle_{\gamma}.$$

The lattice parameter of $M_{23}C_6$ is approximately three times that of austenite, so the electron diffraction patterns are readily identified. The particles usually develop a polyhedral habit, but occasionally in steels deformed at elevated temperatures a more regular cubic morphology is displayed (Fig. 12.10). As the critical temperature range for chromium carbide nucleation and growth is between 500°C and 850°C, any process which allows the steel to pass slowly through this temperature range will render it sensitive to intergranular corrosion in service. Welding, in particular, provides these conditions in the heat affected zone leading to localised attack in certain chemical media. It is, therefore, important to have information about the reaction kinetics for the formation of $M_{23}C_6$. Being a typical nucleation and growth process, the time-temperature-transformation curve is typically C-shaped with the nose at about 750°C (Fig. 12.11). For some steel compositions the minimum time for the formation of $M_{23}C_6$ sufficient to give

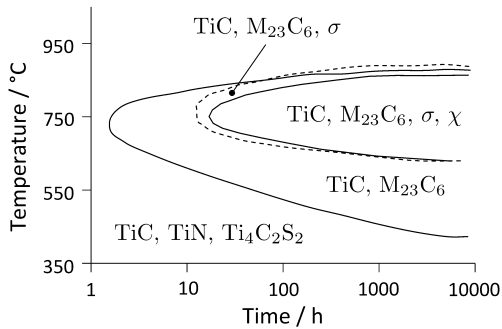


Figure 12.11 Time-temperature-precipitation diagram for 316 TM stainless steel, solution treated and aged as a function of time and temperature. σ -phase is typically an intermetallic compound FeCr but may contain other solutes such as Mo. The χ -phase is another such compound but with a different crystal structure (after Grot and Suruiell [14], with permission of Springer).

subsequent intergranular corrosion, i.e. time to achieve *sensitisation*, is as short as 100 s. Several ways of reducing or eliminating the formation of $M_{23}C_6$ are available. The term *stabilisation* is used to describe these processes:

1. Solution treatment: after welding, the steel can be reheated to 950–1100°C to allow $M_{23}C_6$ to redissolve, and further precipitation is then prevented by rapid cooling to avoid the C-shaped curve.
2. Reduction of the carbon content: this can be reduced below 0.03 wt% by modern steel-making methods involving oxygen lancing. For complete immunity from intergranular corrosion in 18–8 steels, a carbon level of 0.02 wt% should not be exceeded.
3. Control of $M_{23}C_6$ reaction kinetics: addition of molybdenum to Cr/Ni stainless steels markedly lengthens the sensitisation time. An increase in nickel content has an adverse effect, while increasing chromium has a beneficial effect.
4. Use of strong carbide-forming elements, niobium and titanium form carbides which are much more stable than $M_{23}C_6$, so they preferentially combine with the available carbon and thus lessen the opportunity for $M_{23}C_6$ to nucleate.
5. Introduce a crystallographic texture such that there is a large fraction of low-energy grain boundaries in the steel.

12.4 PRECIPITATION OF NIOBIUM AND TITANIUM CARBIDES

In normal practice, sufficient niobium or titanium is added to the steel to combine with all the carbon, the stoichiometric ratios being:

	Ti:C	Nb:C
Atomic weights	48:12	93:12
Ratios	4:1	8:1

However, the additions are in excess of these proportions to allow for some solid solution of Ti or Nb, and for combination with any nitrogen which may be present. Titanium and niobium carbides are much less soluble in austenite than is chromium carbide, so they will form at much higher temperatures as relatively stable particles. These should remain relatively inert during commercial heat treatments involving solution temperatures no higher than 1050°C, and thus minimise the possible nucleation of $M_{23}C_6$. However, TiC and NbC have some solubility in austenite at 1050°C and can subsequently precipitate at lower temperatures. During high-temperature processes such as welding, these carbides dissolve to a greater extent in austenite and can then reprecipitate at lower temperatures. Therefore, NbC and TiC will not always form inert dispersions, and are often likely to be redistributed by heat treatment. They do, however, have the great advantage of not depleting the matrix of chromium, particularly at sensitive areas such as grain boundaries. The ability to form dispersions of NbC and TiC has a further advantage in that these dispersions can remain very fine at temperatures in the range 500–750°C, and so provide a means of dispersion strengthening austenitic steels to achieve greater strength in this temperature range. The development of creep-resistant austenitic steels owes much to the properties of these carbide dispersions.

The formation of NbC and TiC in austenite is most conveniently studied by subjecting the steel to high-temperature solution treatment (1100–1300°C), followed by rapid cooling to room temperature. On subsequent ageing in the range 650–850°C precipitation takes place. The carbides are both fcc of the NaCl crystal type with lattice parameters within 2–3% of each other, but differing from that of austenite by 20–25%. They both exist over a range of stoichiometry $MC_{0.6}$ – $MC_{1.0}$. Precipitation in each case occurs in several different ways.

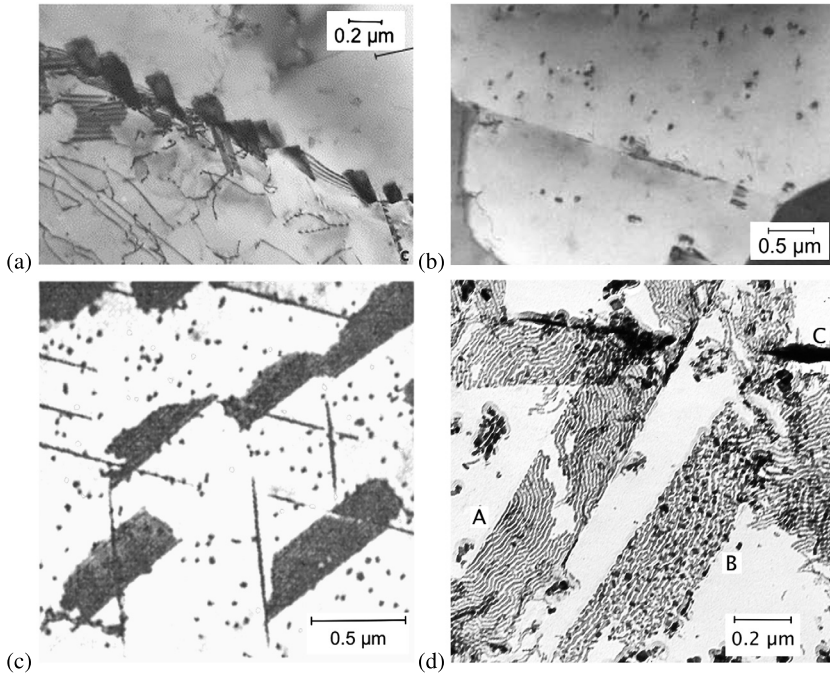


Figure 12.12 Different modes of precipitation in austenitic stainless steel. (a) Grain boundary precipitation of $M_{23}C_6$ in a 304 stainless steel containing 0.05 wt% carbon, following ageing at 670°C for 50 h (after Trillo and Murr [15], with permission from Elsevier). (b) Intragranular TiC precipitation in 326 TiM stainless steel following ageing at 750°C for 20 h (after Grot and Suruiell [14], with permission of Springer). (c) TaC precipitates in Fe-18Cr-12Ni-2Ta-0.1C wt% aged at 700°C for 25 h (Froes). (d) NbN precipitation in association with stacking faults (A, B) and $M_6\text{N}$ at 'C' in Fe-18Cr-12Ni-1.25Nb-0.04N aged at 700°C for 500 h (courtesy of Borland).

Grain boundary:

Grain boundaries are preferred sites, but because chromium diffuses more rapidly in austenite than does Nb or Ti, $M_{23}C_6$ usually forms first (Fig. 12.12a). This emphasises that NbC or TiC should not be taken into solution if full stabilisation is to be achieved. In Fig. 12.12, TTT curves for $M_{23}C_6$ and (NbTi)C illustrate that, at lower temperatures and shorter times, the chromium carbide forms first, but at longer times it can redissolve and be replaced by (NbTi)C.

Dislocations:

NbC and TiC nucleate extensively on dislocations (Fig. 12.10), an important mechanism relevant to the precipitation of equilibrium phases which

have not been preceded by GP zone formation. It should also be noted that a significant part of the creep resistance of this group of alloys arises from nucleation of alloy carbides on dislocations generated by deformation at elevated temperatures (e.g. Fig. 12.10). The carbides always have a cube-cube Widmanstätten orientation relationship with the matrix, as do other MC carbides such as VC, TaC. Since the lattice parameter of austenite is 20–25% less than that of the carbides, a flux of vacancies into the precipitates is needed to reduce internal stresses resulting from growth of the particles. Only a few of these vacancies can be quenched in, so carbide particles will grow most readily in situations where further vacancies are generated, e.g. at dislocations or boundaries.

Precipitation in association with stacking faults:

It is often the case that NbC, TaC and TiC precipitate on $\{111\}_\gamma$ plates as thin discs which exhibit stacking fault contrast in thin foils in the electron microscope (Fig. 12.12). These discs grow very substantially on ageing, e.g. at 700°C. Analysis has shown that the discs are formed by the climb of partial dislocations (Frank type), which by climbing generate a continuous source of vacancies. The (NbTi)C precipitate particles nucleate on the partial dislocations and make use of the vacancies in growing, a process which is repeated many times as the partial dislocation escapes from the rows of particles it has nucleated. The final result is a pseudo-Widmanstätten array of discs on $\{111\}_\gamma$ planes, which contain very fine dispersions of (NbTi)C. This complex precipitate morphology can occur side by side with normal nucleation on undissociated dislocations.

Matrix precipitation:

Random precipitation of (NbTi)C in the matrix, not on dislocations, is occasionally observed, but it is the rarest morphology encountered. The particles still exhibit the cube-cube orientation relationship with the matrix, and are apparently nucleated on solute atom/vacancy clusters. Consequently, they are only obtained after heat treatments which result in high supersaturations of vacancies in the austenite matrix, i.e. very high solution temperatures and rapid quenching (Fig. 12.12b). However, there is some evidence that certain elements, e.g. phosphorus, encourage this type of precipitation by trapping vacancies, the phosphorus atoms being 20% smaller than the other atoms in the austenite solid solution, and so cause localised strain fields.

The carbide morphologies have been presented in decreasing order of occurrence. The evidence suggests that this order is dictated by increasing degree of supersaturation, which is a function of the solution temperature. In practice, high solution temperatures can usually be avoided, except in welding, so grain boundary precipitation and dislocation precipitation are the dominant mechanisms observed.

12.5 NITRIDES IN AUSTENITIC STEELS

In simple austenitic steels the role of nitrogen is largely that of a solid solution strengthening element, although it can replace carbon in $M_{23}C_6$. While higher nitrogen concentrations can be maintained without deleterious precipitation than is the case with carbon, in steels with 0.2–0.3 wt% N, Cr_2N can precipitate at grain boundaries, and also within the grains. Exposure of austenitic steels to air at temperatures greater than 600°C can lead to very high (>1 wt%) nitrogen concentrations under the oxide layer, with coarse Cr_2N matrix precipitation, as well as discontinuous lamellar precipitation at grain boundaries. Such regions often lead to cracks under creep conditions.

In the presence of Nb or Ti, more stable nitrides of these elements are formed, which are much less soluble in austenite than Cr_2N . TiN and NbN, isomorphous with the corresponding carbides, have been identified, and also M_6N which can eventually replace NbN during ageing (Fig. 12.12d). These phases can precipitate in the range 650–850°C after rapid cooling from high solution temperatures. They may, therefore, occur as a result of welding or in alloys subject to creep conditions at high temperatures. The modes of nucleation of these nitride phases are similar to those of the corresponding carbides, although there are morphological differences.

12.6 INTERMETALLIC PRECIPITATION IN AUSTENITE

Austenitic steels, as a class, possess relatively modest mechanical properties, which are largely outweighed by their excellent corrosion resistance in many media. However, it is often desirable to develop higher-strength alloys, particularly for use at elevated temperatures where deformation by creep needs to be minimised. Carbide dispersions offer one solution, but the volume fraction of precipitate is limited by solubility considerations and

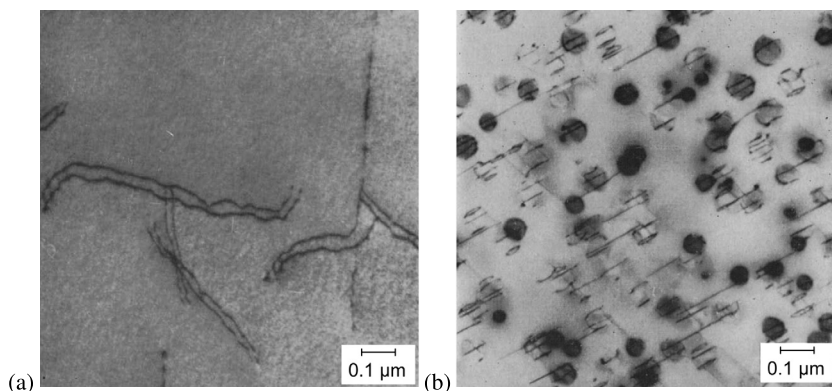


Figure 12.13 Fe-24Ni-17Cr-2Ti wt%. (a) Superdislocations penetrating fine γ' particles, in a sample aged at 675°C for 20 h. (b) Dislocation loops around coarsened γ' precipitates in a sample aged at 775°C for 75 h. After Singhal and Martin [16], reproduced with permission of Elsevier.

there are also problems associated with high-temperature ductility and the stability of the dispersions.

The highly alloyed matrices of many austenitic alloys have allowed the development of intermetallic phases as suitable dispersions to achieve high temperature strength. The most important of these phases is the γ' fcc phase $\text{Ni}_3(\text{AlTi})$ first found in nickel-base alloys, with an fcc matrix analogous to austenite, containing titanium and aluminium which can replace each other in the precipitate. The γ' precipitate is obtained in stable austenitic steels, e.g. 20Cr25Ni with an (Al + Ti) content of 1–5 wt% by quenching from a solution temperature of 1100–1250°C, and ageing in the range 700–800°C. The dispersion developed in this way has two important advantages. Firstly, the precipitate particles have the cubic crystal structure similar to that of the matrix with which they have a cube-cube orientation relationship. Moreover, the lattice parameters are similar, so that the interfaces between precipitate and matrix are coherent, and therefore, of low energy. The familiar Lifshitz-Wagner Equation (9.6) shows that the coarsening rate is directly related to the interfacial energy. Secondly, this type of reaction allows a large volume fraction (0.3–0.5) of precipitate particles to be achieved, the particles being strong, but not catastrophically brittle, cf. sigma phase.

The γ' precipitate normally observed in austenite is spherical when the precipitate is very fine (Fig. 12.13a), and indeed there is evidence for the formation of pre-precipitation spherical zones. However, on prolonged

ageing at 750°C, the γ' particles gradually adopt a more complex morphology as they lose coherency with the austenitic matrix (Fig. 12.13b). By varying the ratio of Ti to Al in γ' the coarsening characteristics can be substantially modified. Addition of Al to γ' Ni₃Ti decreases the lattice parameter from about 3.590 Å for 25Ni-15Cr wt%, resulting in greater stability of the precipitate. However, complete replacement of titanium lowers the γ' parameter to 3.559 Å, which results in an increase in mismatch parameter. This helps to explain why an (Al + Ti) content of 1–1.5 wt% Al and 3–3.5 wt% Ti was found to be optimum for high-strength austenitic steels, resistant to coarsening.

The γ' phase is not the equilibrium phase in austenitic steels with Al and Ti. It is replaced eventually by a coarsely dispersed hexagonal phase η (Ni₃Ti) in titanium-containing steels. In steels with a high Al/Ti ratio, the equilibrium intermetallic phase is body-centred cubic β NiAl. Both these phases coarsen excessively, and are undesirable constituents of the microstructure in austenitic creep-resistant alloys.

While a number of other intermetallic phases have been observed in austenitic steels, mention will be made only of sigma phase (σ), as it usually has a catastrophic influence on mechanical properties at room temperature. The phase, which has a tetragonal lattice with parameters 0.8799 and 0.4544 nm [18] dependent on composition, occurs in the binary Fe-Cr system over a wide composition range between 25 and 60 wt% Cr. In CrNi austenitic steel, σ formation is encouraged when the Cr content exceeds 17 wt%, but is discouraged by increasing the nickel content. The phase forms at austenite grain boundaries and requires, for full development, long-term ageing (up to 1500 h) at 750°C. However, in some circumstances, σ has been detected in 25Cr-20Ni steels after 70 h at this temperature. The presence of ferrite in the austenite greatly accelerates the formation of sigma, which has been shown to nucleate at the γ/α boundaries (Fig. 12.14). The ferrite, being richer in chromium, tends to be preferentially absorbed during the growth of sigma phase. Elements such as Mo and Ti achieve a further acceleration of sigma formation, e.g. in an 18Cr-8Ni-3Mo-1Ti wt% steel, the σ -phase can be formed after only 30 min at 870°C.

12.7 AUSTENITIC STEELS IN PRACTICAL APPLICATIONS

The commonest austenitic steel is the so-called 18-8 containing around 18 wt% Cr and 8 wt% Ni. It has the lowest nickel content concomitant

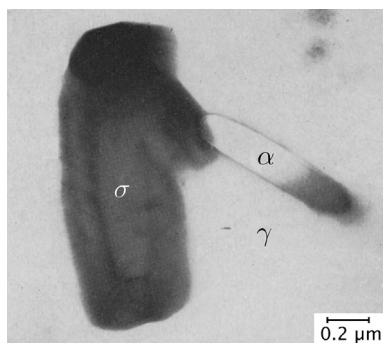


Figure 12.14 Nucleation of sigma phase (σ) at an α/γ interface in a Fe-24Ni-25Cr-0.5Ti wt% stainless steel aged from the austenitic condition at 750°C for 1500 h. After Singhal and Martin [17], reproduced with permission of Elsevier.

Table 12.1 Chemical compositions (wt%) of some austenitic stainless steels

Element	Numerical designation of steel type						
	301	302	304	310	316	321	347
C	0.15 max	0.08 max	0.08 max	0.25 max	0.08 max	0.08 max	0.08 max
N	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Cr	16–18	17–19	18–20	24–26	16–18	17–19	17–19
Ni	6–8	8–10	8–12	19–22	10–14	9–12	9–13
Mo					2–4		
Ti						5 × C	
Nb							10 × C
Mn	1.5	1.5	1.5	1.5	1.5	1.5	1.5

with a fully austenitic structure. However, in some circumstances, e.g. after deformation, or if the carbon content is very low, it may transform partially to martensite at room temperature. Several of the most familiar austenitic steel specifications are given in Table 12.1.

Greater stability towards the formation of martensite is achieved by increasing the nickel content, as illustrated in the 301 to 310 types of steel in Table 12.1. The 18–8 stainless steel owes its wide application to its excellent general resistance to corrosive environments. However, this is substantially improved by increasing the nickel content, and increasing the chromium gives greater resistance to intergranular corrosion. Austenitic steels are prone to *stress corrosion cracking*, particularly in the presence of chloride ions where a few p.p.m. can sometimes prove disastrous. This is a

type of failure which occurs in some corrosive environments under small stresses, either deliberately applied or as a result of residual stresses in fabricated material. In austenitic steels it occurs as transgranular cracks which are most easily developed in hot chloride solutions. Stress corrosion cracking is substantially reduced in high nickel austenitic alloys.

Type 316 steel contains 2–4 wt% molybdenum, which gives a substantial improvement in general corrosion resistance, particularly in resistance to *pitting corrosion*, which can be defined as local penetrations of the corrosion-resistant films and which occurs typically in chloride solutions. Recently, some resistant grades with as much as 6.5 wt% Mo have been developed, but the chromium must be changed to 20 wt% and the nickel to 24 wt% to maintain an austenitic structure. Alloys like these are sometimes known as the *superaustenitic* stainless steels.

Corrosion along the grain boundaries can be a serious problem, particularly when a high-temperature treatment such as welding allows precipitation of $M_{23}C_6$ in these regions. This type of intergranular corrosion is sometimes referred to as *weld-decay* [19]. To combat this effect some grades of austenitic steel, e.g. 304 and 316, are made with carbon contents of less than 0.03 wt% and designated 304 L and 316 L. Alternatively, niobium or titanium is added in excess of the stoichiometric amount to combine with carbon, as in types 321 and 347.

The austenitic steels so far referred to are not particularly strong or ductile materials as illustrated on Fig. 12.3. Typically their 0.2% proof strength is about 250 MPa and the tensile strength between 500 and 600 MPa, showing that these steels have substantial capacity for work hardening, which makes working more difficult than in the case of mild steel. It is the other properties of stainless steels, particularly corrosion resistance, that make them so useful.

12.8 OXIDATION RESISTANT STAINLESS STEEL

The Cr/Ni austenitic steels are resistant to high-temperature oxidation because of the protective surface film, but the usual grades have low strengths at elevated temperatures. Those steels stabilised with Ti and Nb, types 321 and 347, can be heat treated to produce a fine dispersion of TiC or NbC which interacts with dislocations generated during creep. One of the most commonly used alloys is 25Cr–20Ni with additions of titanium or niobium which possesses good creep strength at temperatures as high as 700°C.

Table 12.2 Strengthening of austenitic steels at room temperature

Element	Designation of steel					
	304(N)	347(N)	A286	212	IN744	Experimental
C	0.06	0.08	0.05	0.08	0.05	
N	0.20	0.20				
Cr	18.0	18.0	15.0	13.5	26.0	14
Ni	10.0	11.0	26.0	26.0	6.5	32
Mo			1.2	1.75		
Ti			2.0	3.0	0.3	0.98
Nb		10 × C				2.88
Al			0.15	0.15		4.00
V			0.30			
0.2% Proof stress / MPa	340	415	700	920	570	
Tensile strength / MPa	695	710	1000	1300	740	
% Elongation	46	39	25.0 ^a	23.0 ^b	24	

(N) represents high nitrogen.

^a Aged at 750°C.

^b Aged at 700°C.

To achieve the best high-temperature creep properties, it is necessary first to raise the room-temperature strength to higher levels. This can be done by precipitation hardening heat treatments on steels of suitable composition to allow the precipitation of intermetallic phases, in particular Ni₃(Al Ti). In Table 12.2 the room-temperature strength of two alloys in this category (A286 and Unitemp 212) after ageing at 700–750°C is compared with that of the simpler standard austenitic alloys, e.g. 304. It can be seen that the strength is more than doubled by the precipitation reaction.

Table 12.2 shows an experimental stainless alloy intended for applications in the temperature range 600–900°C where a protective alumina layer forms to protect the steel against further oxidation, especially in the presence of water vapour [20]. The alloy is strengthened primarily by Ni₃Al γ' precipitates but because of the chemical composition rich in niobium, Fe₂Nb Laves phase also forms in addition to some NiAl.¹ However, the primary strengthening mechanism at high temperatures is through the fine γ' particles (Fig. 12.15) which provide for exceptional creep resistance suitable for high steam temperatures in power plant. One of the problems associated with the application of austenitic stainless steels in such circumstances is the

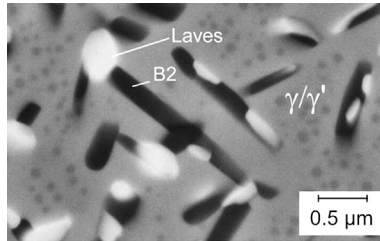


Figure 12.15 The microstructure of the austenitic stainless alloy listed as ‘experimental’ in Table 12.2 following ageing at 750°C for 2000 h. The Laves phase is Fe_2Nb and ‘B2’ is NiAl . After Yamamoto et al. [20], reproduced with the permission of Elsevier.

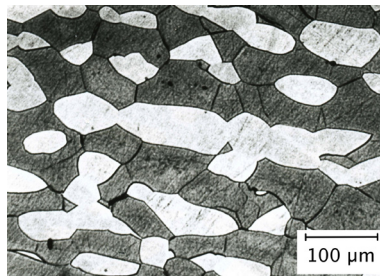


Figure 12.16 Duplex stainless steel with the lighter regions corresponding to austenite and with ferrite in the remaining microstructure. Taken from Fe-22Cr-6Ni-2Mn-0.5Si-3Mo-0.14N-0.03C wt% steel, heat treated to 1200°C and water quenched (courtesy of S. Sharafi).

high thermal expansion coefficient and low thermal conductivity, which can combine to give poor thermal fatigue resistance unless the components concerned are not subjected to significant thermal cycling and are used in thin sections.

12.9 DUPLEX AND FERRITIC STAINLESS STEELS

In Section 12.2, the importance of controlling the γ -loop in achieving stable austenitic steels was emphasised. Between the austenite and δ -ferrite phase fields there is a restricted ($\alpha + \gamma$) region which can be used to obtain two-phase or duplex structures in stainless steels (Fig. 12.16). The structures are produced by having the correct balance between the α -forming elements (Mo, Ti, Nb, Si, Al) and the γ -forming elements (Ni, Mn, C and N). To achieve a duplex structure, it normally is necessary to increase the chromium content to above 20 wt%. However, the exact proportions

Table 12.3 Typical compositions (wt%) of some ferritic stainless steels

Element	Type 409L	Type 430	Type 446	Type 18/2
C	<0.03	0.06	0.08	0.02
Cr	11	17.0	25.0	18.0
Mo				2.0
Mn	1.0	1.0	1.5	
Si	1.0	1.0	1.0	
Ti	$6 \times w_C$			
N				0.25

of α and γ are determined by the heat treatment. It is clear from consideration of the γ -loop section of the equilibrium diagram, that holding in the range 1000–1300°C will cause the ferrite content to vary over wide limits. The usual treatment is carried out between 1050°C and 1150°C, when the ferrite content is not sensitive to the subsequent cooling rate.

The duplex steels are stronger than the simple austenitic steels, partly as a result of the two-phase structure and also because this leads normally to a refinement of the grain size. Indeed, by suitable thermomechanical treatment between 900°C and 1000°C, it is possible to obtain very fine microduplex structures which can exhibit super-plasticity, i.e. very high ductilities at high temperatures, for strain rates less than a critical value. A typical composition, IN744, is shown in Table 12.2 with the mechanical properties at room temperature.

A further advantage is that duplex stainless steels are resistant to *solidification cracking*, particularly that associated with welding. While the presence of δ -ferrite may have an adverse effect on corrosion resistance in some circumstances, it does improve the resistance of the steel to transgranular stress corrosion cracking as the ferrite phase is immune to this type of failure.

The super-duplex stainless steels have even better corrosion resistance than the duplex stainless steels. They are particularly superior in their resistance to localised pitting corrosion, because of their larger concentrations of chromium, molybdenum and nitrogen. To maintain the balanced ferrite/austenite microstructure, it is necessary to also boost the concentration of austenite stabilising elements such as nickel. Super-duplex stainless steels, therefore, typically contain 27Cr–7Ni–4Mo–0.3N wt%.

There is another important group of stainless steels which are essentially ferritic in structure. They contain between 10 and 30 wt% chromium and, by dispensing with the austenite stabilising element nickel, possess consider-

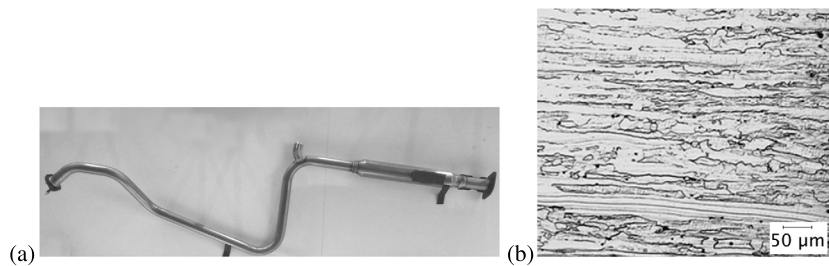


Figure 12.17 (a) An exhaust pipe for an automobile, made using type 409L ferritic stainless steel. (b) The ferritic microstructure in the hot-rolled condition. Micrograph from Ahn et al. [21], reproduced with permission of Elsevier.

able economic advantage. These steels, particularly at the higher chromium levels, have excellent corrosion resistance in many environments and are completely free from stress corrosion. Typical compositions are shown in Table 12.3. For some applications, such as the exhaust system of a car, the chromium concentration can be limited (e.g., type 409L, Table 12.3) because this provides sufficient corrosion and oxidation resistance while at the same time making the alloy formable; ferrite also has a much lower thermal expansion coefficient than austenite, so that fatigue induced by temperature variation can be mitigated, Fig. 12.17.

These steels do have some limitations, particularly those with higher chromium contents, where there can be a marked tendency to embrittlement. This arises partly from the interstitial elements carbon and nitrogen, e.g. a 25 wt% Cr steel will normally be brittle at room temperature if the carbon content exceeds 0.03 wt%. An additional factor is that the absence of a phase change makes it more difficult to refine the ferrite grain size, which can become coarse after high-temperature treatment such as welding (Fig. 12.18). This raises still further the ductile/brittle transition temperature, already high as a result of the presence of interstitial elements. Fortunately, modern steel-making methods such as argon-oxygen refining can bring the interstitial contents below 0.03 wt%, while electron beam vacuum melting can do better still.

The ferritic stainless steels are somewhat stronger than austenitic stainless steels, the yield stresses being in the range 300–400 MPa, but they work harden less so the tensile strengths are similar, being between 500 and 600 MPa. However, ferritic stainless steels, in general, are not as readily deep drawn as austenitic alloys because of the overall lower ductility. How-

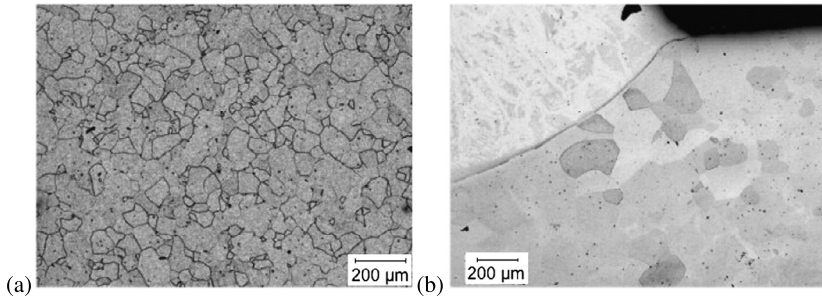


Figure 12.18 Welding-induced grain growth in a ferritic stainless steel of composition Fe-0.015C-17.6Cr-0.2Ni-1.9Mo-0.16Nb wt%. (a) The fine grain structure of the plate. (b) Very coarse ferrite grains in the heat-affected zone of the plate following welding. After Silva et al. [22], with permission of Elsevier.

ever, they are suitable for other deformation processes such as spinning and cold forging.

Welding causes problems due to excessive grain growth in the heat-affected zone but, recently, new low-interstitial alloys containing titanium or niobium have been shown to be readily weldable. The higher chromium ferritic alloys have excellent corrosion resistance, particularly if 1–2 wt% molybdenum is present.

There are two phenomena which may adversely affect the behaviour of ferritic stainless steels. Firstly, chromium-rich ferrites when heated between 400°C and 500°C develop a type of embrittlement, typically known as the 475°C embrittlement. The most likely cause is the precipitation of a fine coherent chromium-rich phase (bcc α') arising from the miscibility gap in the Fe-Cr system (Fig. 12.4), probably by a spinodal type of decomposition involving $\alpha \rightarrow \alpha_{\text{Fe}} + \alpha_{\text{Cr}}$ where the subscripts denote the dominant solute in the separated regions. This phenomenon becomes more pronounced with increasing chromium content. Fig. 12.19 illustrates the phenomenon for an exceptionally rich Fe-38.8Cr wt% alloy that is aged at 475°C. The decrease in toughness is dramatic and in a much shorter time than can be explained simply on the basis of hardness changes due to the decomposition of the solid solution. It is likely that the temperature sensitivity of the flow stress increases during ageing, leading to an elevation of the impact transition temperature. Prolonged ageing leads to the formation of σ -phase, the precipitation rate of which increases with the chromium concentration. As in austenite, the presence of sigma phase can lead to marked embrittlement.

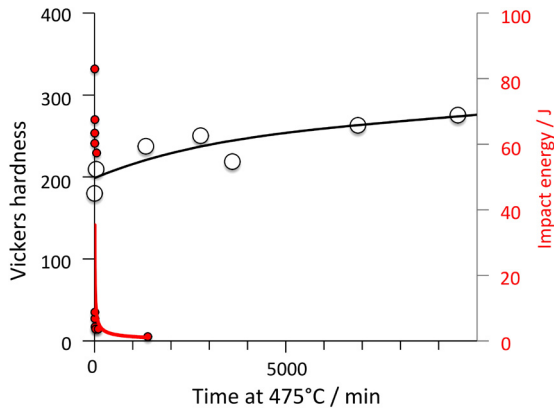


Figure 12.19 Hardness and impact toughness of a Fe-38.8Cr wt% alloy quenched and then aged at 475°C for the period indicated. Selected data from Cortie and Pollak [23].

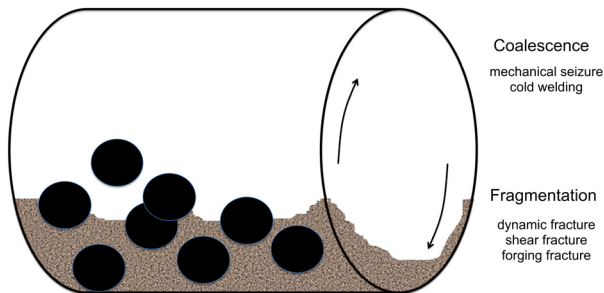


Figure 12.20 Schematic illustration of the mechanical alloying process. The powder consisting of elemental iron, other elemental alloying additions, and yttria powder are placed in a ball mill containing cast-iron balls. The rotation of the mill causes the powders to undergo repeated welding and fragmentation, leading to mechanical mixing.

12.10 MECHANICALLY ALLOYED STAINLESS STEELS

Mechanical alloying is a process in which mixtures of fine powders consisting of elemental metals or master alloys are changed into solid solutions, apparently without any melting, Fig. 12.20. The powders are forced to collide with each other and with much larger, hardened steel balls whilst contained in a ball mill. The collisions are energetic, involve large contact pressures and lead eventually to the formation of an intimate solid solution [24,25]. Refractory oxides, commonly yttrium oxide, can be dispersed into the mechanically alloyed powder in order to obtain dispersion strengthening. The mechanically alloyed powder is finally extruded to form full density bulk samples in rod, sheet or other useful shapes.

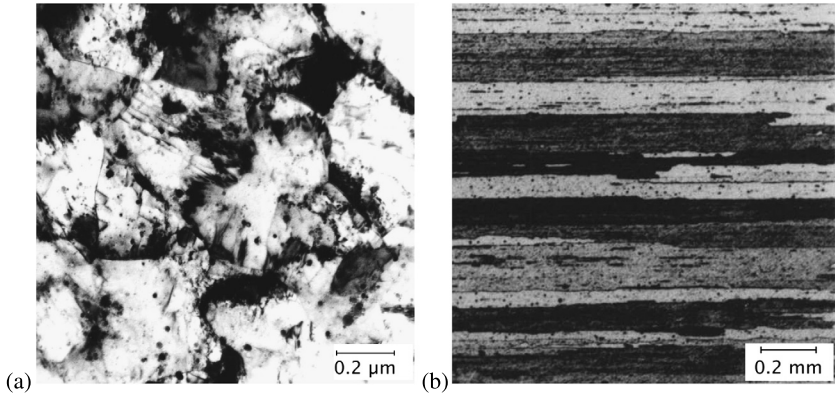


Figure 12.21 (a) Transmission electron micrograph of a mechanically alloyed steel prior to recrystallisation, showing the fine grained microstructure. (b) Light micrograph illustrating the elongated recrystallised grain structure.

After consolidation by extrusion, the alloys are usually hard and possess an extremely small grain size, typically a fraction of a micrometre (Fig. 12.21a). With one exception (Chapter 15), such a small grain size is impossible to achieve by any other process for bulk samples. The material is usually extremely hard in the as-consolidated state, and has to be softened before further fabrication. The grain boundary area locked into the material gives it a large stored energy, which under suitable heat-treatment conditions triggers recrystallisation into a much coarser grain structure. If annealing is carried out by passing the sample through a hot zone (zone annealing), then the recrystallisation front is localised within the high-temperature region. The front then advances at the same rate as the sample, thereby leading to *directional recrystallisation* in which the microstructure consists of huge columnar grains parallel to the zone annealing direction (Fig. 12.21b). It resembles sometimes the microstructure obtained during directional solidification. The columnar grains are highly anisotropic, usually restricted only by the size of the sample, and can reach lengths in excess of a metre. In some instances, even isothermal annealing can lead to the development of columnar recrystallised grains. The yttria particles introduced during mechanical alloying are not isotropically dispersed, but tend to align parallel to the extrusion direction [26]. Consequently, anisotropic grain boundary pinning leads to the columnar grain growth during recrystallisation. The grain structure can be manipulated by appropriate processing as illustrated in Fig. 12.22.

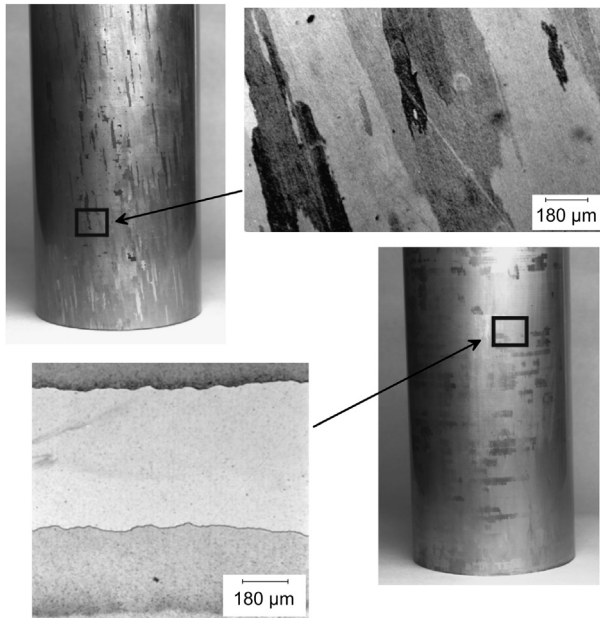


Figure 12.22 Torsion extruded tubes of mechanically alloyed yttria dispersed stainless steel. Heat treatment can then lead to the twisted grain structure along the tube axis, or a circumferential structure depending on the extrusion conditions. Courtesy of C. Garcia Capdevila.

Table 12.4 Chemical compositions of mechanically alloyed oxide dispersion strengthened stainless steels (wt%)

C	Cr	Al	Ti	Mo	Y ₂ O ₃
0.01	20	4.5	0.5	—	0.5
0.01	14	—	1.0	0.3	0.27

There are two kinds of mechanically alloyed ferritic stainless steels available commercially, with many other varieties under development for the fusion reactor programme (Table 12.4). The alloy with the largest aluminium and chromium concentrations naturally has a better oxidation resistance. Its oxide content permits its use as a creep-resistant material to temperatures in excess of 1000°C, whereas normal ferritic steels are not used when the service temperature exceeds about 600°C.

The ferritic state helps make the steels less susceptible to radiation induced swelling. The lower chromium alloys (also without aluminium) are

therefore designed for nuclear reactor applications. The significant titanium concentration, in the absence of carbon, leads to the precipitation of a bcc-FeCrTiMo intermetallic compound (χ -phase) during ageing at around 800°C. This can further boost the creep strength.

12.11 TRANSFORMATION OF METASTABLE AUSTENITE

Some austenitic steels are often close to transformation, in that the M_S temperature may be just below room temperature. This is certainly true for low-carbon 18Cr8Ni austenitic steel, which can undergo a martensitic transformation by cooling in liquid nitrogen or by less severe refrigeration. The application of plastic deformation at room temperature can lead to formation of martensite in metastable austenitic steels, a transformation of particular significance when working operations are contemplated. The increase in M_S by cold work is specified by an M_S^σ temperature below which transformation to martensite occurs when the steel stressed (Fig. 5.23).² In general, the higher the alloying element content the lower the M_S and M_S^σ temperatures, and it is possible to obtain an approximate M_S temperature using empirical equations.

The martensite formed in Cr-Ni austenitic steels either by refrigeration or by plastic deformation is similar to that obtained in related steels possessing an M_S above room temperature.

Manganese can be substituted for nickel in austenitic steels, but the Cr-Mn solid solution then has a much lower stacking fault energy. This means that the fcc solid solution is energetically closer to an alternative close-packed hexagonal structure, and that the dislocations will tend to dissociate to form broader stacking faults than is the case with Cr-Ni austenites. In these circumstances, the martensite which forms first is hexagonal in structure (ϵ -martensite), with a habit plane $\{0001\}_\epsilon$ parallel to the stacking fault plane $\{111\}_\gamma$ (Fig. 12.23). This phase has been shown to nucleate on stacking faults in which the volume decrease associated with the fcc $\rightarrow$ hcp change is directed normal to the fault plane [29,30], with the following orientation relationship with austenite:

$$\begin{aligned}\{0001\}_\epsilon &\parallel \{111\}_\gamma, \\ \langle 11\bar{2}0 \rangle_\epsilon &\parallel \langle 1\bar{1}0 \rangle_\gamma.\end{aligned}$$

This type of martensite forms as parallel-sided plates which can be easily confused with annealing twins, common in fcc matrices with low stacking fault energies. Frequently α' martensite eventually forms, nucleating at the interface between ϵ and the austenitic matrix.

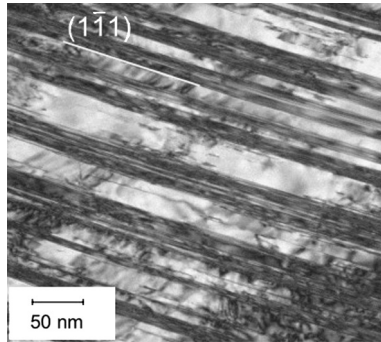


Figure 12.23 The bands, present in a deformed austenitic stainless steel, consist of a mixture of ε -martensite and mechanical twins, as verified using electron diffraction. After Ullrich et al. [31], reproduced with permission of Elsevier.

Manganese on its own can stabilise austenite at room temperature provided sufficient carbon is in solid solution. The best example of this type of alloy is the Hadfield manganese steel with 12 Mn–1.2C wt% which exists in the austenitic condition at room temperature and even after extensive deformation does not form martensite. However, if the carbon content is lowered to 0.8 wt%, then $M_s^{\alpha'}$ is above room temperature and transformation is possible in the absence of deformation at 77 K. Both ε and α' martensites have been detected in manganese steels. Alloys of the Hadfield type have long been used in wear resistance applications, e.g. grinding balls, railway points, excavating shovels, and it has often been assumed that partial transformation to martensite was responsible for the excellent wear resistance and toughness required. However, it is likely that the substantial work-hardening characteristics of the austenitic matrix are more significant in this case.

In general, fcc metals exhibit higher work-hardening rates than bcc metals because of the more stable dislocation interactions possible in the fcc structure. This results in the broad distinction between the higher work hardening of austenitic steels and the lower rate of ferritic steels, particularly well exemplified by a comparison of ferritic stainless steels with austenitic stainless steels. Within the austenitic category, however, there are two factors which influence the extent of work hardening:

- (a) the stacking fault energy of the matrix, determined by the composition;
- (b) the stability of the matrix.

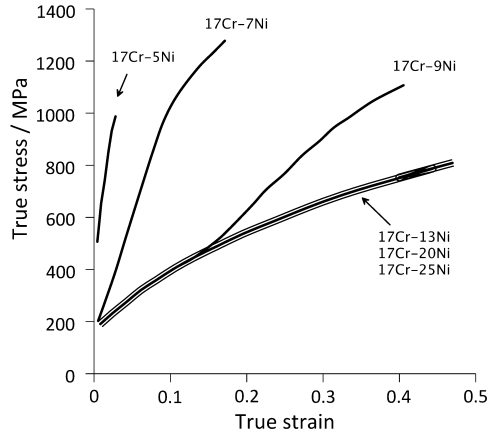


Figure 12.24 Effect of decreasing nickel content on the stress-strain curves of stainless steels (data from Pickering [32]).

The chromium nickel austenitic steels have stacking fault energies in the range $5\text{--}60\text{ mJ m}^{-2}$, and it would be expected that the highest nickel alloys would show the lowest work hardening as nickel is one of the elements that raises the stacking fault energy of austenite. The elements Cr, Mn, Co, Si, C and N tend to lower the stacking fault energy of austenite. This can be deduced from the greater tendency for annealing twins to occur in austenites rich in these elements. Plastic deformation of such solid solutions not only produces stable dislocation interactions but after heavy deformation, many fine deformation twins are introduced into the microstructure. Both of these factors contribute to the high flow stresses observed in the deformed alloys. By severe cold working, e.g. up to 80% reduction in wire drawing, the relatively modest yield strengths of ordinary austenitic steels can be raised to over 1200 MPa although ductility will then be compromised.

However, the largest effect on work-hardening rates is undoubtedly the transformation to martensite, as illustrated by the true stress-strain curves of several austenitic steels of decreasing nickel content, i.e. decreasing stability of austenite (Fig. 12.24). By this means yield stresses of well over 1500 MPa can be achieved, e.g. a metastable austenite containing 17Cr-4Ni-3Mn-0.1C wt% after almost complete transformation following 40% deformation at room temperature has a 0.2% proof stress of 1700 MPa. It should be noted that the increase in strength is accompanied by a substantial decrease in ductility, so such steels should not be used for deep

drawing, an application where stability of the austenite is essential. In contrast, in stretch forming applications unstable austenitic steels can be used because the transformation, by raising the work-hardening rate, also increases the extent of uniform straining, as distinct from localised straining, which the steel will undergo prior to failure.

The advantages obtainable from the easily fabricated austenitic steels led naturally to the development of *controlled transformation* stainless steels, where the required high strength level was obtained after fabrication, either by use of refrigeration to take the steel below its M_S temperature or by low-temperature heat treatment to destabilise the austenite. Clearly the M_S – M_F range has to be adjusted by alloying so that the M_S is just below room temperature. The M_F is normally about 120°C lower, so that refrigeration in the range –75°C to –120°C should result in almost complete transformation to martensite. Alternatively, heat treatment of the austenite can be carried out at 700°C to allow precipitation of $M_{23}C_6$ mainly at the grain boundaries. This reduces the carbon content of the matrix and raises the M_S so that, on subsequent cooling to room temperature, the austenite will transform to martensite. This precipitation reaction can be accelerated by designing the steel to include a small volume fraction of δ -ferrite. The δ/γ interfaces then provide very effective nucleating sites for $M_{23}C_6$.

Further heat treatment is then necessary to give improved ductility and a high proof stress; this is achieved by tempering in the range 400–450°C. Typical compositions of these steels and the properties which can be obtained by alternative heat treatments are given in [Table 12.5](#). This category of steels places large demands on metallurgical control, the treatments are complex and the cost high. Consequently, they tend only to be used in critical applications such as highly stressed skins of supersonic aircraft and rocket casings.

Another group of steels has been developed to exploit the properties obtained when the martensite reaction occurs during low-temperature plastic deformation. The TRIP steels was introduced in [Chapter 10](#), with the formation of martensite leading to increases in work-hardening rate and hence of uniform ductility prior to necking. Essentially the principle is the same as that employed in controlled transformation steels, but plastic deformation is used to form martensite and the approach is broader as far as the thermomechanical treatment is concerned.

In one process, the composition of the steel is balanced to produce an M_S^g temperature above room temperature. The steel is then heavily deformed (~80%) above the M_S^g temperature, usually in the range

Table 12.5 Compositions and properties of controlled transformation steels (after Pickering, 1976). 'RT' stands for room temperature

Composition	Heat treatment	0.2% proof stress MPa	Tensile strength MPa	% Elongation
0.1C, 17Cr, 4Ni, 3Mn	1. Solution treated 925°C, cold worked 40% reduced, tempered 3 h at 450°C	1670	1700	0.5
	2. Solution treated 950°C, refrigerated at -78°C, tempered 1 h at 400°C	1200	1440	19
0.06C, 16.5Cr, 5Ni, 2Mn, 1.5Mo, 2Co, 1Al	1. Solution treated 1050°C, aged 2 h at 700°C, cooled to RT, then aged 4 h at 450°C	1270	1430	0
	2. Solution treated 950°C, refrigerated at -78°C, tempered 4 h at 450°C	1240	1520	21
0.07C, 17.5Cr, 3Ni, 2Mn, 2Mo, 2Co, 1Cu	1. Solution treated 1050°C, aged 2 h at 700°C, cooled to RT, then tempered 4 h at 450°C	1110	1250	10
	2. Solution treated 950°C, refrigerated at -78°C, tempered 4 h at 450°C	1240	1360	20

250–550°C, which results in austenite that remains stable at room temperature. Subsequent tensile testing at room temperature gives high strength levels combined with extensive ductility as a direct result of the martensitic transformation which takes place during the test. For example, a steel containing 0.3C–2Mn–2Si–9Cr–8.5Ni–4Mo wt% after 80% reduction at 475°C gives a proof and ultimate tensile strength of 1430 and 1500 MPa respectively, and an elongation of 50%.

Higher strength levels (proof stress ~2000 MPa) with ductilities between 20% and 25% can be obtained by adding strong carbide-forming elements such as vanadium and titanium, and by causing the M_s^g temperature to be below room temperature. As in the earlier treatment, severe thermo-mechanical treatments in the range 250–550°C are then used to deform the austenite and dispersion strengthen it with fine alloy carbides. The M_s^g

temperature is, as a result, raised to above room temperature so that, on mechanical testing, transformation to martensite takes place, giving excellent combinations of strength and ductility as well as substantial improvements in fracture toughness.

Like the controlled transformation steels, the TRIP steels require extremely good metallurgical control and relatively expensive to make. They are only used in applications where high demands are made on mechanical, as distinct from environmental properties. They do, however, illustrate how a combination of basic principles can be carefully balanced and controlled to achieve outstanding mechanical properties in alloy steels.

12.12 SUMMARY

Chromium has a unique role in stainless steels. It has a sufficiently large solubility in iron to passivate the surface and to do this repeatedly when the oxide layer is damaged. The resistance to pitting corrosion can be improved by molybdenum. Aluminium-rich stainless steels have been developed to resist high temperature oxidation by forming stable alumina scales. These are the key characteristics of stainless steels which otherwise have ambient temperature mechanical properties that can be achieved in low-alloy steels that are not stainless. In other words, the class itself is defined by the ability of the stainless steel to isolate itself from its environment.

The phase mixtures present in stainless steels and the mechanisms by which these phases form can be manipulated by varying other solutes, given rise to a large variety of alloys suited for different purposes depending on property combinations or economical factors.

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BACKNOTES

1. The main reason for adding niobium at such a large concentration is to improve the stability of the alumina scale.
2. There is often a distinction made between stress induced and plastic-strain induced martensite. However, in all practical scenarios, the strain is achieved by applying a stress, with the stress playing the dominant role [27,28].

CHAPTER 13

Weld Microstructures

Abstract

Bridges, ships and much of the infrastructure on which modern civilisation depends, rely on the ability to connect pieces of well-engineered and shaped steel by welding. A localised heat source introduces liquid metal into the gap between the pieces of steel, which on solidification forms an integral joint. The process is complex with phenomena embracing all states of matter that are ordinarily observable, to wit: plasma, gas, liquid and solid. It requires an understanding of many aspects of metallurgy, heat and fluid flow in order to achieve a reliable joint. There also exist processes that do not involve fusion but nevertheless fall within the remit of welding.

13.1 INTRODUCTION

Fusion welding is of greatest importance in the fabrication of engineering structures. There are many ways in which fusion welding can be carried out, but all of them involve the deposition of a small amount of molten steel between the components to be joined or coated (Fig. 13.1a, b). When the steel solidifies, it welds the components together. The metallurgy of the welded joint can be categorised into two major regions, the fusion zone and the heat-affected zone (HAZ), Fig. 13.1c. The fusion zone represents both the deposited metal and the parts of the steel component melted during the process, and is a solidification microstructure. The HAZ, on the other hand, represents those regions in the close proximity of the weld, where the heat input during welding changes the microstructure without melting the steel. This chapter describes the development of microstructure in both zones, beginning with the fused regions. Virtually every aspect of phase transformation in steels is relevant to the subject of welding. There is an opportunity for a whole series of transformations to occur successively as the weld cools from the liquid state.

13.2 FUSION ZONE

13.2.1 Weld solidification

Iron is ferritic at temperatures just below the melting point. As it cools, the ferrite then transforms into austenite, only to revert back to ferrite on continued cooling. Most steels contain modest concentrations of alloying

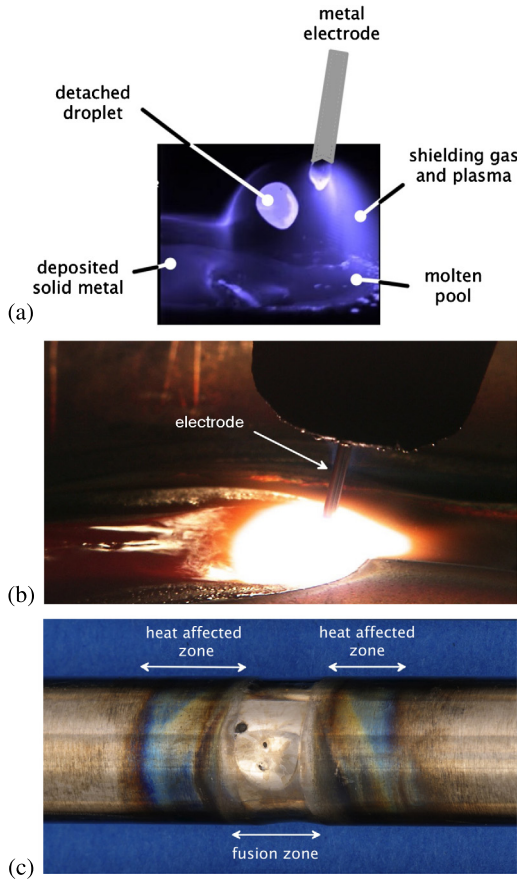


Figure 13.1 A process using a wire electrode that is consumed as the weld is deposited. An electrical arc is struck between a metal electrode and the steel. This melts the consumable electrode with droplets detaching and falling into the weld pool below – some of the steel also melts and contributes to the weld pool while protected by a shielding of inert gas (image courtesy of Stuart Guest, Julien Chapuis and Patricio Mendez). (b) The electrode moves along the welding direction, leaving behind the solidified weld metal. There are many variations on this process [1,2]. Image courtesy of Kamellia Dalaei, ESAB AB. (c) The heat-affected zone highlighted by the oxide interference colours on a welded stainless steel tube. Photograph courtesy of Drs Yanhui Zhang and Simon Condie of TWI, Cambridge.

elements, and hence show similar crystal structure changes as pure iron. Weld deposits, therefore begin solidification with the epitaxial growth of columnar delta-ferrite (δ -ferrite) from the hot-grain-structure of the parent plate at the fusion surface, Fig. 13.2a [3–5]. The grains are anisotropic

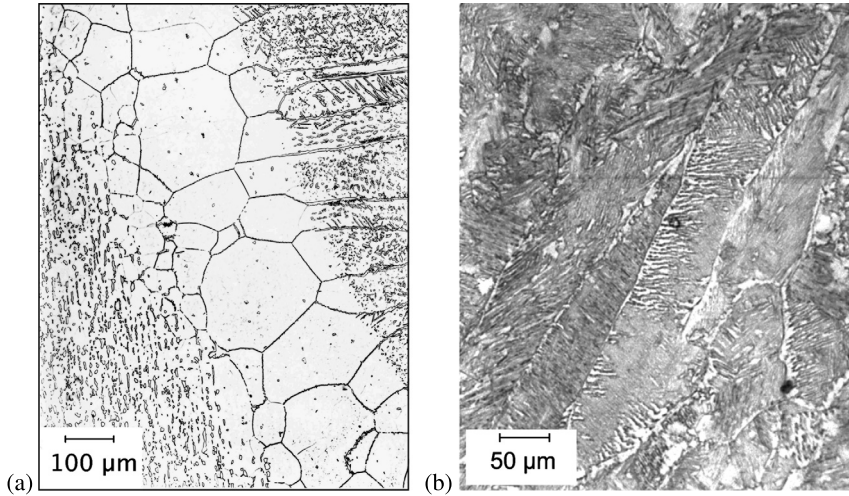


Figure 13.2 (a) Illustration of the epitaxial growth of columnar grains from the fusion boundary of a stainless steel weld (courtesy of Honeycombe and Gooch). (b) Optical micrograph showing the columnar prior-austenite grain structure typical in steel weld deposits (courtesy Carrie Walsh).

because they grow into the liquid along the direction of heat flow. Those grains with their $\langle 100 \rangle$ directions parallel to the heat-flow direction grow fastest and hence stifle the growth of unsuitably oriented grains. The width of the columnar grains therefore increases with distance away from the fusion boundary.

As already pointed out, the δ -ferrite undergoes a solid-state transformation to austenite as the temperature decreases. The austenite nucleates at the δ - δ grain boundaries and develops into a columnar austenite grain structure which strongly resembles that of the original δ -grains (Fig. 13.2b).

The detailed shape and size of the austenite grains is of importance in the evolution of the final microstructure. The effect of the austenite grain size is two-fold. Firstly, the number density of austenite grain boundary nucleation sites changes inversely with the grain size. Coarse-grained weld deposits therefore have a higher hardenability. The second, and more subtle effect, arises from the columnar shape of the austenite grains, a shape which is like that of a hexagonal prism. The grains are typically about 100 μm wide and about 5000 μm in length [6]. This is quite unlike an equiaxed grain structure, and because of the fewer grain junctions involved, allows the hardenability of a weld to be larger than that of a wrought alloy.

Table 13.1 A comparison of the chemical composition (wt%) of a submerged arc weld with that of the plate being welded, and the wire used as the consumable electrode. The welding conditions used were 34 V, 900 Amp (direct current positive), at a welding speed of 0.005 m s^{-1} , with a calcium silicate flux

	C	Mn	Si	Cu	Al	N	O
Plate	0.21	1.0	0.2	0.05	0.04	0.01	0.004
Wire	0.14	1.5	0.2	0.31	0.01	0.01	0.001
Weld	0.16	1.1	0.3	0.16	0.01	0.01	0.053

Solidification does not occur under equilibrium conditions during welding. Solidification-induced chemical segregation, and composition variations due to uncontrolled changes in the welding conditions, make the solidification microstructure inhomogeneous. The amplitude of these variations becomes larger as the alloy concentration increases.

Mineral fluxes or inert gas shrouds are employed in order to protect the hot metal against environmental attack during welding. Such protection is not entirely effective, with the result that the oxide content of welds tends to be much larger than that of wrought steel (Table 13.1). The oxide particles are entrapped in the fusion zone during solidification. As discussed later, these non-metallic particles serve as heterogeneous nucleation sites and hence are of considerable importance in the evolution of the microstructure. Table 13.1 reveals some other interesting differences between the plate and weld compositions. The copper concentration of the weld is large because in this case, the welding wire has a copper coating to enable better electrical contact. The silicon concentration in the weld is larger than both the wire and the plate, because the excess silicon is acquired by decomposition of the protective flux. These observations emphasise the complexity of the welding process, in which the chemical composition of the final weld deposit depends on many variables, including the plate, wire and flux compositions.

13.2.2 As-deposited microstructure

The microstructure obtained as the weld cools from the liquid phase to ambient temperature is called the *as-deposited* or *primary* microstructure. Its major components include allotriomorphic ferrite, Widmanstätten ferrite, and acicular ferrite (Fig. 13.3). There may also be some martensite, retained austenite or degenerate pearlite. These latter phases occur in very small fractions, and are known by the collective term *microphases*. Bainite, consisting of sheaves of parallel platelets, is not generally found in well-designed weld-

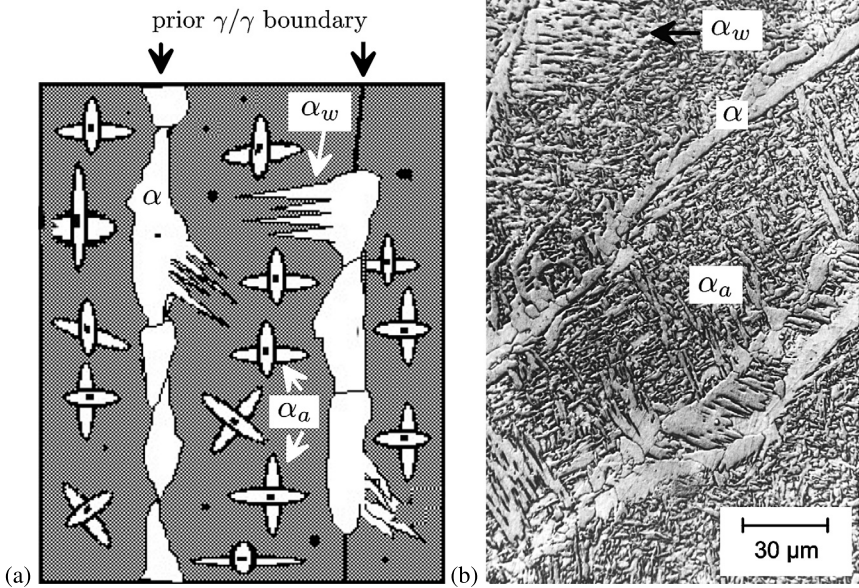


Figure 13.3 (a) Schematic illustration of the essential constituents of the primary microstructure in the columnar austenite grains of a steel weld deposit. (b) Scanning electron micrograph of the primary microstructure of a steel weld (courtesy of Rees). The terms α , α_w and α_a refer to allotriomorphic ferrite, Widmanstätten ferrite and acicular ferrite, respectively.

ing alloys. Instead, acicular ferrite is induced to nucleate heterogeneously on non-metallic inclusions [7].

In practice, the gap between the components to be joined often has to, for thick steels, be filled by a sequence of several weld deposits. These multirun welds have a complicated microstructure (Fig. 13.4). The deposition of each successive layer heat treats the underlying microstructure. Some of the regions of original primary microstructure are reheated to temperatures high enough to cause the reformation of austenite, which during the cooling part of the thermal cycle transforms into a different microstructure. Other regions may simply be tempered by the deposition of subsequent runs. The microstructure of the reheated regions is called the *reheated* or *secondary* microstructure.

13.2.3 Allotriomorphic ferrite

Allotriomorphic ferrite (α) is the first phase to form on cooling the austenite grains below the A_{e3} temperature. It nucleates at the columnar austenite

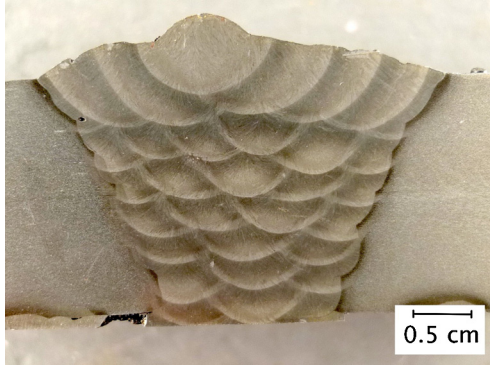


Figure 13.4 The macrostructure of a multirun weld, made by sequentially depositing a number of beads in each of the 7 layers (courtesy of Kamellia Dalaei, ESAB AB).

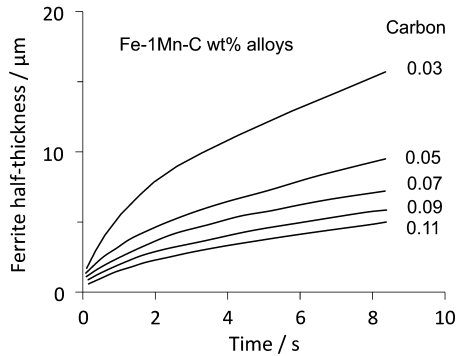


Figure 13.5 An illustration of the parabolic thickening of ferrite during isothermal transformation at 740°C. Each curve represents a Fe-1Mn-C wt% steel with the carbon concentration as indicated on the diagram.

grain boundaries. Because these boundaries are easy diffusion paths, they become decorated with thin, continuous layers of ferrite. The layers then thicken at a rate which is controlled by the diffusion of carbon in the austenite ahead of the transformation interface. Under isothermal conditions, the ferrite thickness z^* changes parabolically with time t (Chapter 3):

$$z^* = \alpha_1 t^{1/2}, \quad (13.1)$$

where α_1 is the parabolic rate constant. This is illustrated in Fig. 13.5 for alloys with different carbon concentrations; note that the growth kinetics become sensitive to the carbon concentration as the latter approaches the solubility of carbon in the ferrite.

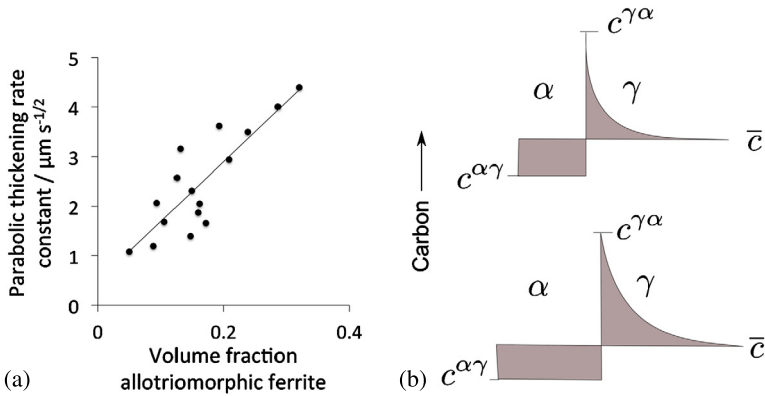


Figure 13.6 (a) The correlation between the calculated parabolic thickening rate constant (a variable related to the growth rate) and the volume fraction of allotriomorphic ferrite obtained in a series of manual metal arc weld deposits, fabricated using similar welding parameters but with different chemical compositions. The rate constant is calculated for transformation at 700°C. (b) The diffusion distance increases as the ferrite layer thickens, slowing down the rate of growth.

The magnitude of the parabolic rate constant depends on the equilibrium compositions of the austenite and ferrite, and on the diffusivity of carbon in austenite (Chapter 3). Alloying elements such as manganese, which stabilise austenite, are associated with a smaller value of α_1 . Because nucleation is not rate limiting in the case of the majority of low-alloy steel weld metals, the fraction of allotriomorphic ferrite obtained correlates directly with the parabolic rate constant (Fig. 13.6a). Nevertheless, welding does not involve isothermal transformation. The cooling rate of the weld metal once it is in the solid-state is given approximately by [8]:

$$\frac{dT}{dt} = \frac{C_{12}}{q\eta} (T - T_i)^{C_{13}} \quad (13.2)$$

where q in the case of arc welding is the electrical energy input per unit length of the weld, η is the arc energy transfer efficiency (≈ 0.8), T_i is the temperature of the steel being welded and C_i are empirical constants. Although the discussion in the Chapter is limited to the essential concepts, it is routinely possible to integrate the development of microstructure over a range of temperatures to properly represent welds [9] or steels in general [10].

The fact that during isothermal transformation the thickness of the ferrite varies with the square root of time, means that the rate of growth

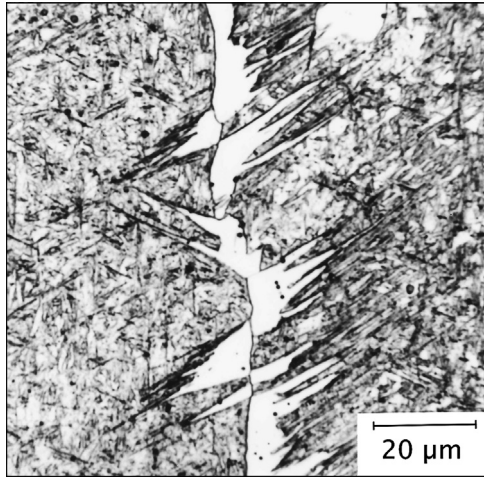


Figure 13.7 Widmanstätten ferrite plates growing from allotriomorphic ferrite in a partially transformed steel weld which was quenched from the transformation temperature. The matrix is martensitic (courtesy of Barritte).

decreases as the ferrite layer gets thicker. This is because the distance over which carbon has to diffuse increases with time (Fig. 13.6b). The growth rate for a given alloy goes through a maximum as a function of temperature, because the driving force for transformation increases with undercooling whereas the diffusivity decreases. Consequently, as the weld cools to temperatures less than about 600°C, the diffusional growth of ferrite slows down so much that the layers of allotriomorphic ferrite reach a limiting thickness. Widmanstätten ferrite formation does not involve the diffusion of substitutional solutes, and therefore its growth is not sluggish at low temperatures. The remaining austenite, therefore, begins to transform into Widmanstätten ferrite (Fig. 13.7).

13.2.4 Widmanstätten ferrite and acicular ferrite

Although substitutional solutes and iron atoms do not diffuse during the growth of Widmanstätten ferrite, carbon does partition during transformation. Because of its plate shape, much of the carbon can be accommodated at the sides of the growing plate, so that the plate tip always encounters fresh austenite. This is unlike the case for allotriomorphic ferrite, where the partitioned carbon builds up ahead of the interface and progressively slows down the rate of growth. Widmanstätten ferrite plates therefore lengthen at a constant rate.

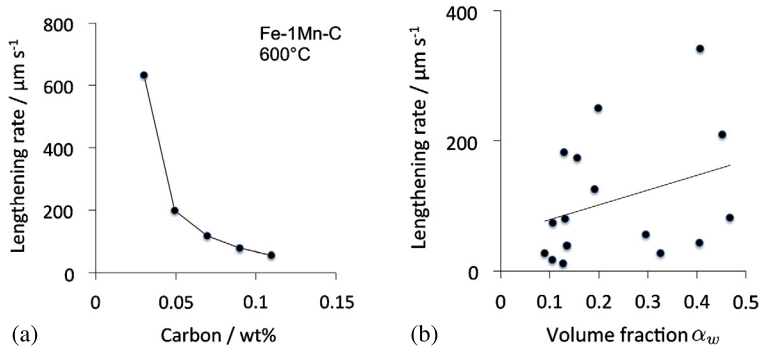


Figure 13.8 (a) The isothermal growth rate of Widmanstätten ferrite in a series of Fe-1Mn-C wt% alloys as a function of carbon concentration. Notice that the growth rates are so large, that the plates could grow right across typical austenite grains within a fraction of a second. (b) Poor correlation of the volume fraction of Widmanstätten ferrite against the calculated growth rate.

The growth rates are found to be so large for typical weld compositions, that the formation of Widmanstätten ferrite is usually completed within a fraction of a second. Hence, for all practical purposes, the transformation can be regarded as being isothermal (Fig. 13.8a).

Unfortunately, the fraction of Widmanstätten ferrite that forms in weld deposits correlates badly with the plate lengthening rate, as illustrated in Fig. 13.8b [11]. This is because there is an interference between the plates of Widmanstätten ferrite that grow from the austenite grain boundaries, and acicular ferrite plates which nucleate at non-metallic particles dispersed throughout the weld (Fig. 13.9). The formation of Widmanstätten ferrite and acicular ferrite is therefore competitive. Anything that increases the number density of inclusion nucleation sites relative to austenite grain nucleation sites, favours the formation of acicular ferrite at the expense of Widmanstätten ferrite. Hence, the refinement of austenite grain size, or a reduction in the oxide content of the weld below a limiting value, both lead to a decrease in the acicular ferrite content.

By the time the weld deposit cools to about 500°C, most of the austenite has been consumed. The small quantity of remaining austenite (about 5%) is enriched in carbon and either transforms to martensite, or into pearlite, which is degenerate because it does not have the opportunity to establish a lamellar structure. Slower cooling rates favour the formation of pearlite relative to martensite. Some austenite may also be retained to ambient temperature. Because of their small volume fractions in the overall mi-

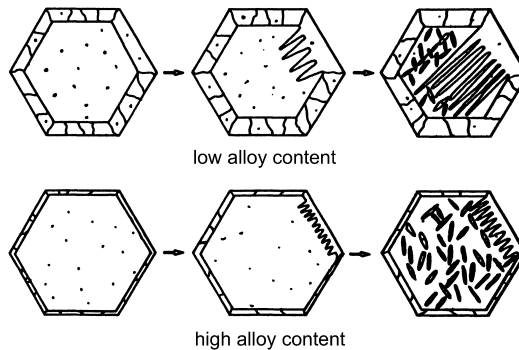


Figure 13.9 Diagrams illustrating the development of microstructure in two weld deposits with different chemical compositions. The hexagons represent cross-sections of columnar austenite grains whose boundaries first become decorated with uniform, polycrystalline layers of allotriomorphic ferrite, followed by the formation of Widmanstätten ferrite. Depending on the relative transformation rates of Widmanstätten ferrite and acicular ferrite, the former can grow entirely across the austenite grains or become stifled by the intragranularly nucleated plates of acicular ferrite [9].

crostructure, these phases are, in welding terminology, called ‘microphases’. The microphases are relatively hard and behave in many respects like brittle inclusions. They are, therefore, of importance in determining the toughness of weld deposits. However, this is not a generic conclusion, the ability of such local zones to be brittle depends also on the following factors [12]:

- (a) the hardness of the local zone relative to its surroundings;
- (b) the size relative to the average microstructural scale;
- (c) the shape of the zone; thus films of carbon-rich austenite can be beneficial to toughness whereas large blocks that decompose readily into untempered, high-carbon martensite, are not [13];
- (d) the number density of the local brittle zones relative to the fracture criteria important in the engineering design.

13.2.5 Sensitivity to carbon

It is striking that small variations in carbon concentration can have a major influence on the microstructure of welds, especially since the average carbon concentration of a weld is usually kept very small [14]. It is apparent from the previous discussions of the growth rates of allotriomorphic and Widmanstätten ferrite, that the sensitivity of growth kinetics to carbon becomes larger as the concentration of carbon decreases.

These are important observations given that the general trend in the steel industry is to reduce the carbon concentration, sometimes to levels approaching the maximum solubility of carbon in ferrite. The rate at which ferrite grows increases sharply as the carbon concentration of the steel approaches its solubility in ferrite. This is because there is no need for the carbon to diffuse ahead of the γ/α interface, since it can all be accommodated in the ferrite.

Hence, the effect of carbon is seen to be larger (Figs 13.5 and 13.8a) when its concentration changes from 0.03 $\rightarrow$ 0.05 wt%, when compared with the change from 0.09 $\rightarrow$ 0.11 wt%. Changes in mechanical properties are found to reflect this behaviour, the strength of low-carbon steels being particularly sensitive to the carbon concentration. This increased sensitivity of the γ/α transformation to carbon at low concentrations, leads to a corresponding decreased sensitivity to substitutional alloying elements. Carbon in effect controls the kinetics of transformation.

In welding, the hardenability of the steel is often expressed as a carbon equivalent (CE). The concentration of each solute is scaled by a coefficient which expresses its ability, relative to carbon, to retard the γ/α transformation. Steels with a CE in excess of about 0.4 wt% cannot easily be welded because of their increased tendency to form martensite. There are in fact two popular expressions for the CE, one due to the International Institute for Welding (IIW), and the other attributed to Ito and Besseyo, covering the high and low ranges of carbon, respectively:

$$\text{IIW} > 0.18 \text{ wt\% C,}$$

$$\text{CE} = w_{\text{C}} + \frac{w_{\text{Mn}} + w_{\text{Si}}}{6} + \frac{w_{\text{Ni}} + w_{\text{Cu}}}{15} + \frac{w_{\text{Cr}} + w_{\text{Mo}} + w_{\text{V}}}{5} \text{ wt\%,} \quad (13.3)$$

$$\text{Ito-Besseyo} < 0.18 \text{ wt\% C,}$$

$$\text{CE} = w_{\text{C}} + \frac{w_{\text{Si}}}{30} + \frac{w_{\text{Mn}} + w_{\text{Cu}} + w_{\text{Cr}}}{20} + \frac{w_{\text{Ni}}}{60} + \frac{w_{\text{Mo}}}{15} + \frac{w_{\text{V}}}{10} + 5w_{\text{B}} \text{ wt\%.} \quad (13.4)$$

The Ito-Besseyo CE formula has smaller coefficients for the substitutional solutes when compared with the IIW formula. It is believed to be more reliable for low-carbon steels. The IIW formula shows much smaller tolerance to substitutional alloying elements than the Ito-Besseyo equation. As already discussed, with low carbon concentrations the kinetics of transformation are more sensitive to carbon than to substitutional solutes. Hence, it is logical that there should be two different empirical expressions

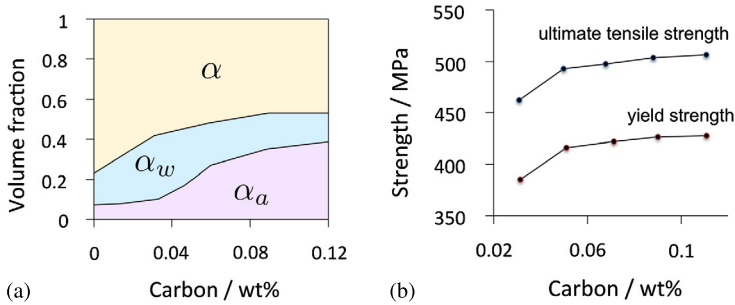


Figure 13.10 Variations in microstructure and mechanical properties as a function of carbon concentration in Fe-1Mn-C wt% steel weld deposit using manual metal arc welding (1 kJ mm^{-1}).

for the CE for the low- and high-carbon weldable steels. Fig. 13.10 illustrates that, as expected, both the microstructure and mechanical properties change more rapidly at low carbon concentrations.

13.3 HEAT-AFFECTED ZONE

The HAZ is the portion of the material which has not been melted, but whose microstructure and mechanical properties are altered by the heat of welding.

13.3.1 Heat flow

All welding processes involve a source of heat, the prime purpose of which is to cause melting.¹ Subsequent solidification should lead to the formation of an integral joint. Much of the heat manages to diffuse from the fusion zone into the adjacent solid regions. As a consequence, those regions experience a heating and cooling cycle, the severity of which depends on the distance from the fusion boundary (Fig. 13.11). The peak temperature and the heating rate decrease with distance away from the fusion boundary. The cooling rate, on the other hand, is less sensitive to this distance, and can be stated as the time Δt_{8-5} taken to cool over the range $800\text{--}500^\circ\text{C}$. For many weldable steels, this defines the temperature range within which austenite decomposes by solid-state transformation.

The nature of the thermal cycle at any position within the HAZ can be characterised by two parameters, the peak temperature T_p and the time

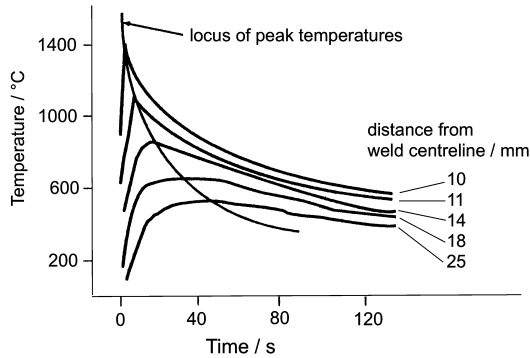


Figure 13.11 Temperature-time curves representing typical thermal cycles experienced in the HAZ of a weld (adapted from data published in the *Welding Handbook* [15]).

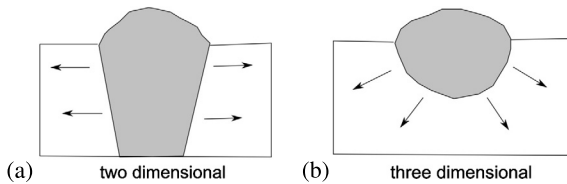


Figure 13.12 Illustration of (a) two-dimensional and (b) three-dimensional heat-flow conditions.

period Δt_{8-5} . Both of these parameters increase with the heat input q :

$$T_P \propto \frac{q}{r}, \quad (13.5)$$

$$\Delta t_{8-5} \propto q^n, \quad (13.6)$$

where r is the distance from the fusion boundary and n has a value (1 or 2) which depends on whether the component being welded is thick compared with the size of the weld bead. The relative thickness determines whether the flow of heat is two- or three-dimensional (Fig. 13.12). The heat input q is per unit length of weld, and typically is in the range about 1–5 kJ mm⁻¹.

13.3.2 Microstructural zones

There is a well-defined gradient of microstructure in the HAZ, as a function of the distance from the fusion boundary (Fig. 13.13):

1. Those regions immediately adjacent to the fusion boundary are heated to very high temperatures and hence transform completely to austenite. During continuous heating, austenite begins to form at a temperature

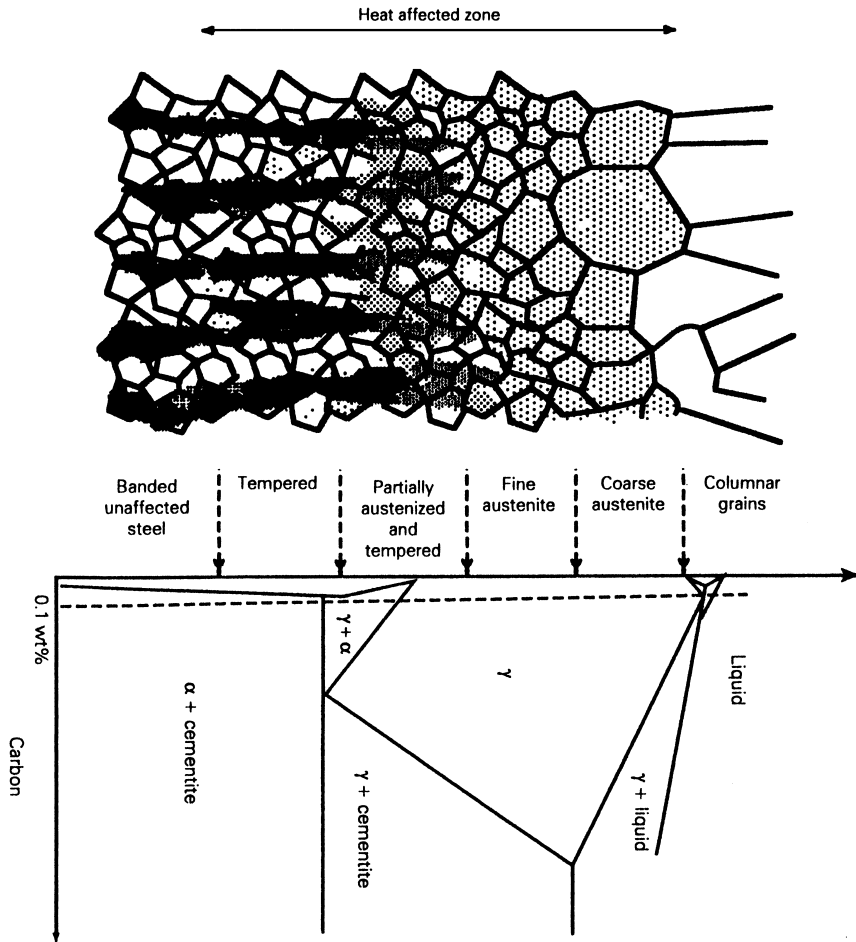


Figure 13.13 Schematic illustration of the microstructural variation to be expected in the HAZ of steel welds. Notice that the microstructural zones do not, and should not coincide with the equilibrium transformation temperatures since heating and cooling rates during welding do not approach equilibrium rates.

$A_{c1} \simeq 800^{\circ}\text{C}$, and the samples become fully austenitic at $A_{c3} \simeq 950^{\circ}\text{C}$. These temperatures are different from the corresponding equilibrium temperatures A_{e1} and A_{e3} because they increase with the heating rate. The peak temperatures in the HAZ close to the fusion boundary are well in excess of the A_{c3} temperature of weldable steels. Consequently, the austenite that forms is annealed during heating beyond A_{c3} , giving rise to a very coarse grain structure. This forms the *coarse-grained austenite zone*.

Table 13.2 Characteristic temperature ranges for the variety of microstructural regions within the HAZ of steel welds

HAZ microstructure	Temperature range
Coarse-grained austenite	$1500^{\circ}\text{C} > T_p > 1200^{\circ}\text{C}$
Fine-grained austenite	$1200^{\circ}\text{C} > T_p > A_{c3}$
Partially austenitised zone	$A_{c3} > T_p > A_{c1}$
Tempered regions	$A_{c1} > T_p$

2. The austenite grain size decreases sharply with distance from the fusion boundary. It is necessary to distinguish this as the *fine-grained zone* because its mechanical properties tend to be superior to those of the coarse zone.
3. As the peak temperature decreases, regions of the HAZ further away from the fusion boundary become only partially austenitic during the heating part of the thermal cycle. The austenite that forms has a rather high carbon concentration, due to the increase in the solubility of carbon in γ with decreasing temperature. The part that does not transform into austenite becomes tempered.
4. When the peak temperature becomes less than the A_{c1} temperature, the only effect of the heat input is to temper the microstructure, the extent of tempering decreasing with distance from the fusion boundary.

The individual microstructures are illustrated in [Fig. 13.14](#), and discussed in detail in the sections that follow ([Table 13.2](#)).

13.3.3 Coarse-grained austenite

The formation of austenite during heating is in many ways different from transformations which occur during cooling below the equilibrium temperature. As discussed in [Chapter 3](#), the formation of ferrite follows a C-shaped curve kinetic behaviour on a time-temperature-transformation diagram; the overall transformation rate, therefore, goes through a maximum as a function of the supercooling below the equilibrium temperature. This is because of two opposing effects; the diffusion coefficient decreases as the temperature falls, but the driving force for transformation increases.

During heating, however, both the diffusion coefficient and the driving force increase with temperature. The overall rate of transformation, therefore, increases continuously as the transformation temperature is raised, [Fig. 13.15](#).

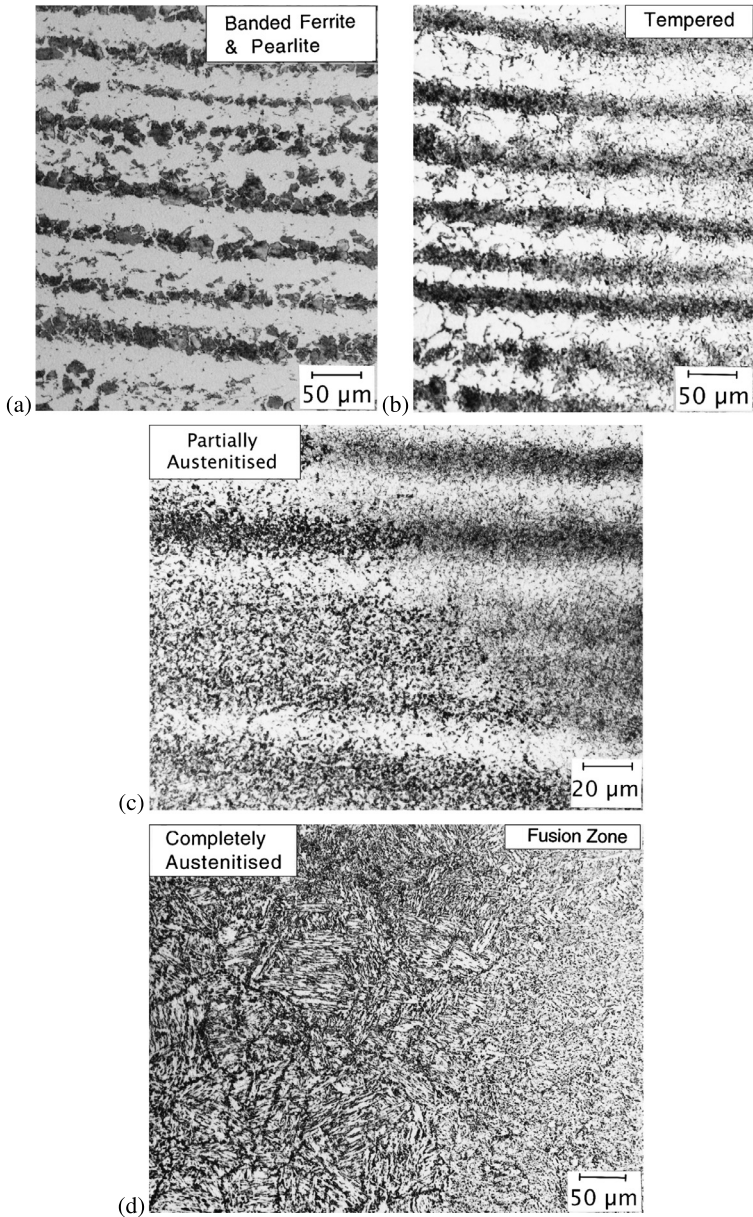


Figure 13.14 The gradient of microstructure in the HAZ of a mild steel plate (courtesy of C. Davis). (a) The plate microstructure far away from the weld, completely unaffected by welding. The bands of ferrite/pearlite are typical of many structural steels which are chemically inhomogeneous. (b) The tempered region. (c) The partially austenitised region. (d) The fully austenitised region merging into the fusion zone.

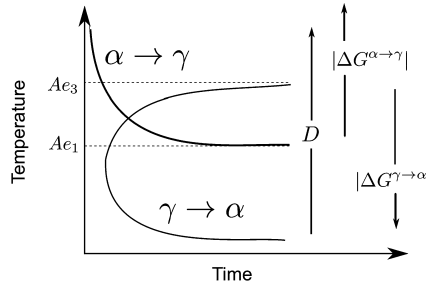


Figure 13.15 A comparison of the TTT curves for the $\gamma \rightarrow \alpha$ transformation, and for the reverse $\alpha \rightarrow \gamma$ transformation. ΔG represents the driving force for transformation and D is the diffusion coefficient.

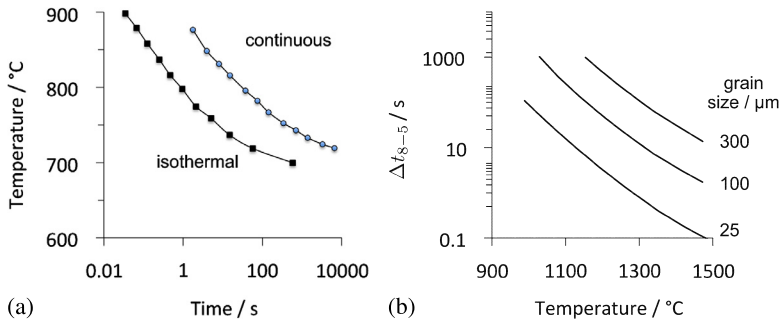


Figure 13.16 (a) The TTT and CHT diagrams for the beginning of austenite growth in a Fe-0.15C-0.5Si-1.5Mn wt% alloy (courtesy of Suzuki). (b) Schematic austenite grain growth diagram for the heat-affected zone of a microalloyed steel that is welded. Δt_{8-5} is the cooling time over the temperature range 800–500°C, and the peak temperature reached is plotted on the horizontal axis. The lines therefore represent contours of constant austenite grain size (adapted from Ashby and Easterling [16]).

For practical purposes, the formation of austenite during heating can be represented by a continuous heating transformation (CHT) diagram, analogous in concept to the continuous cooling transformation (CCT) diagrams so useful in illustrating the formation of ferrite (Fig. 13.16a). The CHT diagram is displaced to longer times when compared with the isothermal transformation diagram for austenite formation. For typical heating rates encountered in the region adjacent to the fusion boundary, the formation of austenite should be completed when the temperature has exceeded the A_{c3} temperature by about 100°C. Since the peak temperature in this zone is much higher than A_{c3} , the austenite grains coarsen rapidly as T_p is approached. In steels which are microalloyed, it may necessary for the grain

boundary pinning particles (e.g. niobium carbonitrides) to dissolve before substantial grain coarsening occurs. In any case, once the coarsening begins, it proceeds very rapidly because the effect of temperature increases exponentially during heating. The austenite grain growth can be expressed conveniently in the form of grain growth diagrams (Fig. 13.16b) which contain contours of equal grain size as a function of the peak temperature and Δt_{8-5} .

The importance of the coarse-grained austenite zone is in the mechanical properties which develop as the austenite transforms during the cooling part of the thermal cycle. The coarse grain structure leads to an increase in hardenability, because it becomes easier to avoid intermediate transformation products, so that untempered martensite or other hard phases can form during cooling. The welding process introduces atomic hydrogen into the weld metal, which is able to diffuse rapidly into the HAZ. Hard microstructures are particularly susceptible to embrittlement by hydrogen, the fracture occurring shortly after the weld has cooled to room temperature. This hydrogen-induced phenomenon is called ‘cold-cracking’. This is why the carbon equivalent of the steel has to be kept low enough to prevent the hardness in the coarse-grained region from becoming unacceptably large.

13.3.4 Fine-grained austenite zone

This region is typified by austenite grains some 20–40 μm in size. The grain structure and hardenability are, therefore, not very different from those associated with control-rolling operations during the manufacture of the steel. The fine austenite grains thus transform into more desirable ferritic phases, with lower hardness values and higher toughness.

13.3.5 Partially austenitic regions and local brittle zones

At a sufficiently large distance from the fusion boundary, the peak temperature is such that the steel cannot transform completely to austenite. The small amount of austenite that does form has a larger carbon concentration. This is because the solubility of carbon in austenite, which is in equilibrium with ferrite, increases as the temperature decreases (Fig. 1.9). The subsequent transformation behaviour of this enriched austenite is then quite different, since it has a higher hardenability.

If the cooling rate is sufficiently large, then the carbon-enriched austenite transforms partially into hard martensite, the remaining austenite being retained to ambient temperature. These minute regions of hard martensite

are known as 'local brittle zones'. They are located in much softer surroundings consisting of tempered ferrite. Consequently, they do not cause a general reduction in toughness, but lead to an increase in the scatter associated with toughness tests. This is because the test specimen only sometimes samples the local brittle zone, in which case the recorded toughness can be poor. On other occasions, the measured toughness can be very high, presumably because the test region does not include a local brittle zone. Such scatter in mechanical property data is not only disconcerting, but also makes design difficult because of the existence of a few very low values.

When the cooling rate in this region is not high enough to induce martensitic transformation, the carbon-enriched austenite can decompose into a mixture of coarse cementite and ferrite. The cementite particles again constitute local brittle zones and increase the variability in mechanical properties.

13.4 FRICTION STIR WELDING OF STEELS

Friction stir welding is a solid-state, process [17–19] in which a rotating tool with a shoulder and terminating in a threaded pin, moves along the butting surfaces of the two plates that are to be joined, Fig. 13.17. Heat generated by friction with the plates, at the shoulder and to a lesser extent at the pin surface, softens the material being welded. The flow of this plasticised metal as a result of tool rotation and translation accomplishes the joint. During the process, material is transported from the front of the tool to the trailing edge where it is forged into a joint.

Since its discovery in 1991 [17], friction stir welding has evolved as a technique of choice in the routine joining of aluminium components because the aluminium softens rapidly with heat, making the process easy to implement with steel tools; its applications for joining difficult metals and metals other than aluminium are growing, albeit at a much slower pace. 'Difficult' in this context means metals that do not plasticise easily because they are strong relative to the material used to make the tool. This is because the steel is strong even when red-hot but the process requires it to be plastic to enable a sound weld to be fabricated. Hence, expensive tools have to be used to survive the high temperatures, between 800–1200°C and severe wear. Fig. 13.18a illustrates the problem.

The microstructural gradients expected in a friction-stir weld and its proximity are different from conventional welds because the process does not involve melting but does include plastic deformation which is intrinsic

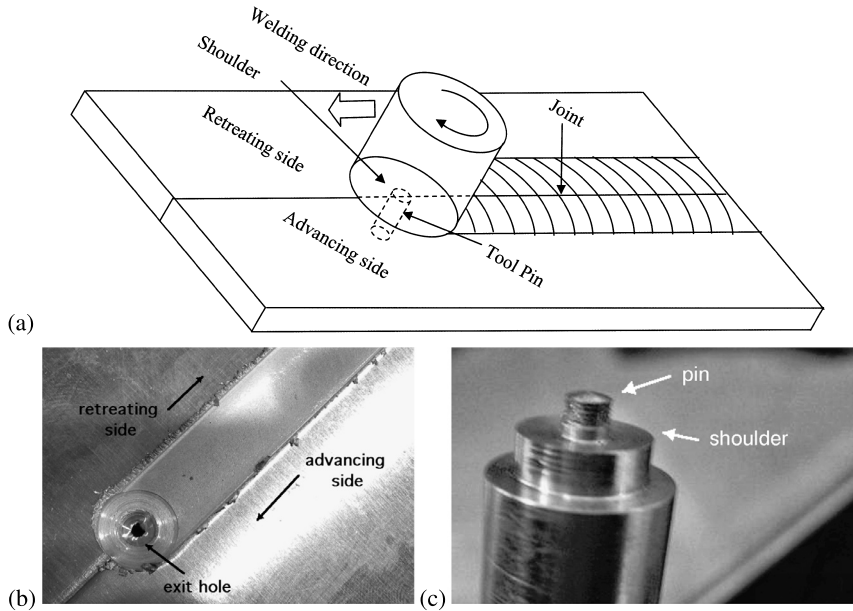


Figure 13.17 (a) The friction stir welding process. The advancing side has the direction of rotation along the welding direction. (b) A friction stir weld between aluminium sheets. (c) A tool, with a threaded-pin. After Nandan et al. [20], reproduced with permission of Elsevier.

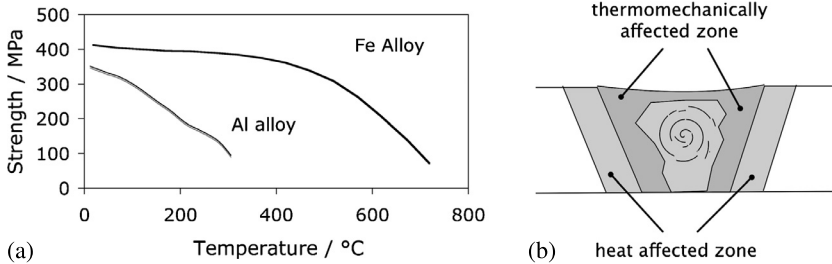


Figure 13.18 (a) Typical temperature dependence of the hot-strength of aluminium alloys and steels [21,22]. (b) Schematic of the microstructural zones expected in friction stir welds.

to its operation, Fig. 13.18b. The heat-affected zone, however, is as in conventional welds, except that the peak temperatures reached are lower than those associated with fusion welding. Furthermore, the HAZ tends to extend less into the parent plate and the austenite grains created by the heat are fine. The central nugget region containing the flow-pattern, the so-called

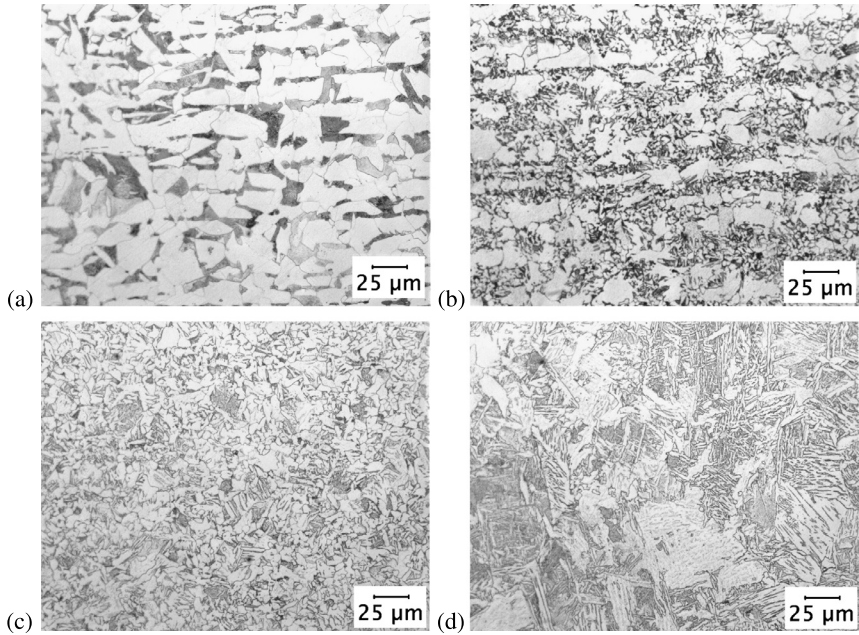


Figure 13.19 Typical microstructure of an FSW weld in a C-Mn steel. (a) Parent steel, with bands of allotriomorphic ferrite and pearlite. (b) Intercritically heated region of HAZ. (c) TMAZ (fine-grained region near stir zone). (d) Stir zone. Micrographs courtesy of P. Threadgill [23], reproduced with permission of Elsevier.

onion rings, is the most severely deformed region, although it frequently seems to dynamically recrystallise, so that the detailed microstructure may consist of equiaxed grains of austenite that transform on cooling. The layered (onion-ring) structure is a consequence of the way in which a threaded tool deposits material from the front to the back of the weld. It seems that cylindrical sheets of material are extruded during each rotation of the tool, which on a weld cross-section give the characteristic onion-rings.

The thermomechanically-affected zone lies between the HAZ and nugget; it too becomes fully austenitic and in spite of the deformation, for most steels, the austenite grain structure is of a recrystallised nature. The top surface of the weld has a different microstructure, a consequence of the shearing induced by the rotating tool-shoulder. Fig. 13.19 shows the variations in microstructure for a low-alloy steel, with banding retained in the partially austenitised region because the austenite forms in the manganese-rich regions of the chemically segregated steel. The thermomechanically affected zone shows a fine microstructure when compared with the stir

zone which reaches higher temperatures. Further details and dependence on alloy composition are discussed in [20].

It is likely that the friction stir welding method will be useful for steels when conventional methods, which have served well for so long, cannot be applied. This might include specialised applications [24]. The process is offered to join steel strip ends before being formed into a coiled tube [25]. The enhanced fatigue properties, reduced susceptibility to galvanic corrosion due to the absence of a filler, and the ability to join difficult-to-weld steels is the basis for the application of friction stir welding in this instance. A variation of the process is applied to steel cutting edges to improve the chipping resistance [26].

For large scale applications, the economic viability of the process has not been demonstrated. An analysis [27] indicates that the cost of the tool (£ $\approx$ 2900) would require it to survive a weld length of 120 m to achieve even a 20% reduction in production cost; present tools are not capable of achieving this [28,29]. The friction stir welding of ship steels reduces distortion, but current distortion levels with arc welding are manageable [30].

13.5 SUMMARY

Steels that cannot be welded because they are too strong or if their composition results in the production of brittle phases on the application of heat have their uses, for example in the manufacture of shafts, bearings, gears and armour. However, the ability to weld vastly increases the possibilities so it is not surprising that the un-weldable steels occupy a hardly noticeable proportion of the total volume of steels manufactured annually.

Wrought steels are produced using thermomechanical processing and careful heat treatment to ensure their properties. However, weld metal usually has to achieve matching or better properties in the cast state. This places limitations on the concentrations and variety of solutes that can be added to weld metal. Impurities such as oxygen will be present in most weld metals at greater concentrations than in the steel being joined. Some of the resultant non-metallic particles turn out to be useful in acting as intragranular nucleation sites that stimulate acicular ferrite which is good for toughness.

Although friction welding, which does not involve melting, has been known for some time, the radically different friction stir welding process has revolutionised the joining of aluminium and its alloys. Whether this process will prove as useful for steels remains to be demonstrated.

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BACKNOTES

1. Or in the case of friction stir welding to locally plasticise the steel.

CHAPTER 14

Nanostructured Steels

Abstract

The prefix 'nano' refers to a billionth of some quantity, whereas 'structure' refers to the way in which objects are organised. Nanostructure therefore is an arrangement of objects that are very small indeed. There are additional caveats in our case, because the individual objects are crystals that must fill space so that the resulting agglomerates can be used in engineering structures. In practice, this means that there is a huge density of intercrystalline interfaces that interrupt the ordered arrangements of atoms, making the steel incredibly strong. However, engineering design requires an appropriate combination of properties, economic viability and the ability to scale-up production. As a consequence, the few applications of nanostructures that have had limited success, can all be described within the space of this chapter.

14.1 INTRODUCTION

The idea that a fine structure is always good for ambient temperature properties, and in particular the expectation that strength and toughness should simultaneously improve, became engrained in metallurgy following the tremendous success of microalloyed, thermomechanically processed steels. We shall see, however, that unexpected difficulties arise when the grain size becomes so small that a substantial proportion of atoms is located at the boundaries. Conventional wisdom then fails, but before discussing the details, it is worth considering what constitutes a nanostructure.

Some guidance is necessary in order to make a rational use of the term 'nanostructure' in the present context. For example, the introduction of a large number density of closely spaced precipitates does not correspond to a nanostructure. Such precipitates would be coherent, their strain fields would interact, and as in the theory of concentrated solid solutions [1], the algebraic mean of their stress fields would tend to zero so that dislocation lines appear unpinned.¹

Fig. 14.1 shows how the grain boundary area per unit volume increases as the grain size is reduced. The relationship is inverse ($S_V = 2/\bar{L}$) so there is a sharp increase as $\bar{L} \lesssim 40$ nm. This also means that there is a corresponding dramatic change in properties as the grain size becomes smaller than about 40 nm (or $S_V \gtrsim 0.05 \text{ nm}^{-1}$) as illustrated in Fig. 14.1b. It follows that a grain size less than 40 nm is a good practical definition of when a steel can be said to be nanostructured.

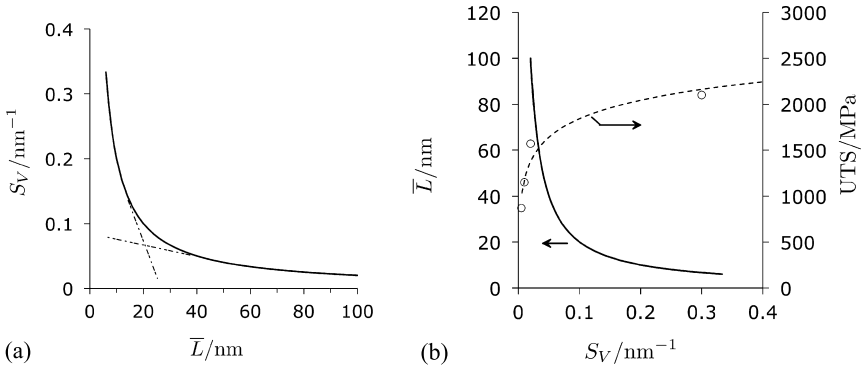


Figure 14.1 (a) Calculation of the grain boundary surface per unit volume (S_V) as a function of the mean linear intercept ($\bar{L}$) that defines the size of equiaxed grains. (b) The S_V - $\bar{L}$ data plotted alongside selected experimental data on the ultimate tensile strength as a function of $\bar{L}$ from a compilation by Bhadeshia [2].

14.2 WHY THE YEARNING FOR EXCEEDINGLY FINE GRAINS?

Extreme brittle behaviour occurs when fracture leads only to the creation of new surfaces that are flat on a microscopic scale. Some polycrystalline ceramics fall in this category, but the toughness increases as the grain size is reduced. This is because the material can be assumed to contain a crack that is effectively the grain size and the stress concentration at the atomically sharp crack tip scales with the grain size. Brittle cracks occur on planes that are easiest to fracture and are at the same time suitably oriented relative to the applied stress. Therefore, conventional wisdom is that a finer grain size results in the more frequent deflection of the crack tip into cleavage planes that are not optimally oriented with respect to the applied stress [3].

It also is possible that the re-initiation of cleavage in an adjacent grain requires a modicum of plasticity, which would add to the work of fracture. Indeed, the work of fracture in the case of steel which is tested in its brittle regime is about $14\text{--}80\text{ J m}^{-2}$ [4,5] compared with a typical surface energy of 2 J m^{-2} , indicating a strong role of microplasticity in the propagation of cleavage cracks.

Most steels contain a substantial quantity of allotriomorphic ferrite, and some cementite may be present at the ferrite grain boundaries. This cementite then fractures under stress and the resulting microcrack is the basis for cleavage crack extension in the microstructure as a whole [6]. The cementite thickness is found to scale with the ferrite grain size as illustrated in Fig. 14.2. Since the stress required to propagate the cleavage crack from the

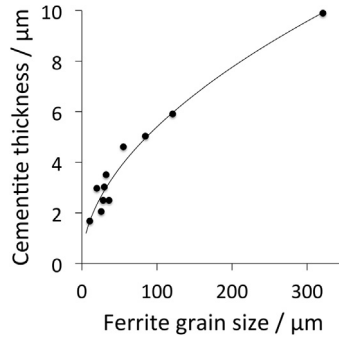


Figure 14.2 The coarsest observed cementite thickness versus the ferrite grain size in a variety of steels. Grain refinement leads also to thinner cementite particles so the toughness is expected to improve. Data from a compilation by Curry and Knott [4].

fractured cementite scales with the thickness^{-1/2}, the toughness increases as the ferrite grain size is refined [4]. Similar logic must apply to mixtures of bainitic ferrite and carbon-enriched retained austenite – the latter transforms into high carbon, untempered martensite which is then the source for cleavage fracture. It is well-established that an overall refinement of the mixture ($\alpha_b + \gamma$) leads to an improvement in toughness (Chapter 15).

Ductile fracture in tension usually involves the nucleation, growth of voids, which when they coalesce leads to ultimate failure. But tensile elongation contains two components, first the plastic strain that is distributed homogeneously so that the sample deforms uniformly. Deformation of course hardens the steel, but at some point the rate at which it hardens is not sufficient to compensate for the reduction in area, so the deformation becomes focused leading to necking. This is the point where the engineering stress reaches a maximum and fracture then becomes inevitable. The majority of elongation should be uniform in a good steel.

Fig. 14.3 shows two tensile tests conducted on fully ferritic steel. The strength obviously increases when the grain size is reduced, but there is no uniform elongation observed because plastic instability sets in as soon as yielding occurs. In contrast, the same steel when it has a coarser grain structure shows steady work hardening and considerable uniform ductility. The mechanism of work hardening is primarily the multiplication of dislocations. The fine-grained sample clearly lacks an ability to work harden because dislocation interactions may not have the space to develop in the same way as in a coarse grained sample, and because the dislocation density may be reduced by the defects sinking into adjacent boundaries. Therefore,

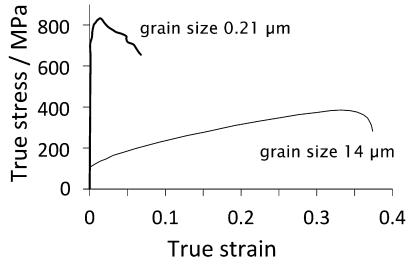


Figure 14.3 Tensile tests on interstitial-free ferritic steel with two different ferrite grain sizes. Selected data from Tsuji et al. [7].

a serious shortcoming of ultra-fine grains is the loss of work hardening capacity, which any design procedure must address if nanostructured steels are to be utilised.

14.3 PRODUCTION OF NANOSTRUCTURED STEEL

14.3.1 Shape preserving deformations

Nanostructured steels are often made in laboratories using severe plastic deformation [8]. The plastic deformation that can be achieved without fracture is often in excess of a von Mises strain of $\epsilon_{vM} = 20$.² This obviously cannot be while the material is in tension, so ingenious processes have been invented to maintain the overall shape without inducing fracture.

A particular shape-preserving process is illustrated in Fig. 14.4a where the constrained sample material is sheared by the conjoint action of torsion and compression. The shear strain per rotation is the displacement $2\pi r$ divided by the thickness l , where r is the radial distance; it follows that the total shear strain for N rotations is given by [9]:

$$\gamma = 2\pi \frac{rN}{l} \quad \text{with} \quad \epsilon_{vM} = \frac{\gamma}{\sqrt{3}}. \quad (14.1)$$

The equation implies that the shear strain is zero at the centre but this is inconsistent with observations because there is likely to be some sliding involved between the sample and the torsion support or rotating member [8].

The torsion test-sample is typically less than a centimetre in diameter and a millimetre thick. While such samples are big enough for structural characterisation, the only assessment of mechanical properties is usually with hardness testing. Fig. 14.4b, c shows the *microstructure* obtained in severely sheared samples of Armco iron and a fully pearlitic rail-steel. The

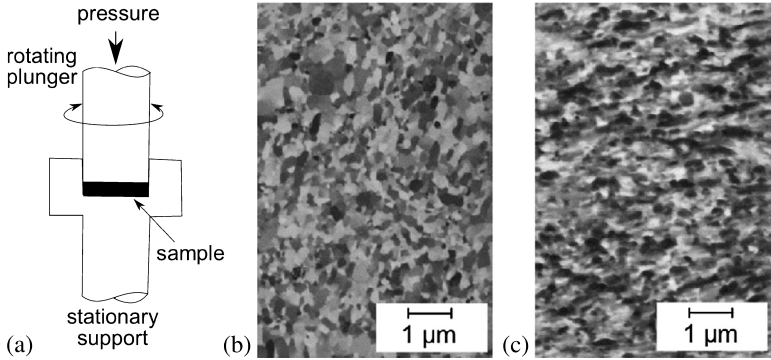


Figure 14.4 (a) Schematic diagram of compression-torsion severe plastic deformation equipment. The sample experiences severe shear strains and because of the constraint, it retains its essential shape. (b) Commercially pure iron torsion-deformed to $\epsilon_{vM} = 36$. (c) Fully pearlitic steel torsion-deformed to $\epsilon_{vM} = 16$. Adapted images from Wetscher et al. [10], reproduced with the permission of Elsevier.

emphasis on the adjective ‘micro’ is because the deformation failed in both cases to achieve a structural scale less than 100 nm for the pearlitic steel and 250 nm in the Armco iron. It is not therefore surprising that the Armco iron achieved a hardness of just 350 HV following $\epsilon_{vM} = 36$. In the case of the pearlite, the deformation led to the fragmentation of the cementite, which was still present after $\epsilon_{vM} = 16$, with a final hardness of 612 HV.

These properties are a consequence of both the fine structure and the defects such as dislocations, but they are not particularly interesting since these levels of hardness can be achieved routinely through heat treatment. The technique therefore is limited to basic studies. Although publications (e.g. [8]) refer to the material produced using torsion as ‘bulk nanostructured’, it is neither bulk nor nanostructured.

Equal channel angular processing [11] can be applied to somewhat larger samples, Fig. 14.5. The sample is forced through a die such that it experiences redundant work by being bent through an angle ϕ , but with the bend propagating along the entire length so that the original shape is recovered. The equivalent strain is then given by [12]:

$$\epsilon_{vM} = \frac{2}{\sqrt{3}} N \cot \{\phi/2\}. \quad (14.2)$$

The process can be repeated on the same sample in order to accumulate strain. The relatively large samples that can be processed permit a better characterisation of the mechanical properties. Studies on austenitic stainless

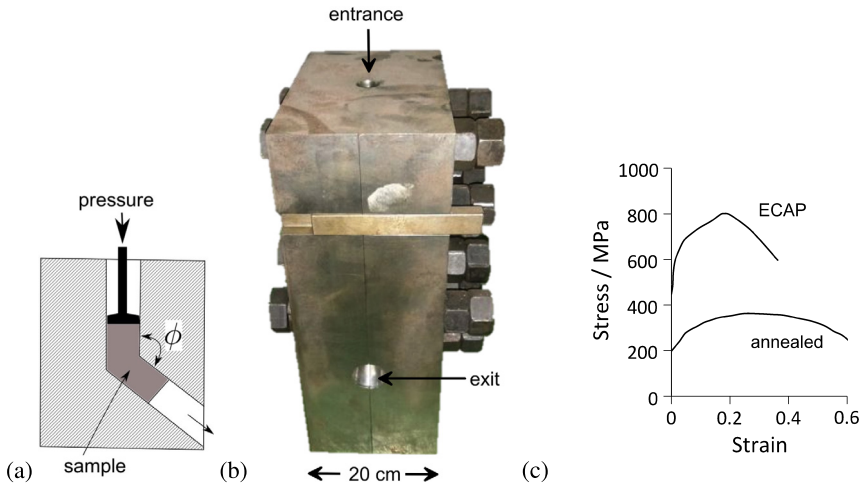


Figure 14.5 (a) Schematic diagram of equal channel angular processing (ECAP). The steel is introduced at the top and is deformed through the angle ϕ but exits the die with the same shape that it started with. The process can be repeated if desired. (b) An actual ECAP die for producing severely deformed cylindrical samples. The die is in two halves which are bolted together for inspection and maintenance of the cavity. (c) Comparison of the behaviour in tension of a mild steel containing 0.08C wt%, in its annealed and processed conditions (selected data from Fukuda et al. [14]).

steel [13] suggest that there is a deterioration in the fatigue properties even though the yield strength increases due to the refinement of the structure. Similarly, a 0.08C wt% ferritic steel exhibited a refinement of microstructure to about $0.2\mu\text{m}$ size, an increase in strength but a large decrease in elongation (Fig. 14.5c). The strength that is obtained is not remarkable and once again, is routinely accessible in mass produced commercial steels.

Accumulative roll-bonding [7,15] involves plane strain deformation by rolling, of two separate pieces of steel which become cold-bonded as they emerge from the rolls. The final thickness is identical to that of the individual pieces (Fig. 14.6). The von Mises equivalent strain for this case is [16]:

$$\epsilon_{vM} = N \times \frac{2}{\sqrt{3}} \ln \left\{ \frac{1}{2} \right\} \quad (14.3)$$

where N is the number of times the rolled sample is re-introduced into the roll after stacking.

Accumulative roll bonding is an interesting process because it can in principle be scaled up and can be implemented on conventional large

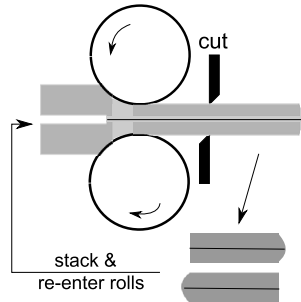


Figure 14.6 Schematic description of accumulative roll bonding. Separate samples of steel are cold-welded by rolling, the emerging steel is the cut, cleaned, stacked and re-rolled a number of times to accumulate plastic strain.

Table 14.1 Some properties of steel made using the accumulative roll bonding process

Material	N	UTS / MPa	% elongation	Reference
Interstitial-free steel	0	274	57	[16]
Interstitial-free steel	6	751	6	[16]
Interstitial-free steel	0	255	51	[17]
Interstitial-free steel	8	850	3	[17]
Fe-24Ni-0.3C wt% TRIP steel	0	1017	153	[18]
Fe-24Ni-0.3C wt% TRIP steel	6	1395	39	[18]

rolling equipment that exists already in industry. Obviously, the productivity of conventional single-pass rolling would not be matched but the cost-benefit analysis depends on whether exceptional properties can be achieved. Table 14.1 lists some of the mechanical properties reported for interstitial-free steel. It is not surprising that the strength increases but ductility decreases since the material is essentially in a cold-deformed state following accumulative rolling, so that much of the ductility that existed in the annealed state is exhausted. It can of course be recovered by annealing but at the cost of strength.

14.3.2 Shape altering deformations

One of the most successful engineering products has been steel wire and rope made from pearlitic steels. Attempts have been made to take the process of wire drawing to extremes in the hope of greatly enhancing the strength.

One such product is a wire with a strength in excess of 5 GPa [19]. The chemical composition is Fe-0.2C-0.8Si-1.5Mn wt% and the alloy must be

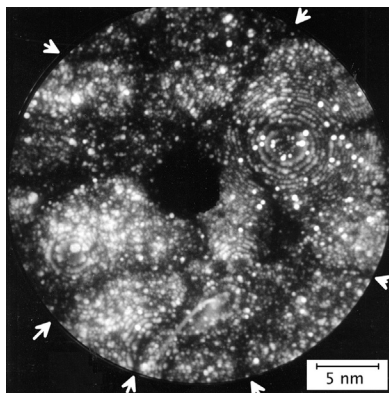


Figure 14.7 Field-ion microscope image of wire in its cold drawn condition, with the positions of some of the cell boundaries highlighted by the arrows. The black hole approximately in the center is an artefact of the imaging technique. Each dot represents the position of an atom.

made with sufficient impurity control so that the drawability is not compromised by inclusions, given the final diameter of the wire is less than $10\text{ }\mu\text{m}$. The processing begins with 10 mm diameter rods which are initially martensitic; intercritical annealing induces the formation of layers of austenite which become enriched in carbon. On quenching to ambient temperature, a mixture of martensite tempered at the intercritical annealing temperature, untempered high-carbon martensite formed on cooling and retained austenite results [20].

Following wire drawing to a true strain of 8.85, the initial microstructure of martensite and tempered martensite becomes both chemically and mechanically homogenised by the mechanical work and acquires an ultra-fine dislocation cell structure as illustrated in Fig. 14.7. It has been shown that much of the strength of the wire comes from this fine structure [21]. Because the cross section of the wire is only $10\text{ }\mu\text{m}$, it behaves in a ductile manner, failing in tension by necking, in spite of its strength.

Obtaining strength by deformation has the advantage that the material becomes insensitive to size as long as the deformation is homogeneous, which is mostly the case when dealing with wires. Fig. 14.8a shows that the strength of the wire varies a lot less with diameter, than does the strength of tiny single crystals of iron in which case strength relies on perfection through the absence of dislocations. Flawlessness typical in small crystals cannot be maintained as the size increases because of entropy considerations [22]; this of course is the reason why carbon nanotubes and graphene

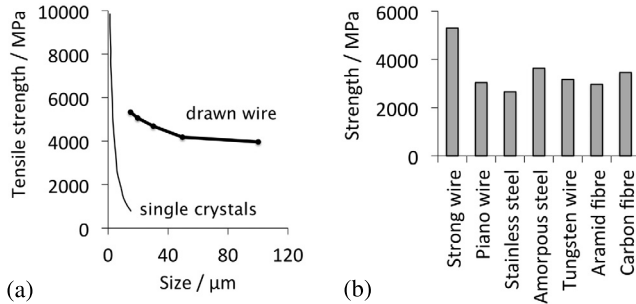


Figure 14.8 (a) A comparison of the size sensitivity of strength, for single crystals of iron (whiskers, Chapter 2) and for wire in its cold-deformed state. (b) A comparison of the strength of the cold-drawn wire against other fibres.

are never going to have the strength levels measured on the nanometre dimensions (section 2.9.2).

In terms of strength, steel wire competes well with a number of other wires or fibres, Fig. 14.8b, although when it comes to specific strength which is normalised by the density, the polymer and carbon fibres reign supreme. None of these materials on their own can be large in all dimensions. In order to produce a nanostructured material that is bulky in all three dimensions requires a different approach, based on solid-state phase transformation.

14.3.3 Nanostructure without deformation

It often is necessary to make components that are three dimensional shapes of substantial dimensions and with a combination of properties, including strength, that enables technology. The material and production cost must be reasonable if large quantities of such steel are required. As we shall see, a steel design is possible, whose structure is intricately subdivided by interfaces and yet is not generated by deformation or rapid cooling, could fulfil these demanding criteria.

A nanostructured material is here defined as one containing an exceptionally large density of strong interfaces, so much so that the strength exceeds 2 GPa – this would require approximately 100 million square metres of interface inside one cubic metre of material [23]. The desire for such materials in the engineering context comes from the yearning for pushing engineering marvels such as the jet engine to extremes of efficiency and performance. Strong nanostructured materials must nevertheless address the following issues if they are to be utilised:

- (i) It should ideally be possible to make samples which are large in all dimensions, not simply wires or thin sheets; this is necessary in order to manufacture components with complex shapes, such as bearings, shafts with keyways and armour.
- (ii) The processing should not involve rapid cooling since the structure would not then be uniform in large sections. Harmful residual stresses and distortion often accompany rapid cooling.
- (iii) The processing should not involve deformation except when the steel is fully austenitic. Deformation limits the shapes that can be produced and the ductility of the final structure is compromised by cold deformation.
- (iv) The material concerned must be cheap to produce if it is not to be limited to niche applications. A good standard for an affordable material is that its cost must be similar to that of bottled water when considering weight or volume.
- (v) Unlike formable steels where crystallographic texture is a key performance parameter, the strong steel needs to be mechanically isotropic for applications where the integrity relies on the whole object rather than a specific feature of that object.

It should be admitted at the outset that strong steels of this kind are unlikely ever to be exploited on a large scale in the context of the 1.4 billion tonnes of steel used annually, because high strength can only be exploited if lower cross sections can be tolerated. Reducing the cross section of a component compromises properties such as the engineering stiffness, the susceptibility to buckling, the corrosion life etc. But for specialist applications such as bearings where the world wide production amounts to just 60,000 tonnes, but represent components critical in dealing with rotational motion, the value added by specialist steel determines the success of the product.

It turns out that it is possible to accommodate all of the utilisation issues listed above, with the design of a nanostructured steel in which the effective size of each crystal is finer than that of a carbon nanotube [24–27]. The fine crystals are generated by solid-state phase transformation with the following design rules:

- (a) the material must have a significant work-hardening mechanism to avoid the early onset of plastic instability once yielding occurs;
- (b) the transformation must be induced at a low homologous temperature³ in order to avoid coarse microstructures;
- (c) there should be a mechanism for avoiding an excessive release of heat due to the enthalpy of transformation since in large components, this

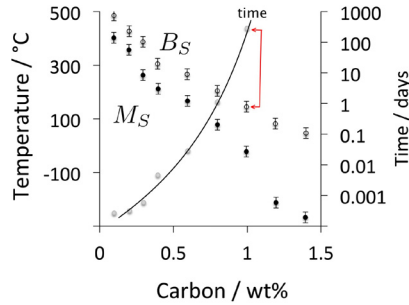


Figure 14.9 Calculated transformation-start temperatures in Fe-2Si-3Mn wt% steel as a function of the carbon concentration, together with the calculated time required to initiate bainite. The red arrow correlates $B_S = 140^\circ\text{C}$ with a transformation time of about one year. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this chapter.)

heat raises the temperature of the steel and hence negates the need to transform at a low temperature. This effect, where the temperature of the steel rises as the crystal structure changes is known as *recalcescence*.

- (d) The transformation should occur at a slow rate to allow any residual heat of transformation to dissipate, thus maintaining the intended transformation temperature.

Crystals that are fine enough cannot be generated by reconstructive transformation because the atoms are too mobile at the temperature where these reactions occur. And in the case of displacive transformations, martensite can be ruled out for large components because its formation either requires a high cooling rate or sufficient alloying to ensure sufficient hardenability. Displacive transformations have the advantage that the energy associated with the shape deformation is stored within the material, thus reducing the enthalpy change during transformation, and hence the propensity to recalcescence. The bainite transformation is an ideal candidate – after all large power plant turbines are able to be made with a bainitic microstructure by slow cooling from the austenite phase field. Furthermore, the rate of the reaction can be controlled more effectively than is the case for martensite.

The question then arises as to what is the lowest temperature at which bainite can form whilst at the same time avoiding the formation of martensite. The fundamental theory for calculating these transformation temperatures is routinely available [28,29].⁴ Fig. 14.9 shows some example calculations for a steel containing 2Si-3Mn wt%, that illustrate how the B_S

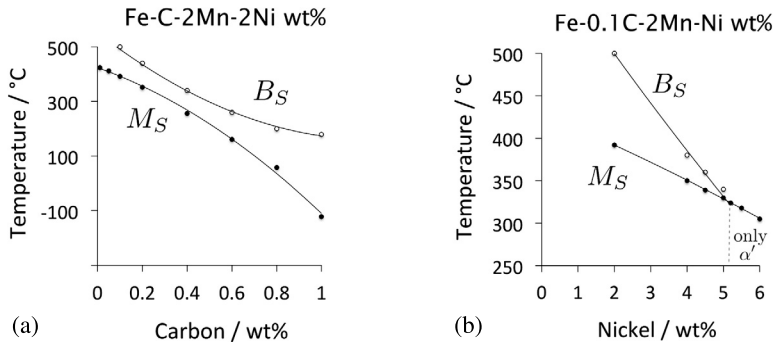


Figure 14.10 Calculated variation in the martensite and bainite-start temperatures as a function of composition.

and M_S temperatures vary as a function of the carbon concentration of the austenite. Surprisingly, there appears to be no lower limit to the temperature at which bainite can be generated but the time required to initiate the reaction increases dramatically as B_S is reduced, so much so that it would take about a year at 140°C (red arrow on Fig. 14.9).

One interesting feature is that the martensite-start and bainite-start temperatures are both suppressed by the addition of carbon (Fig. 14.9). A similar result is obtained for a different steel, Fig. 14.10a. However, if an attempt is made to suppress B_S using substitutional solutes in low carbon steel, then $B_S \rightarrow M_S$ and at some concentration only martensitic transformation is possible. In other words, martensite will precede bainite [30]. The reason for this is that substitutional solute do not partition during displacive transformations so bainite and martensite are similarly affected. However, the nucleation of bainite requires the partitioning of carbon, which adds to the available driving force, one of the reasons why bainite forms at higher temperatures than martensite (which is diffusionless in nucleation and growth). However, the difference in kinetics vanishes if the carbon concentration is reduced and hence the gap between M_S and B_S decreases to the point where it vanishes [28,31]. The bainite transformation then does not occur at all.

Apart from their role in the suppression of transformation temperature, substitutional solutes have other roles to play in achieving the totality of requirements for nanostructured steels. Sufficient silicon must be added so that the partitioning of carbon from the supersaturated bainitic ferrite does not lead to cementite precipitation. The carbon then enriches the

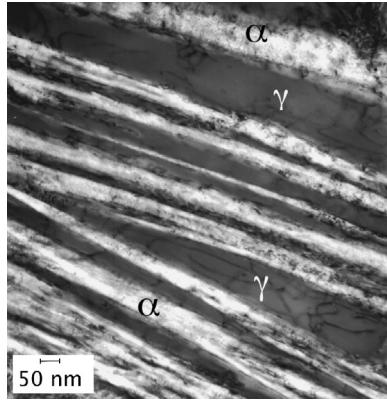


Figure 14.11 A high magnification image of Fe-0.98C-1.46Si-1.89Mn-0.26Mo-1.26Cr-0.09V wt%, transformed at 200°C for 15 days. A corresponding optical micrograph would show the slender plates of ferrite in many different orientations, so the material exhibits isotropic mechanical properties. Stereological measurements show that the true width of the plates is in the range 20–40 nm, which compares with the width of carbon nanotubes.

residual austenite and stabilises it to ambient temperature. A small concentration of molybdenum is added to prevent grain boundary embrittlement by phosphorus [32–37], and chromium to retard the pearlite reaction during cooling to B_S .

Fig. 14.11 shows the structure obtained following isothermal transformation at 200°C, consisting of platelets of bainitic ferrite only 200–400 Å thick, with intervening regions of the parent austenite [24,25,27]. This *retained* austenite is important because when it undergoes stress or strain-induced martensitic transformation, it enhances the work-hardening capacity of the material, thereby avoiding the usual problem of fine-grained metals where ductility diminishes as the grain size is reduced.

The bainite obtained by low-temperature transformation is harder than ever achieved, with values in excess of 700 HV. Some strength, ductility and toughness data are illustrated in Fig. 14.12. The simple heat treatment involves the austenitisation of a chunk of steel (at say 950°C), followed by a gentle transfer into an oven at the low temperature (say 200°C) to be held there for ten days or so. There is no rapid cooling – consequential residual stresses are avoided. The size of the sample can be large because the time taken to reach 200°C from the austenitisation temperature is much less than that required to initiate bainite. This is an important commercial

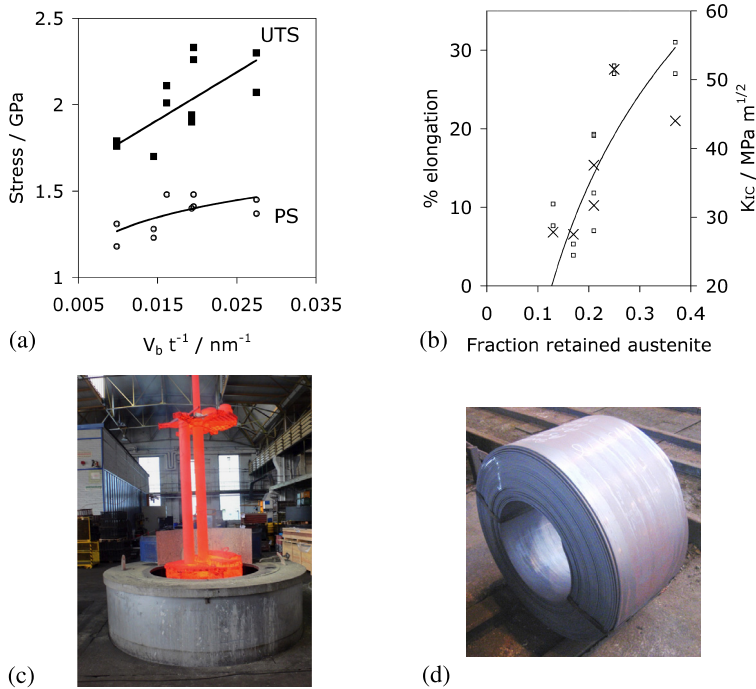


Figure 14.12 Some mechanical properties of a few nanostructured bainitic steels. (a) The ultimate tensile strength and 0.2% proof strength as a function of the volume fraction of bainitic ferrite (V_b) divided by the ferrite platelet thickness t . (b) Ductility (points and curve) and toughness K_{IC} represented as crosses. (c, d) Large scale manufacture of nanostructured bainite.

advantage. And the material can be manufactured in huge quantities with uniform properties across large dimensions (Fig. 14.12c, d).

There are significant limitations to such steels, discussed elsewhere in more detail [29], but which can be summarised as follows:

- (a) It is not possible to weld the steel except by using highly specialised techniques which cannot reasonably be applied in practice. This is because the steels of this kind rely on a high carbon concentration so brittle martensite is produced in the heat-affected zones of the weld.
- (b) Although the fracture toughness is good, the Charpy impact toughness is not, for reasons related to the nature of the test [38]. Since the Charpy test forms the basis of many acceptance criteria, applications of the steel are limited to cases where such tests are not a deciding factor, for example armour.

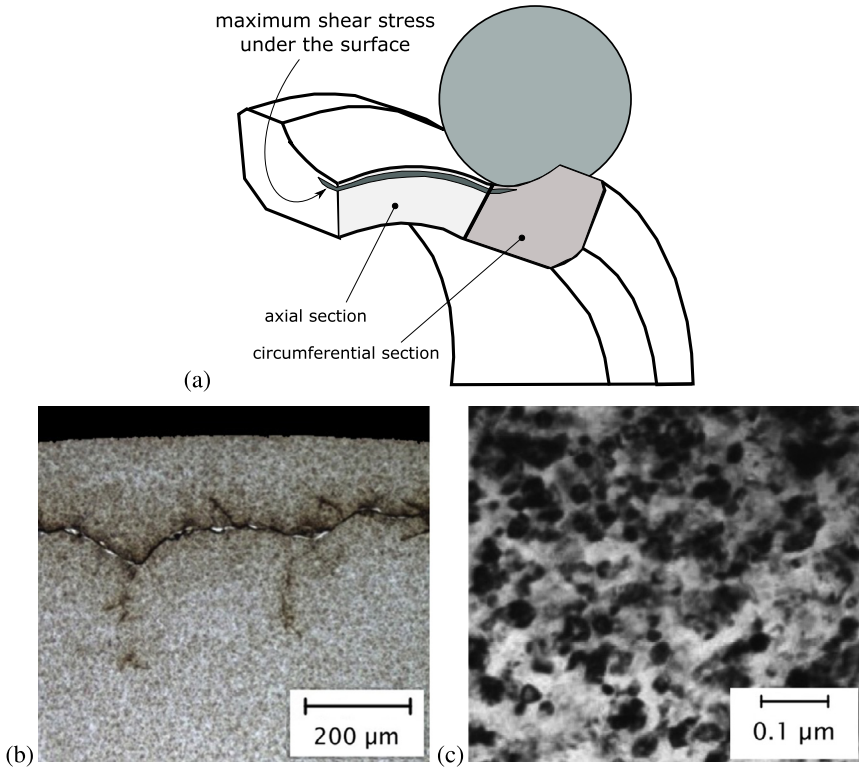


Figure 14.13 (a) Schematic illustration of a ball traversing a bearing raceway; the contact pressure causes the shear stress to be maximum below the surface as illustrated in the axial section. (b) A sub-surface crack showing small, disconnected white-etching regions. After Evans et al. [39], with permission of Elsevier. (c) High resolution image of a white-etching region showing the nanostructure that develops. After Evans et al. [40], with permission of Elsevier.

- (c) The nanostructured steel is not stable at high temperatures ($>400^{\circ}\text{C}$) over long periods because of the tendency for the retained austenite to decompose into a mixture of cementite and ferrite.

Some of these weaknesses apply to all nanostructured metals.

14.4 DETRIMENTAL NANOSTRUCTURES IN STEELS

There are particular steels that have to sustain millions of locally applied pulsating loads at contact stress levels that are typically 2 GPa. Bearings fall into this category – when a rolling element moves over a particular location on the raceway (Fig. 14.13a), it induces a momentary system of Hertzian

stresses that reach a maximum *below* the contact surface. This stress pulse is felt by a point on the bearing on each occasion that the rolling element traverses, as a combination of cyclic torsion and uniaxial compression superimposed in phase.

Bearing steels are relatively brittle because they have to be hard (≈ 650 HV) in order to sustain the high contact stresses. A typical chemical composition contains 1C–1.5Cr wt% and a microstructure of cementite particles in a lightly tempered martensitic matrix [41]. As a result, micro-cracks develop and the crack faces, when suitably oriented with respect to the stress, beat against each other. This localised mechanical deformation causes the cementite to dissolve and greatly refines the original microstructure. When examined in an optical microscope, these mechanically homogenised regions respond less to chemical attack by etchants compared to the surrounding unaffected material. This is why they are called *white-etching regions*, Fig. 14.13b. Because of the refined structure (Fig. 14.13c) and the fact that the carbon that was originally in the cementite is now in solution, the white-etching regions are extremely hard, typically in excess of 1000 HV. The original crack that initiated the rubbing of crack faces therefore propagates as the white matter develops. When the crack reaches the surface, spalling occurs leading to bearing failure.

White matter of the kind described here, and varieties in which the deformation involves both rolling and sliding, occurs in many different applications, for example, on rails and during machining.

14.5 SUMMARY

Studies of nanostructured steels have revealed many new phenomena not described here, for example an inverse Hall-Petch effect, the nature of the equilibrium between tetragonal ferrite and austenite and the peculiarly small work hardening capacity of single-phase nanostructured metals. Some of these ideas fire the imagination but the practical consequences of these steels are negligible to date. This is because strength is not the only property of consequence in design, it is usual that a basket of performance parameters must reach specified levels to ensure integrity during service. Many of the processes used are not capable of being scaled; even the nanostructured bainite which does not have this limitation has few applications because of the lack of weldability. So from a commercial point of view, the nanostructured steels for which information is openly available, are not particularly

relevant. These conclusions sound pessimistic but the purpose here is to educate and hopefully solutions may or may not emerge in the future which change the paradigm, but that as they say, is food for thought.

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BACKNOTES

1. The level of strengthening expected would therefore be small. Nickel superalloys are an example, where high-performance versions contain some 70% by volume of coherent γ' precipitates. These contribute to strength but not to the levels typical of the strongest of nanostructured materials.
2. The von Mises equivalent strain is given by $\epsilon_{vM} = \frac{2}{3}\sqrt{\frac{3}{2}(\epsilon_{xx}^2 + \epsilon_{yy}^2 + \epsilon_{zz}^2) + \frac{3}{4}(\gamma_{xy}^2 + \gamma_{yz}^2 + \gamma_{zx}^2)}$ where ϵ_{xx} are normal and γ_{xy} are normal and shear strains etc.
3. A homologous temperature is the absolute temperature divided by the absolute melting temperature of the material concerned.
4. The algorithms for doing this are freely available on www.msm.cam.ac.uk/map/mapmain.html.

CHAPTER 15

Modelling of Structure and Properties

Abstract

Mathematical models are not a panacea in the study or design of steels. This is because we simply do not understand many aspects of physical metallurgy, nor can we express all that is known into a quantitative framework. There is no 'theory of everything' in any subject. But the fact is that models are useful in reducing the amount of work necessary to create new steels, sometimes quite dramatically, and at other times in pointing experiments into the right direction. We discuss here the essence of the methods now available to cover a wide range of structure and properties.

15.1 INTRODUCTION

There is much to be gained by creating theory that is experimentally verifiable and which does not compromise with the complexity of technology. Such theory can, and is, used routinely in the design of new steels [1–3]. This is particularly so in the case of alloys where the number of variables involved is sufficiently large to make the problem interesting and the outcomes novel and tangible. However, it is worth emphasising at the outset that mathematical models are rarely sufficiently robust or versatile enough to enable complete solutions. The primary reason for their limitations is our inability to express everything using the language of mathematics. The models that exist are mere tools, rather like microscopes, which help understanding and reduce the task in creating new alloys.

Models can be classified into four main categories [4]:

- (i) those which lead to an unexpected outcome that can be verified, for example, the creation of the δ -TRIP steel concept [5] or insight into the barriers to the formation of solid solutions in steel by the mechanical alloying process [6].
- (ii) Those that are created or used in hindsight to explain diverse observations; the quasicchemical model that explains why the diffusivity of carbon in austenite is particularly sensitive to concentration is one such case [7].
- (iii) Existing models which are adapted or grouped to design materials or processes, one example being the design of blast-resistant naval steels [8,9].

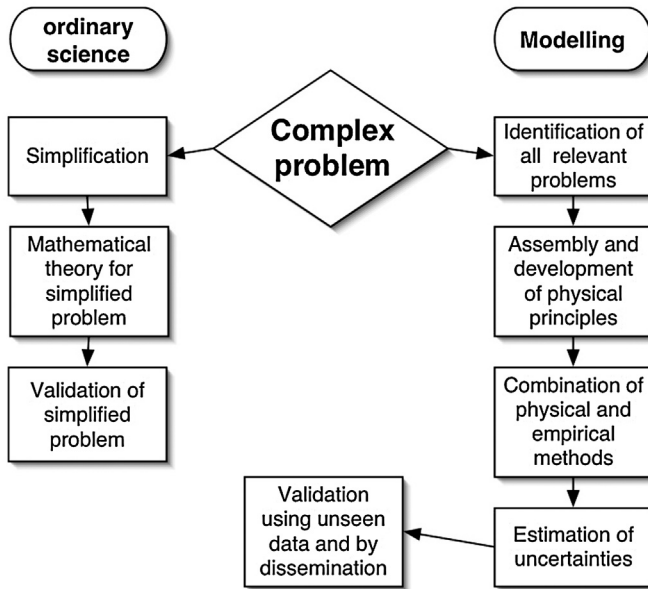


Figure 15.1 Defining qualities of a model compared with the conventional scientific method.

- (iv) Models that are used to express data, reveal patterns, or for implementation in control algorithms; examples that fall in this category have been reviewed [10].

These categories highlight the applications of models, with the emphasis being on quantitative expression. Fig. 15.1 illustrates how the concept of mathematical modelling as described here, differs from ordinary science, which also yearns for the mathematical formulation of Nature. The ordinary scientific method has the purpose of revealing mechanisms to throw light on the workings of nature with the possibility of making unexpected discoveries [11]. However, this scheme often involves simplification to a point where complexity, which also is a part of Nature is dismissed. The claim in cosmology that there is a ‘theory of everything’, neglects the detail that matters to us in our every day lives; and yet, it excites because there may be a plausible explanation of the origins of humanity.

Modelling, in contrast, deals with technology where simplification or dissociation of the problem can make the problem mundane. The method excites when it leads to tangible products that can advance technology. We

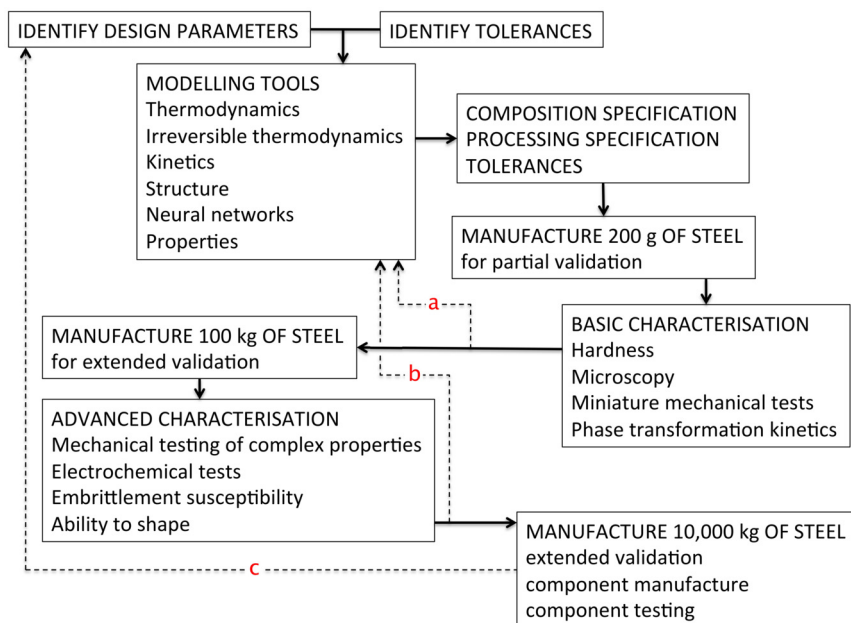


Figure 15.2 Procedure for the efficient design of novel steels. Paths a, b, c are return points in case the ideas generated at the early stages do not work. The costs of the development increase as the samples are scaled to component level testing. The costs of failure also increase in the order of the return paths $a < b < c$.

shall discuss the mathematical methods in the context of steel development although many of the concepts are of generic value.

The process of modelling begins with a need that cannot be met with existing technologies. There is a wide consultation to identify design parameters and tolerances for the problem concerned, Fig. 15.2. For example, in the case of a hydrogen resistant steel to be developed for undersea applications, two targets might be set, one of which exceeds current technologies and the other much more ambitious and more risky. The thickness of the components produced by forging might range from 100–150 mm so the steel would need to be designed to be insensitive to a wide range of cooling rates, with the latter simulated using finite element methods. The strength, ductility, Charpy toughness to sub-zero temperatures, the crack-tip opening displacement (another standard measure of toughness), the resistance to hydrogen, weldability with and without post-weld heat treatment and structural stability to service up to 250°C over a period of some 25 years, would all need to be specified at the outset.

The modelling tools are then assembled and developed, and if necessary combined with empirical techniques and experience in order to create an overall procedure, taking considerable care to estimate uncertainties. Validation of the model is by testing against unseen data which either are in the public domain or available from industrial partners, is useful at this stage in order to gain confidence in the design procedure. Any principles embedded in the software need to be exposed to a wide range of scenarios to assess its limits.

Design in complex problems usually leads to many solutions for the same specification. Therefore, a screening process begins with the manufacture of small samples of steel, typically 200 g each, which are then processed in a limited way. These samples can usually be made in a University environment. A variety of elementary tests can then be carried out to see whether the concepts are proven. If not, then there is a return path to the modelling ('a' in Fig. 15.2), but it may turn out that it simply is not possible to meet the design criteria in which case there has to be a rethink of the technology. Assuming this is not the case and that the small melts show promise, proper mechanical characterisation requires larger quantities of steel that may also need to be thermomechanically processed, so 100 kg samples can be ordered from specialist suppliers. If all is well at that time the considerable resources necessary for component level testing are justified.

In this way, the technological goal is hopefully achieved, and problems may be identified with the models, which in the longer term need to be resolved using the scientific approach. Like ordinary science, the proper use of models leads to insight, but by tackling complexity at the level that is posed, it can reveal issues which are lost during the simplification characteristic of ordinary science. For example, it is unlikely that the existence of a detrimental phase in high-strength steel weld deposits would have been revealed without the creation of a model which uncompromisingly accounts for the full range of variables that influence the Charpy toughness [12–16].

It is important to understand that modelling is not simply an application of a computer program, but rather the combination of a deep understanding of physical principles and quantitative scientific method.

These issues are illustrated by two examples concerning steels, one an elementary microstructure model, and the other dealing with the mechanical properties of mixed microstructures.

The first example illustrates how phase transformation theory can be used in the optimisation of a microstructure consisting of a mixture of bainite and austenite. The problem is first identified to be associated with

the occurrence of large regions of carbon-enriched austenite which are detrimental to toughness. The mechanism of transformation is then utilised to reduce the fraction of this detrimental phase. The major component of this model is the physical metallurgy of the transformation. The model is quantitative, in the sense that it requires the calculation of a phase boundary for a multi-component steel.

The second example helps to understand what is at first sight a strange result, that the strength of a mixed microstructure of martensite and bainite peaks as a function of the volume fraction of martensite. It illustrates how a variety of approximations can be made in order to formulate a model, both by searching the published literature for relationships and data, and by adopting a pragmatic approach.

15.2 EXAMPLE 1: ALLOY DESIGN

High-strength bainitic steels have not in practice been as successful as quenched and tempered martensitic steels, because the coarse cementite particles in bainite are detrimental for toughness (Chapter 6). However, it is now known that the precipitation of cementite during bainitic transformation can be suppressed. This is done by alloying the steel with about 1.5 wt% of silicon, which has a low solubility in cementite and therefore retards its growth.

An interesting microstructure results when this silicon-alloyed steel is transformed into upper bainite. The carbon that is rejected into the residual austenite, instead of precipitating as cementite, remains in the austenite and stabilises it down to ambient temperature. The resulting microstructure consists of fine plates of bainitic ferrite separated by carbon-enriched regions of austenite (Fig. 15.3).

The potential advantages of the mixed microstructure of bainitic ferrite and austenite can be listed as follows:

- (i) Cementite is responsible for initiating fracture in high-strength steels. Its absence during plastic deformation makes the microstructure more resistant to cleavage failure and void formation.
- (ii) The bainitic ferrite is almost free of carbon, which is known to embrittle ferritic microstructures.
- (iii) The microstructure derives its strength from the ultrafine grain size of the ferrite plates, which are less than $1\text{ }\mu\text{m}$ in thickness. It is the thickness of these plates which determines the mean free slip distance, so that the effective grain size is less than a micrometre. This cannot

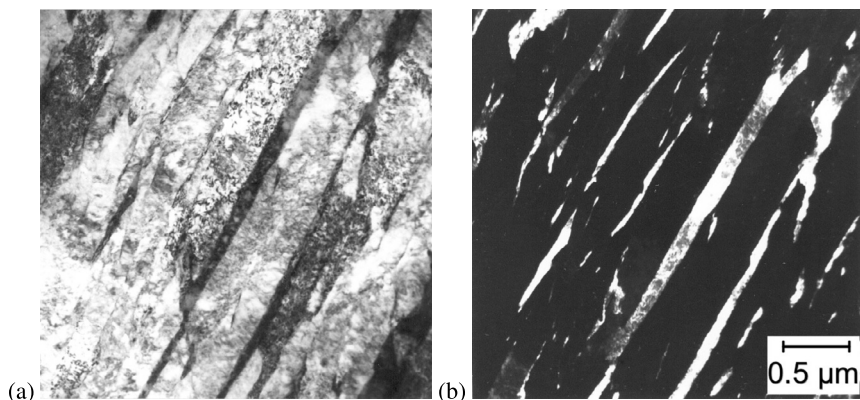


Figure 15.3 Transmission electron micrograph of a mixture of bainitic ferrite and stable austenite. (a) Bright field image. (b) Retained austenite dark field image.

be achieved by any other commercially viable process. It should be borne in mind that grain refinement is the only method available for simultaneously improving the strength and toughness of steels.

- (iv) The ductile films of austenite which are intimately dispersed between the plates of ferrite have a crack blunting effect. They add to toughness by increasing the work of fracture as the austenite is induced to transform to martensite under the influence of the stress field of a propagating crack. This is the TRIP, or transformation-induced plasticity effect (Chapter 12).
- (v) The diffusion of hydrogen in austenite is slower than in ferrite. The presence of austenite can, therefore, improve the stress corrosion resistance of the microstructure.
- (vi) Steels with the bainitic ferrite and austenite microstructure can be obtained without the use of any expensive alloying additions. All that is required is that the silicon concentration should be large enough to suppress cementite.

In spite of these appealing features, the bainitic ferrite/austenite microstructure does not always give the expected good combination of strength and toughness. This is because the relatively large ‘blocky’ regions of austenite between the sheaves of bainite (Fig. 15.4) readily transform into high-carbon martensite under the influence of stress. This untempered, hard martensite embrittles the steel.

The blocks of austenite clearly are detrimental to toughness, and anything that can be done to reduce their fraction, or increase their stability to

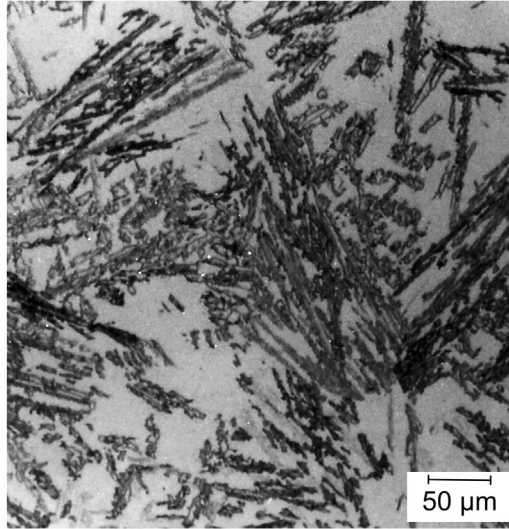


Figure 15.4 Optical micrograph of upper bainite in a Fe-0.43C-3Mn-2.02Si wt% showing the large blocks of untransformed retained austenite between the dark sheaves of bainite.

martensitic transformation, would be beneficial. Both of these effects are controlled by the T'_0 curve of the phase diagram (Chapters 5 and 6). This curve determines the composition of the austenite at the point where the reaction to bainite stops. By displacing the curve to larger carbon concentrations, both the fraction of bainite that can form, and the carbon concentration of the residual austenite can be increased. Modifications to the T'_0 curve can be achieved by altering the alloy composition. It is therefore necessary to calculate the effect of substitutional solutes on the T'_0 curve.

15.2.1 Calculation of the T_0 curve

At the T_0 temperature, the free energies of austenite and ferrite of the same chemical composition are identical (Chapter 6). A simplified method is for the calculation of the T_0 temperature is presented here for multi-component steels. At the T_0 temperature point, the change in free energy as austenite transforms to ferrite is zero:

$$\Delta G^{\gamma \rightarrow \alpha} = 0. \quad (15.1)$$

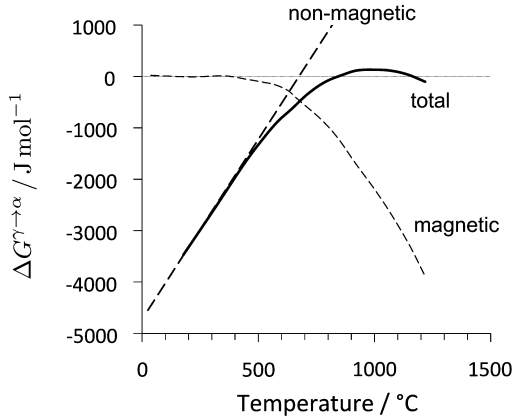


Figure 15.5 Zener's factorisation of the free energy difference between the austenite and ferrite phases into magnetic and non-magnetic components.

Table 15.1 Approximate representations of the free energy components for the $\gamma \rightarrow \alpha$ transformation in pure iron

Function	a	b	Temperature range
$\Delta G_{NM}^{\gamma \rightarrow \alpha} = a + bT \text{ J mol}^{-1}$	-6660	7	$900 > T > 300 \text{ K}$
$\Delta G_{NM}^{\gamma \rightarrow \alpha} = a + bT \text{ J mol}^{-1}$	650	-1	$900 > T > 620 \text{ K}$
$\Delta G_M^{\gamma \rightarrow \alpha} = a + bT \text{ J mol}^{-1}$	0	0	$T < 620 \text{ K}$

Zener argued that the free energy difference can be factorised into two components, the magnetic ($\Delta G_M^{\gamma \rightarrow \alpha}$) and non-magnetic ($\Delta G_{NM}^{\gamma \rightarrow \alpha}$) terms:

$$\Delta G^{\gamma \rightarrow \alpha} = \Delta G_M^{\gamma \rightarrow \alpha} + \Delta G_{NM}^{\gamma \rightarrow \alpha}. \quad (15.2)$$

The non-magnetic component varies approximately linearly with temperature (Fig. 15.5) but the magnetic component varies non-linearly, becoming nearly zero at low temperatures. However, over a restricted temperature range (in which bainite usually forms), both functions can be represented approximately as in Table 15.1.

The Zener factorisation of the free energy into magnetic and non-magnetic components helps to account for the effects of alloying elements, via a modification of the temperature at which the free energy is evaluated¹:

$$\Delta G^{\gamma \rightarrow \alpha}\{T\} = \Delta G_M^{\gamma \rightarrow \alpha}\{T - x\Delta T_M\} + \Delta G_{NM}^{\gamma \rightarrow \alpha}\{T - x\Delta T_{NM}\}. \quad (15.3)$$

ΔT_M and ΔT_{NM} are temperature changes due to a unit concentration (x) of substitutional solute (Table 15.2). The T_0 temperature is therefore cal-

Table 15.2 Values of ΔT_M and ΔT_{NM} for a variety of substitutional solutes (after Aaronson et al. [17])

Alloying element	ΔT_M / K per at%	ΔT_{NM} / K per at%
Si	-3	0
Mn	-37.5	-39.5
Ni	-6	-18
Mo	-26	-17
Cr	-19	-18
V	-44	-32
Co	19.5	16
Al	8	15
Cu	4.5	-11.5

culated by setting $\Delta G^{\gamma \rightarrow \alpha}$ to zero:

$$\Delta G_M^{\gamma \rightarrow \alpha} \{T_0 - x \Delta T_M\} + \Delta G_{NM}^{\gamma \rightarrow \alpha} \{T_0 - x \Delta T_{NM}\} = 0. \quad (15.4)$$

On substituting the expressions listed in Table 15.1, this becomes:

$$a_{NM} + b_{NM} T_0^{\text{Fe}} + a_M + b_M T_0^{\text{Fe}} = 0 \text{ for pure iron,}$$

and

$$a_{NM} + b_{NM} (T_0^{\text{FeX}} - x \Delta T_{NM}) + a_M + b_M (T_0^{\text{FeX}} - x \Delta T_M) = 0 \text{ for an iron alloy.}$$

It follows that the change in the T_0 temperature caused by the addition of a substitutional element is given by the difference between these two equations:

$$\Delta T_0 = \frac{x(b_{NM} \Delta T_{NM} + b_M \Delta T_M)}{b_{NM} + b_M}. \quad (15.5)$$

The effect of several alloying elements can be approximated by assuming additivity:

$$\Delta T_0 = \frac{\sum_i x_i (b_{NM} \Delta T_{NM_i} + b_M \Delta T_{M_i})}{b_{NM} + b_M}. \quad (15.6)$$

To calculate the shift in the T'_0 temperature, we simply set $\Delta G^{\gamma \rightarrow \alpha}$ to the value of the stored energy (say 400 J mol^{-1} for bainite) instead of to zero. The actual T'_0 curve for an alloy, rather than just the shift $\Delta T'_0$ relative to pure iron, can be estimated by noting for a Fe-C alloy, allowing for 400 J mol^{-1} of stored energy:

$$T'_0 (\text{K}) \simeq 970 - 80x_c, \quad (15.7)$$

where x_c is the at% of carbon.

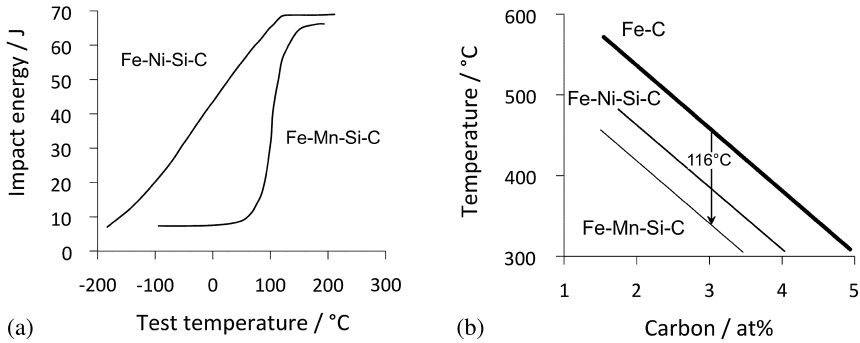


Figure 15.6 (a) Experimentally determined impact transition curves showing how the toughness improves as the amount of blocky austenite is reduced. (b) Calculated T'_0 curves for the Fe-C, Fe-Mn-Si-C and Fe-Ni-Si-C steels.

We can now proceed to apply this methodology to the design of a tough bainitic ferrite/austenite microstructure.

15.2.2 The improvement in toughness

An apparently ideal microstructure consisting of bainitic ferrite and ductile austenite in a Fe-3Mn-2.02Si-0.43C wt% exhibits poor toughness because of the presence of blocky unstable austenite (Fig. 15.6a). It is necessary to increase the amount of bainitic ferrite in the microstructure and to increase the stability of the austenite. Both of these aims can be achieved by changing the substitutional solute concentration such that the T'_0 curve is shifted to higher carbon concentrations (i.e. T'_0 is raised at any given carbon concentration).

Using Equation (15.6), we see that for the Fe-3Mn-2.02Si-0.43C wt% (2.97 Mn, 3.87Si at%) alloy:

$$\Delta T_0 = \frac{\overbrace{2.97[7 \times (-39.5) + (-1) \times (-37.5)]}^{\text{Mn}}}{7 - 1} + \frac{\overbrace{3.87[7 \times (0) + (-1) \times (-3)]}^{\text{Si}}}{7 - 1}$$

$$= 116 \text{ K},$$

the first term on the right-hand side being the effect of manganese and the second the effect of silicon. Hence, for this alloy Equation (15.7) can be modified to give:

$$T'_0(\text{K}) \simeq 970 - 80x_c - 116. \quad (15.8)$$

Manganese is seen to have a large effect in depressing the T'_0 temperature. An examination of Table 15.2 shows that one possibility is to replace all

of the manganese with nickel. Thus, for a Fe-4Ni-2Si-0.4C wt% (3.69Ni, 3.85Si at%) alloy, a similar calculation shows that $\Delta T_0 \simeq 72$ K so that:

$$T'_0(\text{K}) \simeq 970 - 80x_c - 72. \quad (15.9)$$

The remarkable improvement in toughness achieved by doing this, without any sacrifice of strength, is illustrated in Fig. 15.6, along with the T'_0 curves as calculated above.

15.2.3 Precision and limits

The model discussed above has helped in achieving the desired goal of improved toughness, even though the method used is in fact crude. The T'_0 curves are not really linear functions of carbon, and the interactions of carbon with the substitutional solutes are not accounted for. Better methods are available [18,19] and could be used when considering a higher degree of optimisation of steel chemistry. The model also does not incorporate kinetics. This could be a major disadvantage because in commercial practice, microstructures are usually generated using complex non-isothermal heat treatments.

It is likely that the exploitation of these concepts would require several iterations to improve precision, and to adapt the model for complex industrial processing. These examples illustrate the essentials of the modelling technique. Models can be constructed in stages, with significant advances being made at each stage, even though the ultimate problem may not be solved completely. These step-wise successes of the model can be used to justify further development until a point of diminishing returns is reached.

Models can help set the limits to what can or cannot be achieved [20]. Fig. 15.7a is, for carbide-free bainite, a plot of the transformation temperature (T_t) as a function of the transformation time (t). The points are experimental data but the lines which are calculated using a neural network model, define the domain of possible combinations of T_t and t . It is therefore not possible to complete the bainite reaction at 150°C in 40 min (point marked X), it would take much longer. In contrast, it is useful to have a slow transformation rate when making large components because the material can reach a homogeneous temperature before transformation starts, leading to corresponding uniformity of structure and properties. However, the point marked Y shows that slow transformation is not possible if the steel is designed to transform at a high temperature. So if uniformity is required then the alloy composition must be such that the transformation is

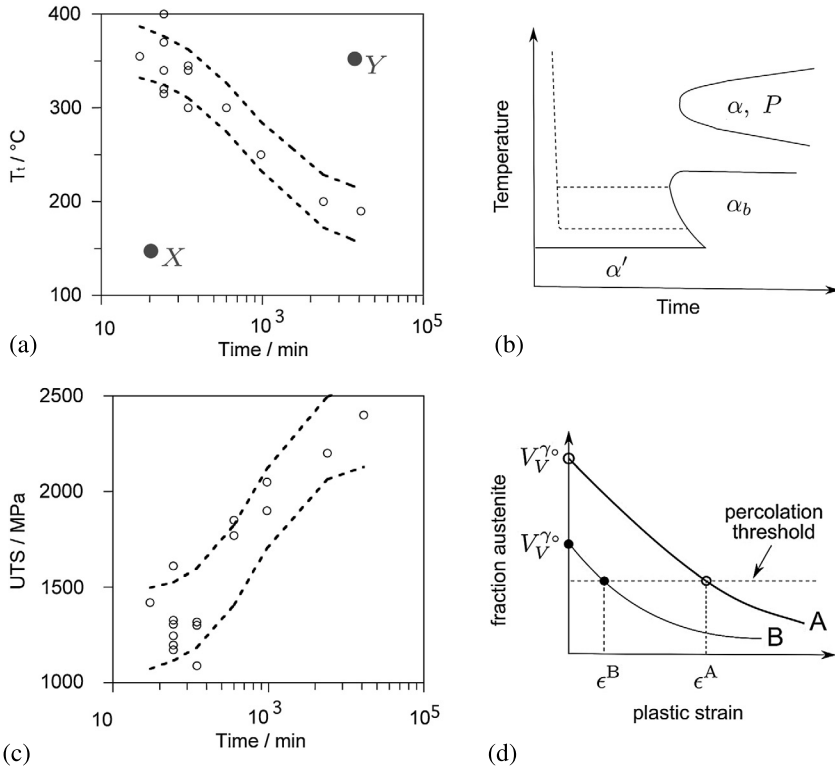


Figure 15.7 Published experimental data on carbide-free bainite (points) [21–25] as a function of transformation time. The curves represent $\pm 1\sigma$ confidence limits obtained by subjecting the data to a neural network analysis. (a) Transformation temperature (T_t) as a function of isothermal transformation time. (b) Calculated TTT diagram. (c) Ultimate tensile strength as a function of isothermal transformation time. (d) The percolation model for the elongation of carbide-free bainite.

suppressed to low temperatures. The reason for definition of the T_t – t domain of possible transformation combinations is that for alloyed steels the transformation time for bainite increases as the transformation temperature is reduced (Fig. 15.7b).

Since the structure in general becomes finer when the transformation is achieved at a lower temperature, Fig. 15.7c illustrates the domain of possible combinations of ultimate tensile strength and transformation time (related to T_t). Obviously, it is not possible to achieve 2 GPa strength in a rapidly transforming steel.

In microstructures consisting of just bainitic ferrite and carbon-enriched austenite, tensile failure is known to occur when the austenite content

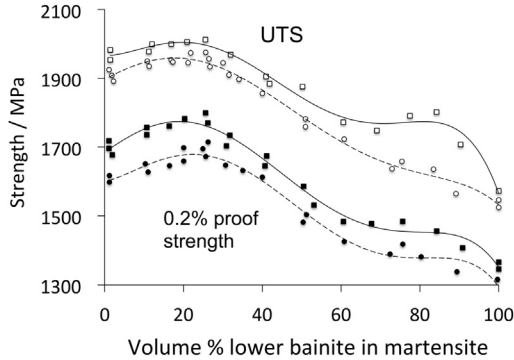


Figure 15.8 Comparison of calculations against experimental data due to Tomita and Okabayashi. The continuous lines represent tests done at 203 K and the dashed line for measurements at 287 K.

decreases to below a threshold value of about $V_V^\gamma \approx 0.1$ [26]. The initial fraction V_V^γ of austenite (Fig. 15.7d) will decrease due to deformation induced martensitic transformation, and the way in which this decomposition occurs as a function of plastic strain can be calculated [27]. It follows that with V_V^γ and the curve defining how it decreases with plastic strain, the elongation to failure is easy to estimate by assuming that failure occurs when the percolation threshold ($V_V^\gamma \approx 0.1$) is breached. Therefore, steel B which has a smaller initial fraction of austenite will exhibit a lower elongation ϵ^B than steel A.

The concepts illustrated in Fig. 15.7 can be used before any design procedure begins, to assess whether the properties demanded by the customer are in fact possible to achieve.

15.3 EXAMPLE 2: MECHANICAL PROPERTIES OF MIXED MICROSTRUCTURES

A peculiar feature of mixed microstructures of bainite and tempered martensite, is that the strength is found to go through a peak as the volume fraction of martensite decreases (Fig. 15.8). This is against intuition in that martensite is usually considered to be the strongest microstructure in steels, in which case the strength should decrease continuously as the fraction of martensite is reduced. However, quantitative modelling, by helping to reveal the mechanisms involved, can explain this anomalous behaviour.

15.3.1 Calculation of the strength of individual phases

It is reasonable to assume that the strength of martensite and bainite can be factorised into a number of intrinsic components²:

$$\sigma = \sigma_{\text{Fe}} + \sum_i x_i \sigma_{\text{SS}_i} + \sigma_C + K_L (\bar{L})^{-1} + K_D \rho_D^{0.5}, \quad (15.10)$$

where x_i is the concentration of a substitutional solute which is represented here by a subscript i . The other terms in this equation can be listed as follows:

K_L = coefficient for strengthening due to lath size, 115 MPa

K_D = coefficient for strengthening due to dislocations, 7.34×10^{-6} MPa

σ_{Fe} = strength of pure, annealed iron, 219 MPa at 300 K

σ_{SS_i} = substitutional solute (i) strengthening

σ_c = solid solution strengthening due to carbon

ρ_D = dislocation density, typically 10^{16} m^{-2}

$\bar{L}$ = measure of the ferrite plate size, typically 0.2 μm .

The individual strengthening contributions are discussed below.

15.3.2 Iron and substitutional solutes

Pure body-centred cubic iron in a fully annealed condition makes an intrinsic contribution σ_{Fe} to the overall strength. Substitutional solutes do not partition during the displacive growth of either martensite or bainite, so their concentrations are fixed by the composition of steel as a whole. Solid solution strengthening contributions, σ_{SS_i} can be estimated as a function of temperature and strain rate from published data. Table 15.3 shows that whereas the strength of pure iron increases as the temperature is reduced, strengthening due to substitutional solutes often goes through a maximum as a function of temperature. Indeed, there is some solution softening at low temperatures because the presence of a foreign atom locally assists a dislocation to overcome the Peierls barrier at low temperatures.

15.3.3 Carbon

Bainitic ferrite ordinarily has only a small amount of carbon dissolved in interstitial solution, assumed to be less than 0.02 wt%. Martensite, on the other hand, can have concentrations well in excess of the average concentration of the alloy, since the prior formation of bainite enriches the residual austenite according to the following relationship derived from a balance of

Table 15.3 Strengthening contributions (MPa) of pure iron and other factors as a function of temperature and solid solution strengthening terms for ferrite, for one wt% of solute. The data are for a strain rate of 0.0025 s^{-1} , calculated as in [28]

	200°C	100°C	Room temperature (23°C)	−40°C	−60°C
Fe	215	215	219	355	534
Si	78	95	105	70	−44
Mn	37	41	45	8	−57
Ni	19	23	37	−2	−41
Mo	—	—	18	—	—
Cr	7.8	5.9	5.8	7.4	15.5
V	—	—	4.5	—	—
Co	1.0	1.8	4.9	9.1	5.8

mass. The total carbon concentration in the alloy is the sum of the concentrations in the austenite (x_γ) and bainitic ferrite (x_{α_b}):

$$\bar{x} = x_\gamma V_V^\gamma + x_{\alpha_b} V_V^{\alpha_b}, \quad (15.11)$$

where V_γ and $V_V^{\alpha_b}$ are the volume fractions of austenite and bainitic ferrite, respectively. It follows that:

$$x_\gamma = \frac{\bar{x} - V_V^{\alpha_b} x_{\alpha_b}}{1 - V_V^{\alpha_b}}, \quad (15.12)$$

x_γ is the concentration in the residual austenite before it transforms into martensite, which is important in determining the hardness of the martensite. Solid-solution theory indicates that the strength increment due to dissolved carbon should vary with the square root of the carbon concentration [29]:

$$\sigma_{SSC} = 1722.5 \times w_C^{1/2}, \text{ MPa}. \quad (15.13)$$

15.3.4 Dislocations

When martensite or bainite form at high temperatures, the shape change due to shear transformation causes plastic deformation, and hence the accumulation of dislocations in both the parent and product phases (Chapter 6). The extent of the plasticity depends on the yield strength, and hence on the temperature. It has therefore been suggested [30] that the dislocation density (ρ_D) of both martensite and bainite can be represented empirically as a function of temperature alone, for the temperature range 570–920 K:

$$\log_{10}\{\rho_D\} = 9.2840 + \frac{6880.73}{T} - \frac{1780360}{T^2}, \quad (15.14)$$

where T is the transformation temperature in Kelvin, and ρ_D is stated in units of m^{-2} . The strengthening σ_ρ due to dislocations is given by:

$$\sigma_\rho = 0.38 \mu b (\rho_D)^{0.5} \simeq 7.34 \times 10^{-6} (\rho_D)^{0.5}, \text{ MPa} \quad (15.15)$$

where μ is the shear modulus and b is the magnitude of the Burgers vector.

15.3.5 Lath size

Martensite and bainite grow in the form of very fine plates or laths. The resulting grain size strengthening σ_G is defined as:

$$\sigma_G \simeq 115 (\bar{L})^{-1} \text{ MPa}, \quad (15.16)$$

where $\bar{L}$ (μm) is the mean linear intercept measured on random sections. This is not the classical Hall-Petch relation (Chapter 2) but another relation due to Langford and Cohen, because at the typically sub-micrometre grain sizes, the mechanism of yield is different, involving the initiation of dislocation sources in the grain boundaries.

15.3.6 Martensite composition and transformation temperature

The excess carbon in the bainitic ferrite partitions into the residual austenite, which then transforms to martensite. The carbon concentration of the martensite can therefore be calculated using Equation (15.11). The martensite-start temperature of the residual austenite can be estimated using Equation (15.18):

$$M_S = \bar{M}_S - 539(x_\gamma - \bar{x}), \text{ } ^\circ\text{C} \quad (15.17)$$

where the concentrations are in wt%, the temperatures in centigrade and $\bar{M}_S$ is the martensite-start temperature of austenite with the average composition of the alloy.

The different contributions to the strength of martensite are illustrated in Fig. 15.9. Carbon is a major contributor since it causes a severe, asymmetrical distortion of the martensite crystal structure and hence interacts strongly with the movement of dislocations. The dislocation density itself makes a significant contribution to the overall strength.

15.3.7 Strength of mixed microstructures

The normal way to calculate the strength of a multiphase alloy is to use a rule of mixtures, i.e. to calculate a mean strength from the strength of

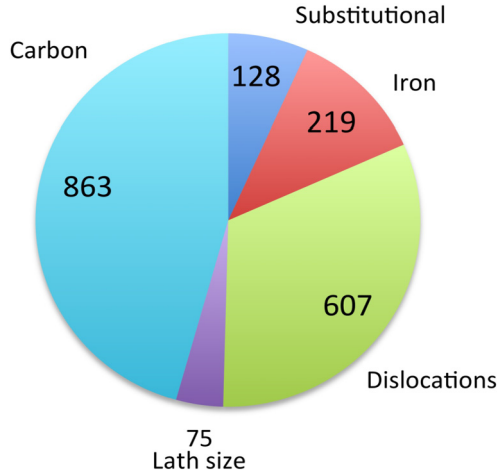


Figure 15.9 Calculated components of the room-temperature strength (MPa) of virgin martensite in Fe-0.4C-0.2Si-0.71Mn-1.9Ni-0.25Mo-0.88Cr wt% alloy. This is a typical strong steel of the type used in the manufacture of gears, gun barrels, etc.

each component phase weighted by its volume fraction. However, this is not adequate for the present purposes because of constraint effects. It is well established in fracture mechanics that the yield strength is increased by plastic constraint. This is why a weak brazing alloy can bond much stronger samples, as long as the thickness of the braze material is small enough to be constrained throughout by the surrounding stronger matrix. Indeed, the strength of the joint increases as the thickness of the braze layer decreases.

Dispersions of bainite plates form in austenite which subsequently transforms to much stronger martensite. The problem can be modelled assuming that deformation of the bainitic ferrite is constrained by the harder martensite in the same way as the braze material is constrained by the surrounding matrix [31]. The constraint can, therefore, be modelled using experimental data available from brazed joints in high-strength steels. The data, in a normalised form, are summarised in Fig. 15.10a. The vertical axis is the joint strength normalised with respect to that of the unconstrained braze material; the horizontal axis is the braze thickness normalised relative to a thickness value where the restraint effect vanishes.

To analyse the properties of a mixed microstructure, it can be assumed that the normalised braze thickness is equivalent to the volume fraction of bainite. Using this assumption, and the form of the normalised strength versus normalised thickness plot (Fig. 15.10a), the strength of constrained

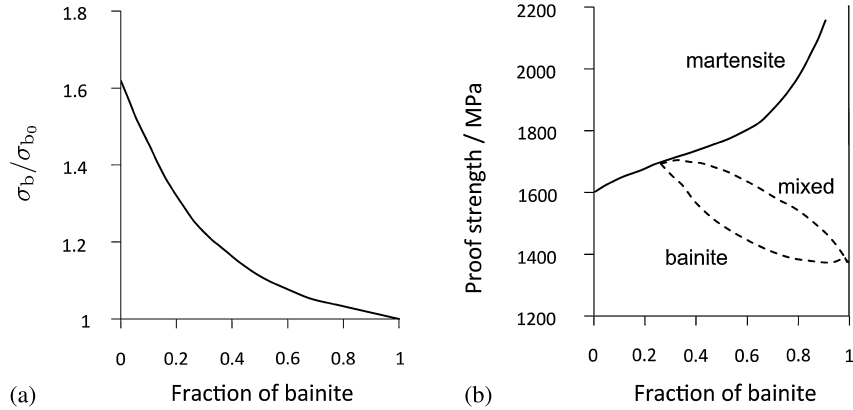


Figure 15.10 (a) Plot of the normalised strength of a brazed joint versus the normalised thickness of the brazing material, the latter being identified with the fraction of bainite in a martensitic matrix. (b) The strength contributions of bainite and martensite in the mixed microstructure.

bainite may be represented by the equation:

$$\sigma \simeq \sigma_0[0.65 \exp\{-3.3 V_V^{\alpha_b}\} + 0.98] \leq \sigma_M, \text{ MPa} \quad (15.18)$$

where σ and σ_0 represent the strengths of constrained and unconstrained bainite, respectively, σ_M is the strength of the martensite and $V_V^{\alpha_b}$ is the volume fraction of the bainite. The strength of bainite is always less than or equal to that of martensite.

When the volume fraction $V_V^{\alpha_b}$ of bainite is small, its strength nearly matches that of martensite (Fig. 15.10b), always remaining above that of bainite on its own. The strength of martensite continues to increase with the fraction of bainite, as the carbon concentration of the residual austenite from which it grows, increases.

Fig. 15.11 shows how the strength of the mixed microstructure is predicted. Line 'a' on Fig. 15.11 shows that a rule of mixtures cannot account properly for the variations observed. The agreement between calculation and experiment improves (curve b) as allowance is made for the change in the strength of martensite as carbon partitions into the austenite, due to the formation of bainite. The consistency between experiment and theory becomes excellent as constraint effects are also included in the calculations (curve c).

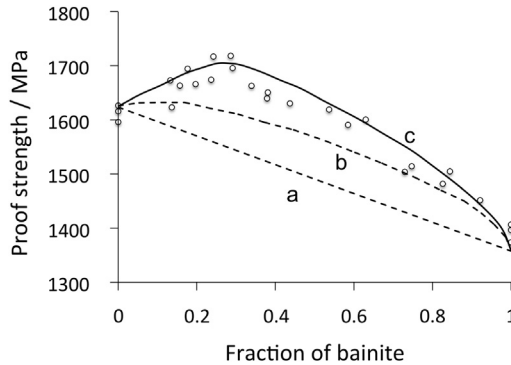


Figure 15.11 Comparison of calculations against experimental data due to Tomita and Okabayashi. The continuous lines represent tests done at 203 K and the dashed line for measurements at 287 K.

15.4 METHODS

The two examples described in the preceding sections are necessarily simplified presentations of quite complex models. It is useful to illustrate some of methods that are now common in the mathematical modelling of steels. It is worth emphasising that in general it is a combination of methods that leads to useful solutions, with the optimum approach to a problem being one that is interdisciplinary.

15.4.1 Electron theory

A metal is created when atoms are brought so close together, that the electrostatic repulsion in transferring a valency electron between the adjacent atoms is offset by the gain due to the delocalisation of electrons. This enables the valency electrons to move within the metal. The delocalised electrons feel a weak electrostatic field from the positively charged cores of atoms because of repulsion by the core electrons. The valence electrons are also screened from each other by positive holes which surround them. All this makes it possible to introduce approximations which allow a single-electron wave function to be exploited in calculating the energy of an electron gas in a metal.

These electrons are able to move, without being scattered by the partly screened potential of the positive ion cores because the latter provide a *periodic* potential whose effect is simply to modulate the free-electron wave function. Difficulties only arise when the electrons satisfy the Bragg condition within the metal. This introduces *band gaps* in the distribution of

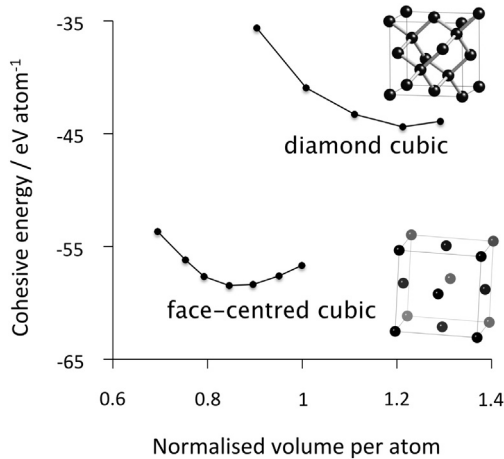


Figure 15.12 The cohesive energy at 0 K versus the volume per atom divided by the volume of an iron atom, for two crystal structures of iron. Selected data from Paxton et al. [32].

electron energies. The metallic state can exist only if the valency bands are partly filled.

Using these concepts, the energy of the electron gas can be expressed in terms of the potential due to the ion cores, Coulomb interactions, kinetic energy and exchange and correlation effects. It is then possible to calculate with an input of the electronic charge and the atomic number of the element, properties such as the cohesive energy of crystals, the elastic moduli, magnetic and acoustic properties. The calculations are known as ‘first principles’ or *ab initio* calculations because they do not require experimental inputs other than the charge on the electron and the types of atoms involved. The calculations are limited to small numbers of atoms because they are extremely computer intensive.

Fig. 15.12 shows some calculations of the cohesive energy at 0 K of two allotropic forms of iron, fcc and the hypothetical structure diamond cubic. In each case the cohesive energy goes through a minimum, which gives the expected density of the allotrope. The calculation of the diamond form of iron shows how it is possible, using electron theory, to estimate the properties of phases which do not exist in reality. Such a form would have a density of only 5 g cm^{-3} , but unfortunately, the energy difference relative to the stable forms of iron is simply too large, meaning that it would be improbable for the fcc $\rightarrow$ diamond transition to be induced, e.g. by alloying.

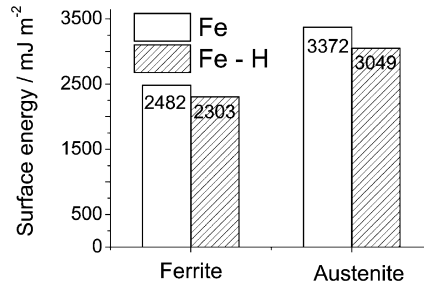


Figure 15.13 Calculated surface energy of ferrite and austenite for pure metal and hydrogen containing system.

Calculations like these are now applied routinely in the context of steels, particularly when clear experiments are impossible – a few examples are listed here for illustration purposes:

- (i) a useful concept that can only be verified using electron theory, states that grain boundaries are embrittled if it is more favourable for a solute to segregate to a free surface [33]. Thus, it has been confirmed using first principles calculations, that phosphorus does in fact have a high tendency to embrittle special boundaries [34].³ The calculations prove that the embrittlement is not due to a reduction in Fe-Fe bonding due to the presence of the phosphorus.
- (ii) Fine titanium carbides in automotive sheet-steel coarsen less if molybdenum is added. This is so even though molybdenum is not favoured in the TiC. The coarsening occurs when the hot steel is coiled as it comes out of the rolling mill. First principles calculations the mechanism, that even though Mo in TiC is thermodynamically unfavourable, its presence reduces the misfit of the carbide with the parent phase, thus making it easier to nucleate [35]. This is why coarsening is retarded because the coarsening rate scales with the interfacial energy per unit area.
- (iii) One theory for the embrittlement of steel by hydrogen is that it reduces the cohesive energy of iron, making it easier to cleave [36]. Iron cleaves on the $\{100\}_\alpha$ planes. To establish whether this is a significant effect, first principles estimates of the change in the energy between hydrogen in the dissolved state and when hydrogen is at the $\{100\}_\alpha$ surface was calculated [37]. If there is a reduction in energy on exposing the cleavage plane then the material can be considered embrittled. As illustrated in Fig. 15.13, the calculations revealed only a

small dependence of the surface energy on hydrogen for the classical cleavage plane in ferrite, much smaller than the profound embrittlement observed at minute concentrations of hydrogen.

- (iv) Silicon has a negligible solubility in cementite. The design of bainitic steels containing retained austenite relies on this because the addition of silicon suppresses cementite and hence the austenite enriched in carbon is retained. The suppression occurs when cementite can only grow by a paraequilibrium mechanism, in which case it is forced to absorb silicon. There are no experimental thermodynamic data for silicon in cementite. First principles calculations have therefore been used to generate the data for subsequent use in phase diagram calculations for alloy design [38,39].

15.4.2 Phase diagram calculations and thermodynamics

Given experimentally determined thermodynamic data, it is possible to estimate in multicomponent, multiphase alloys, the stable phases, their equilibrium fractions and equilibrium chemical compositions as a function of temperature, pressure, magnetic fields and the detailed composition of the alloy. In other words, all the information plotted on phase diagrams.

The free energy of a phase α is simply the weighted mean of the free energies of its component atoms (μ_i) which for a binary solution containing components A and B is:

$$G^\alpha = (1 - x)\mu_A^\alpha + x\mu_B^\alpha,$$

where x is the mole fraction of B . μ_i^α is known as the *chemical potential* of component i in phase α . Although this equation is expressed for a binary solution, it is generally true that equilibrium between any number of phases in contact, containing any number of components, is defined by:

$$\mu_i^\alpha = \mu_i^\beta = \dots \quad \text{for } i = 1, 2, 3, \dots \quad \text{and phase} = \alpha, \beta, \dots$$

The chemical potential must be uniform everywhere at equilibrium.

There are many thermodynamic methods which express the chemical potential as a function of the mixing of solutes in a phase. Most of these methods either are too simple or so complex that they cannot easily be generalised. Therefore, in the computer calculations, the deviation of the free energy of mixing from that of an ideal solution,⁴ i.e. the excess Gibbs free energy, is written as an empirical polynomial equation:

$$\Delta_e G_{AB} = x_A x_B \sum_i L_{AB,i} (x_A - x_B)^i,$$

where L_i are measured interaction coefficients, in this case for a binary solution. For a ternary solution interaction the term would be of the form:

$$\begin{aligned}\Delta_e G_{ABC} = & x_A x_B \sum_i L_{AB,i} (x_A - x_B)^i \\ & + x_B x_C \sum_i L_{BC,i} (x_B - x_C)^i \\ & + x_C x_A \sum_i L_{CA,i} (x_C - x_A)^i.\end{aligned}$$

The advantage of this kind of a polynomial becomes clear, since the relation reduces to the binary problem when one of the components is set to be identical to another, e.g. $B \equiv C$. The method can be extended to deal with any number of components, with the great advantage that few coefficients have to be changed when the data due to one component are improved. It is therefore adopted in many of the phase diagram calculation programs available commercially.

Although thermodynamics is usually associated with the state of equilibrium, the calculation method can also be used to estimate constrained equilibria, e.g. paraequilibrium (Chapter 3) and diffusionless transformation (Chapter 5). Fig. 15.14 illustrates calculated isothermal Fe-Cr-C phase diagrams for both the equilibrium and para-equilibrium states – notice the dramatic change when substitutional solutes are not allowed to partition between the phases.

There is another subtle application of thermodynamics in the design of steels, dealing with steady-state processes in which the system is not at equilibrium but an appropriate observer may not perceive change. An example is diffusion across a constant gradient; neither the flux nor the concentration at any point changes with time, and yet the free energy of the system is decreasing since diffusion occurs to minimise free energy. The rate at which energy is dissipated is the product of the temperature and the rate of entropy production (i.e. $T\sigma_e$):

$$T\sigma_e = JX,$$

where J is a generalised flux of some kind, and X a generalised force. In the case of an electrical current, the heat dissipation is the product of the current (J) and the electromotive force (X). Provided that flux-force sets can be expressed as in this way, it is found that $J \propto X$ for small deviations from equilibrium. In the case of the electrical current, this leads to Ohm's law where the current is proportional to the electromotive force.

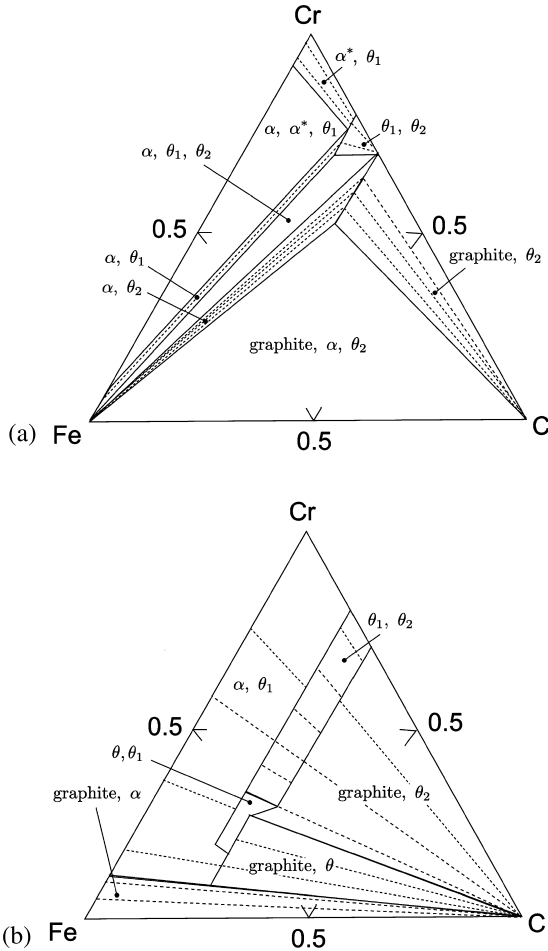


Figure 15.14 Isothermal section of the Fe-Cr-C system. The body-centred cubic phase is ferrite and M stands for a mixture of iron and chromium atoms in a variety of carbide phases (courtesy of J. Robson). θ_1 and θ_2 represent $M_{23}C_6$ and M_7C_6 respectively.

This concept can be applied to the case where a number of irreversible processes occur simultaneously. In a ternary Fe-Mn-C alloy, the diffusion flux of carbon depends not only on the gradient of carbon, but also on that of manganese. Thus, a uniform distribution of carbon will tend to become inhomogeneous in the presence of a manganese concentration gradient. When there is more than one dissipative process, the total energy dissipation

rate is the sum of all the dissipations:

$$T\sigma_e = \sum_i J_i X_i,$$

with

$$J_i = M_{ij} X_j \quad \text{with} \quad i, j = 1, 2, 3 \dots$$

and it is the cross coefficients M_{ij} ($i \neq j$) that drive the diffusion of carbon in a gradient of manganese. The theory is applied widely in computer calculations of the kinetics of phase transformations in steels.

15.5 KINETICS

Almost all the solid-state transformations in steels involve nucleation and growth. The theories for these two processes are well established and have been described in section 3.6.5. The evolution of the volume fraction requires the additional treatment of *impingement* between particles which nucleate at different locations. The change in the real volume of the product phase (α) can be related to the extended volume using Equation (3.13) that was introduced in Chapter 3 as:

$$dV^\alpha = \left(1 - \frac{V^\alpha}{V}\right) dV_e^\alpha,$$

where it is assumed that the microstructure develops at random. The subscript e refers to extended volume, V^α is the volume of α and V is the total volume.

However, it is often the case that different transformation products occur simultaneously from the parent phase, albeit at different rates. The extended volume idea can be generalised to this scenario [40–43]. Suppose α and β precipitate simultaneously, then the relation between extended and real space becomes a coupled set of two equations:

$$dV^\alpha = \left(1 - \frac{V^\alpha + V^\beta}{V}\right) dV_e^\alpha \quad \text{and} \quad dV^\beta = \left(1 - \frac{V^\alpha + V^\beta}{V}\right) dV_e^\beta, \quad (15.19)$$

which in general must be solved numerically.

When martensitic transformation occurs under the influence of an externally applied stress, particular crystallographic orientations that comply better with the applied stress are stimulated first, but this does not rule out the formation of other orientations. The martensite-start temperature

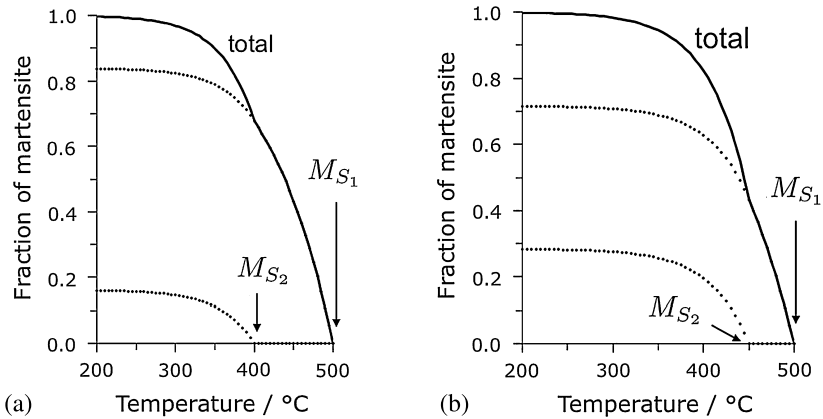


Figure 15.15 Two martensite-start temperatures, (a) 500°C and 400°C, (b) 500°C and 450°C.

of the optimally oriented martensite (M_{S1}) will be greater than of a less favoured orientation (M_{S2}). Both orientations of martensite will grow below M_{S2} and the theory described in Equation (15.19) can be used to follow the evolution of the volume fractions of each kind of martensite as a function of temperature. Fig. 15.15 illustrates such calculations as an example of the simultaneous transformation model [44].

There has in recent years been much prominence given to the phase field method as an alternative technique for calculating the evolution of microstructure.⁵ This begins with the description of the entire microstructure in terms of an *order parameter*. The precipitate and matrix each have a particular value of the order parameter and the interface between these is located by the position where the order parameter changes from its precipitate-value to its matrix-value. The range over which it changes is the *width* of the interface. The set of values of the order parameter over the whole microstructure is the *phase field*.

The free energy per atom is then written for the whole of the (heterogeneous) phase field as a single functional and the evolution of microstructure with time is assumed to be proportional to the variation of this functional with respect to the order parameter.

The method has been extremely successful in dealing with spinodal reactions and in the modelling of solidification, but its utility with respect to solid-state reactions of the kind important in steels has yet to be demonstrated. The definition of the width of the interface and associated coefficients, and handling nucleation are two difficulties which require fit-

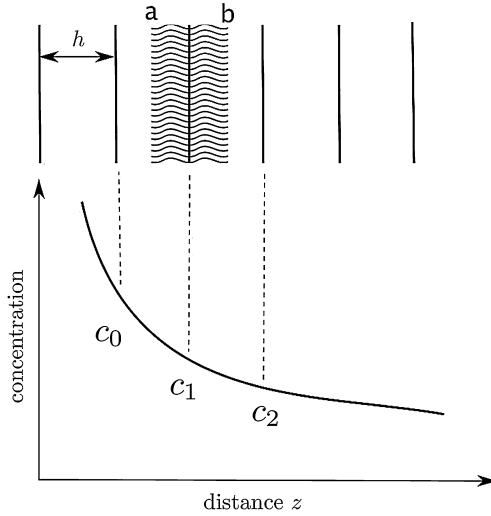


Figure 15.16 Finite difference representation of diffusion.

ting to experimental data. On the other hand, effects such as the overlap of diffusion fields are natural outcomes.

15.5.1 Finite difference method

The finite difference is a discrete analogue of a derivative. Consider one-dimensional diffusion in a concentration gradient along a coordinate z (Fig. 15.16). The concentration profile is divided into slices, each of thickness h . The matter entering a unit area of the face at a in a time increment τ is given approximately by $J_a = -D\tau(c_1 - c_0)/h$. That leaving the face at b is $J_b = -D\tau(c_2 - c_1)/h$. If c'_1 is the new concentration in slice 1, then the net gain in solute is $(c'_1 - c_1)h$ so that:

$$c'_1 - c_1 = \frac{D\tau}{h^2}(c_0 - 2c_1 + c_2). \quad (15.20)$$

This allows the concentration at a point to be calculated as a function of that at the two neighbouring points. By successively applying this relation at each slice, and advancing the time τ , the entire concentration profile can be estimated as a function of time.

The approximation is that the concentration gradient within each slice has been assumed to be constant. This approximation will be better for smaller values of h , but at the expense of computation time. The accuracy

can be assessed by changing h and seeing whether it makes a significant difference to the calculated profile.

15.6 FINITE ELEMENT METHOD

In this, continuous functions are replaced by piecewise approximations. The consequence of applying force to a body represented as a set of springs is illustrated here, assuming that the force F in each spring varies linearly with the displacement δ , with the constant of proportionality labelled the stiffness k . The body is at rest at equilibrium, so for the case illustrated in Fig. 15.17a, $F_1 = -F_2$ so that:

$$\begin{bmatrix} F_1 \\ F_2 \end{bmatrix} = \begin{pmatrix} k & -k \\ -k & k \end{pmatrix} \begin{bmatrix} \delta_1 \\ \delta_2 \end{bmatrix}.$$

The forces at the nodes of the springs illustrated in Fig. 15.17b are therefore

$$\begin{bmatrix} F_1 \\ F_2 \\ 0 \end{bmatrix} = \begin{pmatrix} k_1 & -k_1 & 0 \\ -k_1 & k_1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{bmatrix} \delta_1 \\ \delta_2 \\ \delta_3 \end{bmatrix}$$

$$\begin{bmatrix} 0 \\ F_2 \\ F_3 \end{bmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & k_2 & -k_2 \\ 0 & -k_2 & k_2 \end{pmatrix} \begin{bmatrix} \delta_1 \\ \delta_2 \\ \delta_3 \end{bmatrix},$$

$$\begin{aligned} \begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix} &= \underbrace{\begin{pmatrix} k_1 & -k_1 & 0 \\ -k_1 & k_1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & k_2 & -k_2 \\ 0 & -k_2 & k_2 \end{pmatrix}}_{\text{Component stiffnesses}} \begin{bmatrix} \delta_1 \\ \delta_2 \\ \delta_3 \end{bmatrix} \\ &\equiv \underbrace{\begin{pmatrix} k_1 & -k_1 & 0 \\ -k_1 & k_1 + k_2 & -k_1 \\ 0 & -k_2 & k_2 \end{pmatrix}}_{\text{Overall stiffness}} \begin{bmatrix} \delta_1 \\ \delta_2 \\ \delta_3 \end{bmatrix}. \end{aligned}$$

This illustrates how the properties of the simple elements can be combined to yield an overall response function for a more complex body, which is extremely useful when dealing with intricate industrial problems.

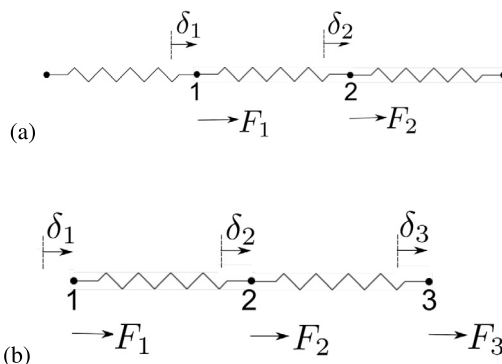


Figure 15.17 Forces on springs.

15.7 NEURAL NETWORKS

The usual approach when dealing with difficult problems is to correlate the results against chosen variables using linear regression analysis; a more powerful method of empirical analysis involves the use of neural networks [46,47], which have had tremendous success in the quantitative treatment of structure-property relationships [10].

In linear regression, fitting data to a specified relationship yields an equation which relates the inputs x_j via weights w_j and a constant θ to obtain an estimate of the output $y = \sum_j w_j x_j + \theta$. Equations like these are used widely in industry, e.g. in the formulation of the *carbon equivalents* (section 13.2.5). It is well understood that there is risk in using the relationships beyond the range of fitted data, but the risk is not quantified.

With neural networks, the input data x_j are again multiplied by weights, but the sum of all these products forms the argument of a flexible mathematical function, often a hyperbolic tangent. The output y is therefore a non-linear function of x_j . The exact shape of the hyperbolic tangent can be varied by altering the weights (Fig. 15.18a). The weights are changed systematically until a best-fit description of the output is obtained as a function of the inputs; this operation is known as *training* the network.

Further degrees of non-linearity can be introduced by combining several of these hyperbolic tangents (Fig. 15.18b), so that the neural network method is able to capture almost arbitrarily non-linear relationships.

Fig. 15.19 illustrates the complexity of the surface that can be produced when representing the output (vertical axis) as a function of two inputs using just four hyperbolic tangents.

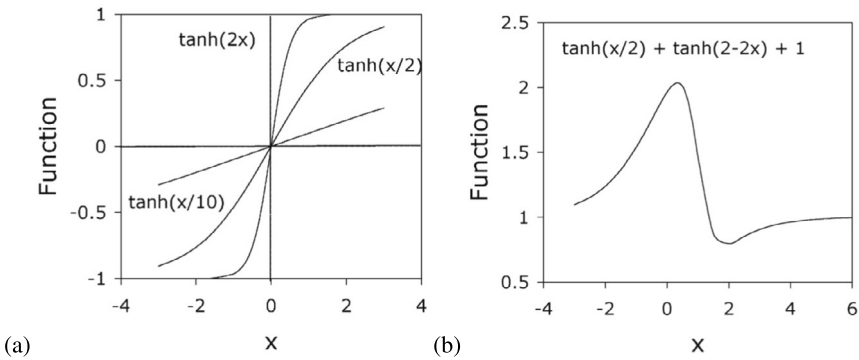


Figure 15.18 (a) Three different hyperbolic tangent functions; the 'strength' of each depends on the weights. The diagram shows how flexible a hyperbolic tangent is. (b) A combination of two hyperbolic tangents to produce a more complex model. Such combinations can be continued indefinitely to produce functions of ever greater complexity.

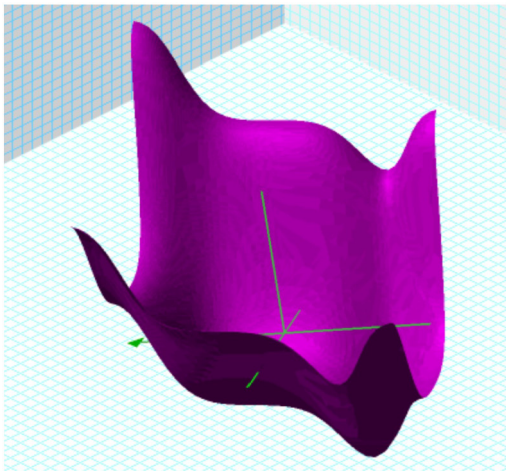


Figure 15.19 Variation in the output z (vertical axis) as a function of two input variables x, y (horizontal axes), the whole surface being generated using just four hyperbolic tangent functions, $z = 0.8[\tanh(wx - 2) + \tanh(x^2 - w) + \tanh(wy + 2) + \tanh(y^2 - w) + 1]$.

A potential difficulty with the ability to produce complex, non-linear functions is the possibility of overfitting of data. To avoid this difficulty, the experimental data can be divided into two sets, a *training* dataset and a *test* dataset. The model is produced using only the training data. The test

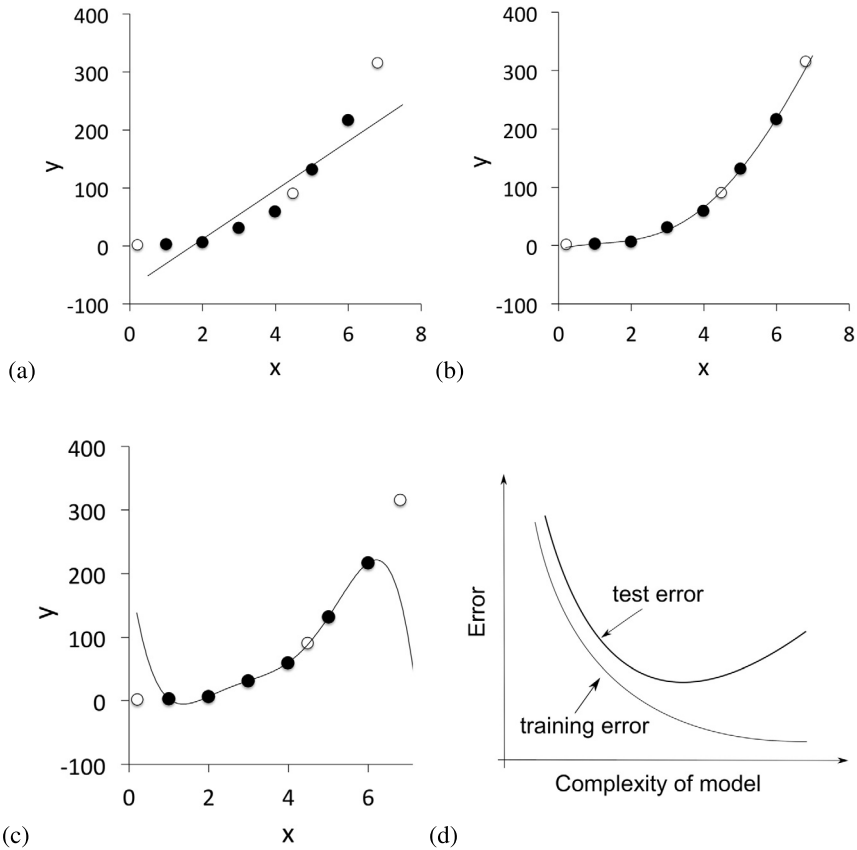


Figure 15.20 Variations in the test and training errors as a function of model complexity, for noisy data. The filled points were used to create the models (i.e. they represent training data), and the circles constitute the test data. (a) A linear function which is too simple. (b) A cubic polynomial with optimum representation of both the training and test data. (c) A sixth-order polynomial which generalises poorly. (d) Schematic illustration of the variation in the test and training errors as a function of the model complexity.

data are then used to check that the model behaves itself when presented with previously unseen data. This is illustrated in Fig. 15.20 which shows three attempts at modelling noisy data for y as a function of x . A linear model (Fig. 15.20a) is too simple and does not capture the real complexity in the data. An over complex function such as that illustrated in Fig. 15.20c accurately models the training data but generalises badly. The optimum model is illustrated in Fig. 15.20b. The training and test errors are shown schematically in Fig. 15.20d; not surprisingly, the training error tends to

decrease continuously as the model complexity increases. It is the minimum in the test error which enables that model to be chosen which generalises best to unseen data.

A neural network like this can capture interactions between the inputs because the hidden units are non-linear. Appropriate measures must be taken to avoid overfitting. With complex networks it is also important to consider the *modelling uncertainty*, i.e. what is the range of models which can adequately represent the known data? A large modelling uncertainty corresponds to the case where these models behave differently when extrapolated.

15.8 SUMMARY

It is now possible to design an innovative steel and to introduce it into service within five years. This is because there is a realisation in academia that there is more than just the measurement of a few properties that makes a usable material. At the same time, industry appreciates the need to devote vast resources in order to take an elementary idea to a stage where the manufacturing capability and technological readiness levels are sufficient. The process towards success can be summarised in stages that are often labelled as readiness levels that are paraphrased here:

1. Principles established based on science or creativity.
2. Technology concept developed, needs defined.
3. Basic characterisation.
4. Prototype development and validation.
5. Major investment to prove component level parameters and scaling.
6. Demonstration in real circumstances.
7. Fully fledged commercial product, which may be developed further with service experience and new knowledge.

If all this is to be achieved in the five year timeframe, then it usually is the case the mathematical models play a role in testing options. The models are rarely sophisticated enough to deal with complex materials so experiments and thought processes based on experience and past literature are essential.

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BACKNOTES

1. The braces used below indicate functional relationship, so $x\{y\}$ indicates the x is a function of y .
2. Although, as pointed out in section 2.7, a linear combination of terms may not always be appropriate.
3. First principles calculations cover a small number of atoms and hence the boundaries simulated are between grains with exact coincidence site lattice orientations, i.e., relatively low-energy configurations. This is a limitation of the method because most boundaries in real steels are not special.
4. An ideal solution is one in which the atoms mix at random at all temperatures.
5. The intrinsic features of the method have been reviewed by Qin and Bhadeshia [45]. The article includes a description of the advantages and disadvantages of the technique.

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