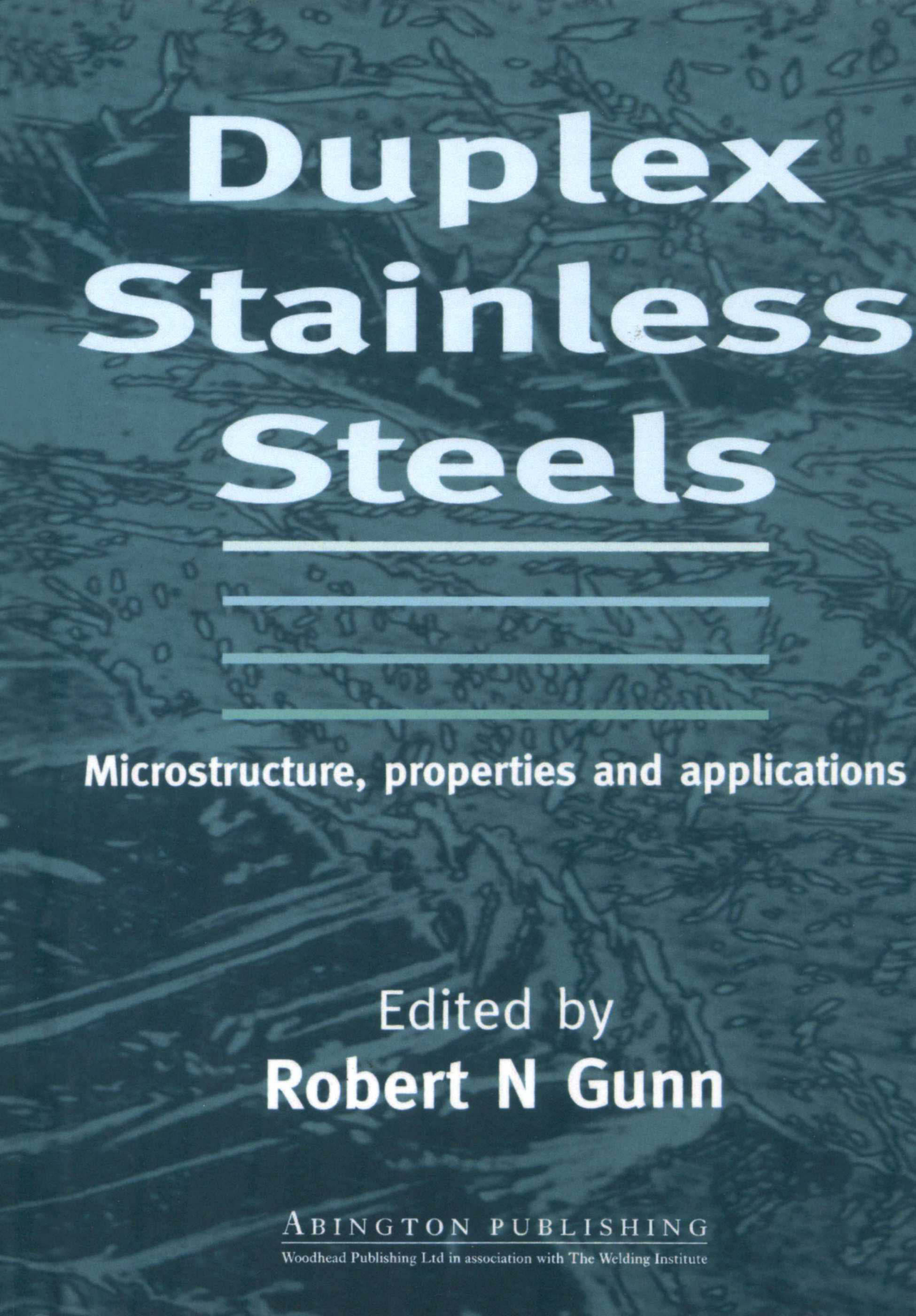


The background of the cover is a dark, teal-colored micrograph showing the characteristic banded structure of duplex stainless steel, with alternating regions of ferrite and austenite.

Duplex Stainless Steels

Microstructure, properties and applications

Edited by
Robert N Gunn

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Duplex stainless steels

1 Developments, grades and specifications

1.1 Historical developments

Stainless steels were developed during the first decades of the twentieth century in the United Kingdom and Germany. The earliest grades were martensitic and ferritic Fe-Cr steels, but quite soon the austenitic Fe-Cr-Ni steels became the largest group. The growth of the austenitic alloys stemmed from their ease of production and fabrication, particularly welding. Minimum carbon levels were high (around 0.08%), due to the existing furnaces and refining techniques. This made the steels sensitive to grain boundary carbide precipitation during heat treatment and welding, and sensitive to intergranular corrosion attack.

A duplex alloy is defined as one that contains a two-phase structure and is more often a descriptor of an alloy where both phases are present in significant quantities. In the context of this book, the term duplex stainless steel covers ferritic/austenitic Fe-Cr-Ni alloys with between 30% and 70% ferrite. The first reference to such alloys appears in 1927, when Bain and Griffith¹ published data on ferritic:austenitic structures. Within the next few years, several foundries in France, Germany, Sweden and the USA explored such steels, initially in the cast form.

Possibly the first commercial product dates from 1929² when Avesta Jernverk produced a grade called 453E with approximate composition 25%Cr-5%Ni. Soon after in 1932 and 1933 a modified grade with 25%Cr-5%Ni-1%Mo (grade 453S) was marketed. Applications included coolers of the Brobeck type (plate and forgings), autoclaves for gunpowder production (castings) and valves for sulphite pulping (castings).

Another record of early duplex products dates back to 1933, when an error during the melting of an 18%Cr-9%Ni-2.5%Mo grade at the Firminy works of the J. Holtzer Company, France, led to a 20%Cr-8%Ni-2.5%Mo steel. Subsequent analysis³ of the casting found it had a high volume fraction of ferrite in an austenitic matrix

and was not sensitive to intergranular corrosion (IGC) in various corrosive media. This was a significant discovery, as the high carbon austenitic grades of the time tended to form a continuous chromium carbide network, leading to rapid corrosion in the surrounding chromium depleted zones.⁴⁻⁷ This observation, combined with the superior strength over the austenitic grades,⁸ encouraged French patents to be issued in 1935 and 1937.⁹⁻¹⁰ The latter patent covered a grade with copper additions to further enhance the corrosion resistance in the most aggressive media. Research was undertaken at several laboratories,¹¹ so that, by the late 1940s, a new family of stainless steel was available which was patented and marketed simultaneously in France, Sweden and the USA.

The Korean war (1950–51) encouraged a nickel shortage, which led to further research into the relatively low nickel-content duplex alloys. It became apparent that a balance of ferrite and austenite had better resistance to chloride stress corrosion cracking (SCC) than a fully austenitic microstructure. Ever since, this has been one of the main exploited advantages of duplex over austenitic stainless steels. In France the UR50 grade with 20–35% ferrite (UNS S32404 in Table 1.1) was marketed in various product forms, including forgings, for such industries as oil refining, food processing, pulp and paper, and pharmaceuticals. These steels were produced in high frequency induction furnaces using precisely weighed alloying additions. A partial vacuum ensured carbon removal, rudimentary deoxidation and restricted nitrogen ingress.¹² Nevertheless, plate products remained sensitive to expensive edge cracks.^{13,14}

Towards the end of the 1950s, the cast alloy CD4-MCu, originally with about 70% ferrite, was marketed (UNS J93370 in Table 1.2), but had relatively poor toughness and ductility. Improvements were made¹⁵ by lowering the chromium content to 22–23% and the introduction of a quench-annealing treatment to increase ductility. And yet, the understanding of physical metallurgy still had not progressed sufficiently to offer a material that was easy to manufacture and fabricate. These factors gave the duplex a reputation for crack sensitivity and left them in a niche market until the 1960s.

During the late 1960s and early 1970s, there were two main factors which advanced the development and use of duplex alloys. First, there was another nickel shortage that pushed up the price of austenitic alloys, combined with increased activity in the offshore oil industry which demanded a stainless material to handle aggressive environments. Second, steel production process techniques improved dramatically with the introduction of the vacuum and argon oxygen decarburisation (VOD and AOD) practices. These techniques led to

Table 1.1 Wrought duplex grades listed in the Unified Numbering System

UNS	Element, wt%			Si	Mn	Ni	Cr	Mo	Cu	W	N
	C	S	P								
Alloy lean											
S31500 (3RE60)	0.030	0.030	0.030	1.40– 2.00	1.20– 2.00	4.25– 5.25	18.0– 19.0	2.50– 3.00	–	–	–
S32304 (2304)	0.030	0.040	0.040	1.0	2.50	3.0– 5.5	21.5– 24.5	– 0.60	0.05– 0.60	–	0.05– 0.20
S32404 (Uranus 50)	0.04	0.010	0.030	1.0	2.0	5.5– 8.5	20.5– 22.5	2.0– 3.0	1.0– 2.0	–	0.20
Standard 22% Cr											
S31803 (2205)	0.030	0.020	0.030	1.00	2.00	4.50– 6.50	21.0– 23.0	2.50– 3.50	–	–	0.08– 0.20
S32205	0.030	0.020	0.030	1.00	2.00	4.50– 6.50	22.0– 23.0	3.00– 3.50	–	–	0.14– 0.20
High alloy											
S31200 (44LN)	0.030	0.030	0.045	1.00	2.00	5.50– 6.50	24.0– 26.0	1.20– 2.00	–	–	0.14– 0.20
S31260 (DP3)	0.03	0.030	0.030	0.75	1.00	5.50– 7.50	24.0– 26.0	2.50– 3.50	0.20– 0.80	0.10– 0.50	0.10– 0.30
S32550 (Ferralium)	0.04	0.030	0.04	1.00	1.5	4.50– 6.50	24.0– 27.0	2.9– 3.9	1.50– 2.50	–	0.10– 0.25
S32900 (329)	0.08	0.030	0.040	0.75	1.00	2.50– 5.00	23.0– 28.0	1.00– 2.00	–	–	–
S32950 (7-Mo Plus)	0.03	0.010	0.035	0.60	2.00	3.50– 5.20	26.0– 29.0	1.00– 2.50	–	–	0.15– 0.35
Superduplex											
S32520 (Uranus 52N+)	0.030	0.020	0.035	0.8	1.5	5.5– 8.0	24.0– 26.0	3.0– 5.0	0.50– 3.00	–	0.20– 0.35
S32750 (2507)	0.030	0.020	0.035	0.8	1.20	6.0– 8.0	24.0– 26.0	3.0– 5.0	0.5	–	0.24– 0.32
S32760 (Zeron 100)	0.03	0.01	0.03	1.0	1.0	6.0– 8.0	24.0– 26.0	3.0– 4.0	0.5– 1.0	0.5– 1.0	0.2– 0.3
S39226	0.030	0.030	0.030	0.75	1.00	5.50– 7.50	24.0– 26.0	2.50– 3.50	0.20– 0.80	0.10– 0.50	0.10– 0.30
S39274 (DP3W)	0.030	0.020	0.030	0.80	1.0	6.0– 8.0	24.0– 26.0	2.50– 3.50	0.20– 0.80	1.50– 2.50	0.24– 0.32
S39277 (AF918)	0.025	0.002	0.025	0.80	–	6.5– 8.0	24.0– 26.0	3.0– 4.0	1.2– 2.0	0.80– 1.20	0.23– 0.33

The chemical compositions listed are for information purposes only.

After 'Metal and Alloys in the Unified Numbering System', SAE/ASTM, September 1996. Values are maxima unless range given.

steels with simultaneously low carbon, sulphur and oxygen contents etc., while allowing for greater control of composition, especially nitrogen. One example of such a steel was UNS S31500 (e.g. 3RE60) which had a maximum carbon content of 0.03%, designed¹⁶ to

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Table 1.2 Common cast duplex grades listed in the Unified Numbering System

UNS	Element, wt%			Si	Mn	Ni	Cr	Mo	Cu	N	Other
	C	S	P								
Standard 22% Cr											
J92205 (2205)	0.03	0.020	0.04	1.00	1.50	4.5– 6.5	21.0– 23.5	2.5– 3.5	1.00	0.10– 0.30	–
J93183 (KCR-D183)	0.03	0.03	0.040	2.0	2.0	4.0– 6.0	20.0– 23.0	2.0– 4.0	1.0	0.08– 0.25	0.5– 1.5 Co
High alloy											
J93345 (Escaloy)	0.08	0.025	0.04	–	1.00	8.0– 11.0	20.0– 27.0	3.0– 4.5	–	0.10– 0.30	–
J93370 (CD-4MCu)	0.04	0.04	0.04	1.00	1.00	4.75– 6.00	24.5– 26.5	1.75– 2.25	2.75– 3.25	–	–
J93371 (3A)	0.06	0.040	0.040	1.00	1.00	4.00– 6.00	24.0– 27.0	1.75– 2.50	2.75– 3.25	0.15– 0.25	–
J93372 (CD-4MCuN)	0.04	0.04	0.04	1.0	1.0	4.7– 6.0	24.5– 26.5	1.7– 2.3	2.7– 3.3	0.10– 0.25	–
J93550 (KCR-D283)	0.03	0.03	0.040	2.0	2.0	–	23.0– 26.0	5.0– 8.0	1.0	0.08– 0.25	0.5– 1.5 Co
Superduplex											
J93380 (Zeron 100)	0.03	0.025	0.030	1.0	1.0	6.5– 8.5	24.0– 26.0	3.0– 4.0	0.5– 1.0	0.2– 0.3	0.5– 1.0W
J93404 (Alloy 958)	0.03	–	–	1.00	1.50	6.0– 8.0	24.0– 26.0	4.0– 5.0	–	0.10– 0.30	–

The chemical compositions listed are for information purposes only.

After 'Metal and Alloys in the Unified Numbering System', SAE/ASTM, September 1996. Values are maxima unless range given.

enhance resistance to SCC. In particular, the chemical composition was more carefully controlled to optimise the ferrite:austenite phase balance. Further, the addition of nitrogen improved corrosion resistance and the high temperature stability of the duplex structure, e.g. the HAZ, by stabilising the austenite. The hot workability and rolling experience was greatly improved,^{17,18} making possible the production of wide sheets and coils.

Another approach taken in the former Soviet Union was to add titanium to the steel (about 0.4%Ti), in a similar manner to stabilised 300-series austenitic grades. The titanium preferentially formed carbides to chromium and reduced the frequency of IGC. Further, the titanium carbides helped to pin the grain boundaries and restricted excessive ferrite grain growth in the HAZ.¹⁹

Even though grades such as S31500 were a breakthrough in alloy design and can be described as the second generation of duplex stainless steel, they were still susceptible to IGC under certain conditions.^{20–22} This was believed²³ to be due to a high Cr/Ni equivalent ratio which led to an almost fully ferritic heat affected zone (HAZ)

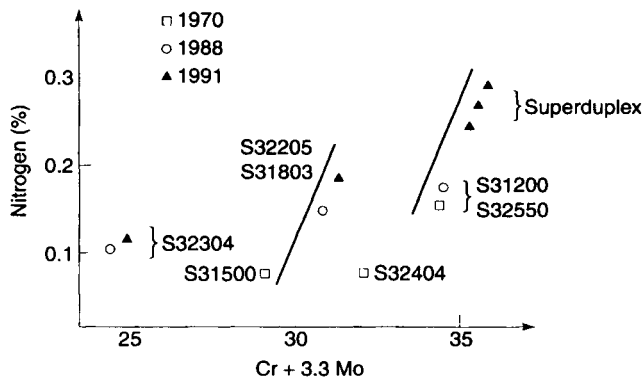
after welding with associated grain growth. As the solubility of carbon and nitrogen is very low in ferrite, carbides and nitrides precipitated along grain boundaries and caused local chromium depletion of the matrix, i.e. sensitisation. To overcome this problem, higher levels of nickel and nitrogen were added and IGC resistance was greatly improved.

1.2 Modern developments

In the early 1970s, the 22%Cr duplex grade was developed in Germany and Sweden, i.e. DIN 1.4462 or UNS S31803 (Table 1.1). One patent²⁴ claimed that this new steel was not sensitive to IGC upon welding due to a balanced chemistry (i.e. Cr/Ni equivalent ratio), including the addition of nitrogen¹² (Fig.1.1). And yet, as the permitted compositional ranges were too wide, highly ferritic HAZs formed with an associated reduction in corrosion resistance.²⁵

Such wide compositional ranges persist in national and international specifications (e.g. S31803), even though most producers and end users commonly specify closer limits to control the weldability. In particular, it is has proved important to keep the nitrogen content towards the upper end of the range, e.g. the limits specified for S32205 (Table 1.1). This latest development has marked the introduction of the third generation of duplex alloys, signalling that the production and welding metallurgy have become established.

More highly alloyed grades have existed for some time with 25%Cr, typified by the S32550 alloys (e.g. Ferralium 255) which also contain



1.1 The development of hot rolled grades in terms of nitrogen against chromium and molybdenum content (after reference 12).

up to 2%Cu. These alloys were originally developed as castings, such as pumps and valves, and have been used extensively in the offshore industry and for sulphuric acid service.

During the 1980s, more highly alloyed duplex grades were developed to withstand more aggressive environments. The so-called superduplex grades contain about 25%Cr, 6-7%Ni, 3-4%Mo, 0.2-0.3%N, 0-2%Cu and 0-2%W (Table 1.1). These grades typically have pitting resistance equivalent numbers (PRE_N) greater than 40, where:

$$PRE_N = \%Cr + 3.3 \times (\%Mo) + 16 \times (\%N) \quad [1.1]$$

PRE_N is derived from an empirical relationship and can take several forms. Nevertheless, the most widely employed for duplex alloys is given above.²⁶ However, due to the introduction of tungsten to some grades of superduplex stainless steel, an element which also improves pitting resistance, a modified form of the PRE relationship has been proposed,²⁷ namely:

$$PRE_W = \%Cr + 3.3 \times (\%Mo + 0.5 \times \%W) + 16 \times (\%N) \quad [1.2]$$

Both forms of the equation will be used in this book (use designated by N or W subscript). Clearly there is no difference between the two PRE forms for those steels with only residual tungsten contents.

In the making of superduplex alloys, the steel makers took care to balance the Cr and Ni forming elements, and added higher levels of nitrogen (Fig. 1.1). These two factors provided the steels with thermal stability during welding and high strength. On the down side, the higher alloy content promotes intermetallic precipitation (leading to a reduction in properties). But this deleterious phenomenon can be avoided by good process control and solution annealing practice, and by limiting arc energies and interpass temperatures during welding.

Another development during the 1980s was a lean alloy grade exemplified by S32304. The lower alloy content, in particular Mo, than the standard grade S31803 means that it is cheaper to produce, but has lower pitting resistance. In this respect, it competes with the high production austenitic grades, such as 304L and 316L, on the grounds of its higher strength, similar pitting resistance in chloride media and better resistance to chloride SCC.

1.3 Specifications and standards

The most comprehensive listing of duplex grades is given by the Unified Numbering System (UNS) from the United States of America.

Although this system only provides information on the composition for each grade, its designations are well recognised and will be referred to throughout this book. Table 1.1 lists the UNS compositional ranges for common wrought products and Table 1.2 provides similar information for castings. In addition, the European coding provided in EN10088-1 covers most of the modern grades and is presented in Tables 1.3 (wrought product) and 1.4 (castings), together with some common tradenames.

Table 1.3 Some common tradenames, EN equivalents and typical PRE_N-values for wrought duplex grades

UNS	Common tradenames	European coding (EN)	Typical PRE _N
Alloy lean			
S31500	3RE60, ¹ A903, ⁹ VLX 569 ³	1.4417	23
S32304	SAF2304, ^{1,11} UR35N, ² VLX534 ³	1.4362	25
S32404	UR50 ²	—	31
Standard 22%Cr			
S31803	2205, ¹ UR45N, ² Falc223, ⁸ AF22, ¹⁰ VS22, ³ VLX562, ³ DP8, ⁴ 318LN, A903, ⁹ 1.4462/PRES35, ¹² NKCr22, ¹³ SM22Cr, ⁴ Remanit 4462 ¹⁴	1.4462	34
S32205	UR45N +, ² 2205 ¹	1.4462	35
High alloy			
S31200	UHB 44LN, UR 47N, ² VLX547 ³	—	38
S31260	DP3 ⁴	—	38
S32550	Ferralium 255, ⁵ UR52N ²	1.4507	38
S32900	AISI 329, UHB 44L, 10RE51, ¹ 453S	1.4460	33
S32950	7Mo Plus ¹⁵	—	36
Superduplex			
S32520	UR52N +, ² SD40 ⁵	1.4507	41
S32750	SAF2507, ^{1,11} UR47N + ²	1.4410	41
S32760	Zeron 100, ⁶ FALC100 ⁸	1.4501	>40
S39226			>40
S39274	DP3W ⁴	—	42*
S39277	AF918, ⁷ 25.7NCu ⁷	—	42

* PRE_w

Manufacturers (in no particular order)

¹ Avesta Sheffield Ltd

² Creusot-Loire Industrie

³ Valourec

⁴ Sumitomo Metal Industries

⁵ Haynes International

⁶ Weir Materials Ltd

⁷ DMV Stainless/Feroni

⁸ Krupp Stahl

⁹ Böhler Edelstahl

¹⁰ Mannesmann

¹¹ AB Sandvik Steel

¹² Fabrique de Fer

¹³ Nippon Kokan

¹⁴ TEW

¹⁵ Carpenter

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Table 1.4 Some common tradenames, EN equivalents and typical PRE_N-values for duplex castings

UNS	Special tradenames	EN	Typical PRE _N
Standard 22Cr			
J92205	2205, ¹ UR45N, ² FALC223, ⁷ AF22, ⁹ VS22, ³ VLX562, ³	1.4462	32–33
J93183	DP8, ⁴ 318LN, A903, ⁸ KCR-D183		
High alloy			
J93345	Escoloy	–	38
J93370	CD4-MCu, ⁶ UR55(M) ²	1.4517	37
J93371	3A	–	35
J93372	CD4-MCuN ⁶	–	35
J93550	KCR-D283	–	49
Superduplex			
J93380	Zeron 100, ⁵ FALC100 ⁷	1.4508	> 40
JU93404	Alloy 958, 4469	1.4469	44
Manufacturers (in no particular order)			
¹ Avesta-Sheffield Ltd, AB Sandvik Steel	⁶ Alloy Casting Institute		
² Creusot-Loire Industries (Usinor Group)	⁷ Krupp Stahl		
³ Valinox	⁸ Böhler Edelstahl		
⁴ Sumitomo Metal Industries	⁹ Mannesmann		
⁵ Weir Materials Ltd			

Duplex stainless steels are relatively new materials with respect to specifications, and so some key documents do not cover these materials completely.²⁸ In particular, corrosion considerations and fabrication problems are not always covered. Furthermore, where certain grades are included, the standards may fall short of user requirements. Nevertheless, this deficiency is being addressed and so the listing of grades provided in material specifications, provided in Table 1.5 (wrought products) and Table 1.6 (castings), should be compared with the latest edition. A further listing of industry specific standards relevant to duplex stainless steels is given in Chapter 12.

Table 1.5 Wrought duplex grades covered in national material standards

Alloy lean			Standard 22%Cr		High alloy				Superduplex				Covers		
UNS	S31500	S32304	S32404	S31803	S32205	S31200	S31260	S32550	S32900	S32950	S32750	S32760	S39274	S39277	
EN	1.4417	1.4362	-	1.4462	1.4462	-	-	1.4507	1.4460	-	1.4410	1.4501	-	-	
ASTM/ASME															
A182				Y	(Y)	Y				Y	Y			Forged flanges, fittings Plate and sheet Tubing Bars and shapes Forging stock Forgings Bars and shapes Pipe and tube Pipe and tube Fittings	
A240			Y	Y	(Y)	Y		Y	Y	Y	Y				
A268				Y	(Y)		Y	Y							
A276				Y	(Y)					Y	Y				
A314				Y	(Y)					Y	Y				
A473				Y	(Y)					Y	Y				
A479				Y	(Y)					Y					
A789	Y	Y		Y	(Y)	Y	Y	Y	Y	Y	Y		Y		
A790	Y	Y		Y	(Y)	Y	Y	Y	Y	Y	Y		Y		
A815				Y	(Y)					Y	Y		Y		
EN															Flat products General Forgings Bars
pr10028	Y			Y	(Y)			Y			Y				
10088	Y			Y	(Y)			Y	Y		Y				
pr10250	Y			Y	(Y)			Y	Y		Y				
pr10272		Y		Y	(Y)			Y			Y				
NACE														Sour service	
MR0175		Y		Y	(Y)		Y	Y			Y	Y	Y		

Table 1.6 Cast duplex grades covered in national standards

UNS EN	J93183 1.4462	J93345 —	J93370 1.4517	J93380 1.4508	J93404 1.4469
ASTM/ASME					
A297					
A351				Y	
A743				Y	
A744			Y		
A872	Y				
A890		Y	Y		Y
NACE					
MR0175			Y	Y	Y

1.3.1 Material standards and specifications

(Also refer to industry specific design/fabrication codes in Chapter 12)

American Petroleum Institute

API 5LC: CRA line pipe, API, August 1991, Second edition.

ASTM/ASME specifications

A182/A182M-94c: 'Forged or rolled alloy-steel pipe flanges, forged fittings, and valves and parts for high-temperature service', ASTM, Vol. 01.01, 1996.

A240/A240M-94a: 'Heat-resisting chromium and chromium-nickel stainless steel plate, sheet and strip for pressure vessels', ASTM, Vol. 01.03, 1996.

A268/A268M-94: 'Seamless and welded ferritic and martensitic stainless steel tubing for general service', ASTM, Vol. 01.01, 1996.

A276-84b: 'Stainless steel bars and shapes', ASTM, Vol. 01.05, 1996.

A297/A297M-93: 'Steel castings, iron-chromium and iron-chromium-nickel, heat resistant, for general application', ASTM, Vol. 01.02, 1996.

A314-94b: 'Stainless steel billets and bars for forging', ASTM, Vol. 01.05, 1996.

A351/A351M-94: 'Castings, austenitic, austenitic-ferritic (duplex), for pressure-containing parts', ASTM, Vol. 01.02, 1996.

A473-94a: 'Stainless steel forgings', ASTM, Vol. 01.05, 1996.

A479/A479M-94a: 'Stainless steel bars and shapes for use in boilers and other pressure vessels', ASTM, Vol. 01.05, 1996.

A743/A743M-93a: 'Castings, iron-chromium and iron-chromium-nickel, corrosion-resistant, for general application', ASTM, Vol. 01.02, 1996.

A744/A744M-94: 'Castings, iron-chromium-nickel, corrosion-resistant, for severe service', ASTM, Vol. 01.02, 1996.

A789/A789M-94: 'Seamless and welded ferritic/austenitic stainless steel tubing for general service', ASTM, Vol. 01.01, 1996.

A790/A790M-94: 'Seamless and welded ferritic/austenitic stainless steel pipe', ASTM, Vol. 01.01, 1996.

A815/A815M-94: 'Wrought ferritic, ferritic/austenitic, and martensitic stainless steel piping fittings', ASTM, Vol. 01.01, 1996.

A872-91: 'Centrifugally cast ferritic/austenitic stainless steel pipe for corrosive environments', ASTM, Vol. 01.01, 1996.

A890/A890M-94: 'Castings, iron-chromium-nickel-molybdenum corrosion resistant, duplex (austenitic/ferritic) for general application', ASTM, Vol. 01.02, 1996.

A928/A928M-94: 'Ferritic/austenitic (duplex) stainless steel pipe electric fusion welded with addition of filler metal', ASTM, 1996.

A949/A949M-95: 'Spray-formed seamless ferritic/austenitic stainless steel pipe', ASTM, 1997.

European Standards

prEN 10028-7: 'Flat products made of steel for pressure vessel purposes. Part 7: Stainless steels', draft 1997.

EN 10088-1: 'Stainless steels – Part 1: List of stainless steels', 1995.

EN 10088-2: 'Stainless steels – Part 2: Technical delivery conditions for sheet/plate and strip for general purposes', 1995.

EN 10088-3: 'Stainless steels – Part 3: Technical delivery conditions for semi-finished products, bars, rods and sections for general purposes', 1995.

prEN 10250-5: 'Open die steel forgings for general engineering purposes – Part 5: Stainless steels', August 1996.

prEN 10272:1996 E: 'Stainless steel bars for pressure purposes', March 1996.

National Association of Corrosion Engineers

MR0175-97: 'Sulfide stress corrosion cracking resistant materials for oilfield equipment, NACE International', 1997.

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2 Alloy design

2.1 Melting and refining

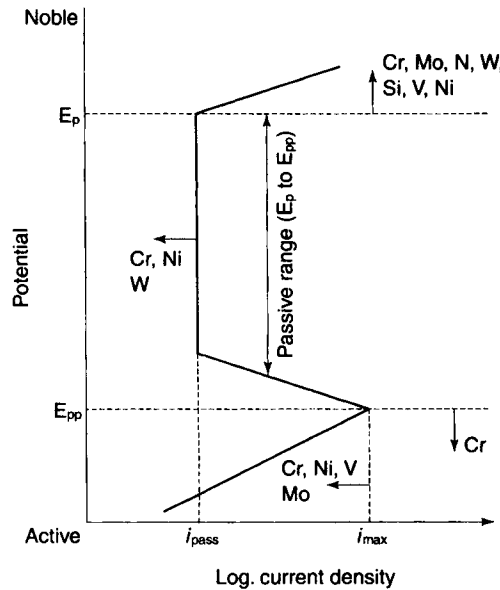
The melt for a duplex alloy can be produced using either high purity material in a conventional induction furnace, or high alloyed scrap in an electric arc furnace (EAF) followed by AOD, VOD or VARP converters.¹ Although both these methods produce high quality materials, the latter method favours lower sulphur contents but the converters do not naturally reduce phosphorus unless reducing conditions, careful scrap selection and good base mix practice are undertaken. Overall, the aim is to reduce sulphur and phosphorus, as far as possible, in order to increase the ultimate corrosion resistance.²

The next stage of refinement involves deoxidation and inoculation by adding a combination of the following agents: SiCaMn, SiCaCe, REM, Al, Ti, Mg, Nb, Zr etc. These additions lead to the precipitation of microscopic oxides which act as multiple nucleation sites for ferrite crystals and provide grain refinement. The precise combination of agents employed depends on the (previous) oxygen and carbon contents, and is selected in view of the final corrosion and mechanical properties.^{3,4} Besides the deoxidants, the cooling rate has a significant effect on grain size which, in the case of castings, remains essentially unchanged during subsequent solution heat treatment and water quenching.

2.2 Alloying additions

2.2.1 Chromium

The main advantage of adding chromium to steel is to improve the localised corrosion resistance, by the formation of a passive chromium-rich oxy-hydroxide film.⁵ Electrochemically this is achieved by extending the passive range (see Fig. 2.1)⁶ and reducing the rate of general corrosion (i_{pass}). However, there is a limit to the level of chromium that can be added to such a steel, as the beneficial effect



2.1 Schematic summary of the effects of alloying elements on the anodic polarisation curve (after reference 6).

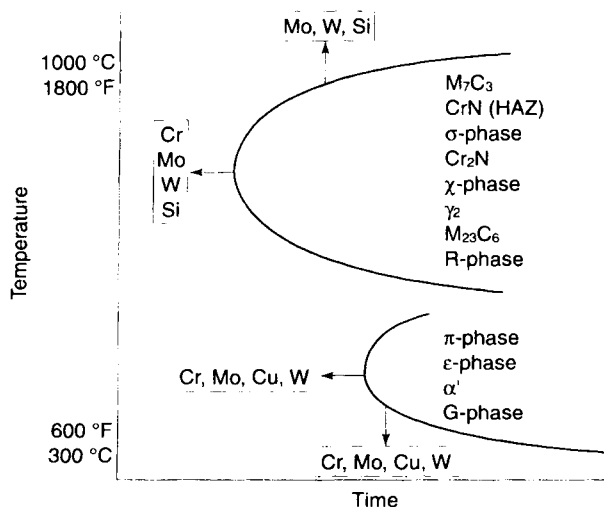
of ever higher levels is negated by the enhanced precipitation of intermetallic phases (Fig. 2.2),⁷ such as sigma. These phases often lead to reduction in ductility, toughness and corrosion properties, and are covered in Section 8.3.4.

Chromium and other elements stabilise ferrite, although the effect of different elements varies. Equations have been derived to quantify elemental effects (the so-called chromium equivalents, Cr_{eq}) of which the most favoured is:

$$Cr_{eq} = \%Cr + \%Mo + 0.7 \times \%Nb \quad [2.1]^8$$

2.2.2 Molybdenum

The beneficial influence of molybdenum on the pitting and crevice corrosion resistance of an alloy in chloride solutions has been recognised for many years (Fig. 2.1). As for chromium, molybdenum extends the passive potential range and reduces the corrosion current density (i_{max}) in the active range. Molybdenum is included in both



2.2 Schematic summary of the effects of alloying elements on the formation of various precipitates (after reference 7).

PRE relationships, Eqs 1.1 and 1.2, and is given a coefficient of 3.3 times that of chromium, while it has a similar effect on ferrite stability as chromium, Eq. 2.1. The mechanism by which molybdenum increases the pitting resistance of an alloy has been examined by a number of workers,⁹⁻¹² and has been found to suppress active sites via formation of an oxy-hydroxide or molybdate ion.¹³

In high temperature sea water, the addition of at least 3%Mo is recommended¹⁴ to prevent crevice corrosion, while an upper limit of about 4%Mo has been quoted.¹⁵ This limit stems¹⁶ from the enhanced sigma forming tendency in the hot working temperature range, i.e. above 1000°C (Fig. 2.2).

2.2.3 Nickel

Counter to the ferrite stabilising effect of chromium (Mo and Nb), there is another group of elements which stabilise austenite:

$$Ni_{eq} = \%Ni + 35 \times \%C + 20 \times \%N + 0.25 \times \%Cu \quad [2.2]$$

In order to maintain about 40% to 60% ferrite, balance austenite, the ferrite stabilising elements, Eq. 2.1, need to be balanced with the austenite stabilisers, Eq. 2.2. For this reason, the level of nickel addition to a given duplex alloy will depend primarily on the chromium content.

At excessive Ni contents, the austenite level increases to well above 50%, with the consequence that Cr and Mo are enriched in the remaining ferrite. As a result, ferrite transformation to intermetallic phases may be enhanced¹⁶ when the alloy is exposed to temperatures in the range 650 to 950°C. Further, high Ni-contents accelerate alpha prime formation,¹⁷ an embrittling intermetallic phase, in the ferrite. In summary, nickel does have some direct effect on corrosion properties, for instance moving E_p in the noble direction and reducing i_{pass} (Fig. 2.1), and yet it appears that the main role of nickel is to control phase balance and element partitioning.

2.2.4 Nitrogen

Nitrogen has a multiple effect on stainless steels by increasing pitting resistance, austenite content and strength. It has a similar influence on pitting as Cr and Mo, moving E_p in the noble direction and thus increasing the passive potential range, Fig. 2.1. This effect is enhanced in the presence of Mo and it has been suggested^{18–20} that Mo and N have a synergistic influence on pitting characteristics. The proposed factor for nitrogen in the PRE_N relationship varies between 13 and 30, but the most widely used value for duplex alloys is 16, Eq. 1.1.

Nitrogen partitions preferentially to the austenite due to the increased solubility in the phase²¹ and also concentrates at the metal-passive film interface.²² During prolonged passivation of stainless steels in acid solutions, surface nitrogen enrichment has been witnessed,^{10,23} which explains how nitrogen can influence repassivation. However, to break down the passive film the anodic current density must be high, in the order of several A/cm². For nitrogen bearing 316L type stainless steel in 4M HCl, nitrogen reversibly impedes active dissolution from reaching these high values, possibly by surface enrichment of nitrogen atoms.²⁴ The inhibitive nature of nitrogen was postulated to result from its dissolution, whereby nitrogen combines with hydrogen ions to form ammonium ions. This is a cathodic reaction, which becomes too slow at high potentials to balance the anodic dissolution of the metal and allows for surface enrichment of nitrogen, leading to the blocking effect observed.

Nitrogen has also been noted to increase the crevice corrosion resistance. Workers have proposed^{25–27} that this is due to nitrogen altering the crevice solution chemistry or by segregating to the surface, which is in keeping with the mechanism for enhanced pitting resistance.²⁴

Another important property of nitrogen is its ability to stabilise duplex alloys against the precipitation of intermetallic phases,²⁸ such as sigma and chi, by reducing Cr-partitioning.²⁹ It is also reported³⁰ that increasing the nitrogen level actually reduces the risk of nitride formation. This may appear contradictory, but is due to an increase in austenite content and so a reduction in the distance between austenite islands.

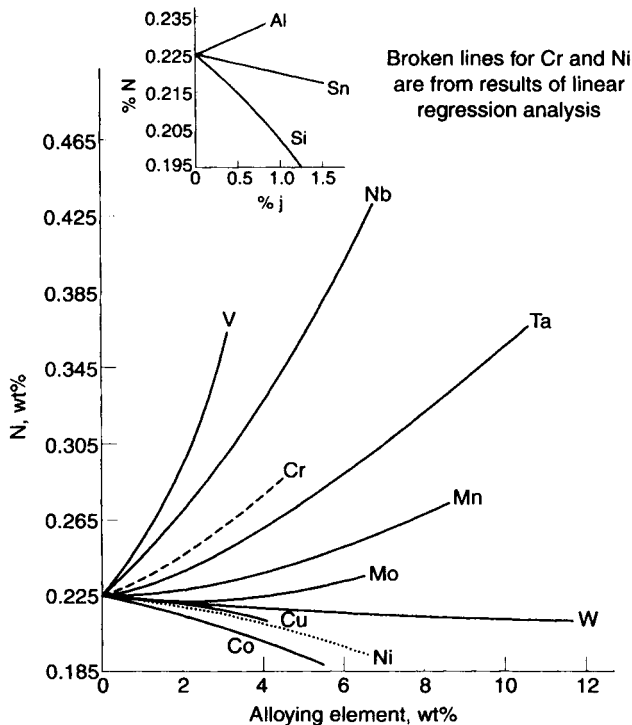
The addition of C and N strengthens both ferrite and austenite by dissolving at interstitial sites in the solid solution.^{31,32} And yet, as carbon is undesirable in stainless steel, due to the risk of sensitisation, the addition of nitrogen is preferred. Further, as nitrogen is a strong austenite stabiliser its addition to duplex stainless steel suppresses austenite dissolution and encourages austenite reformation in the HAZ (see Chapter 9).

Comparison of the nitrogen contents of different duplex stainless steels (Table 1.1), shows that the superduplex grades contain higher levels than the lower alloyed variants. This enhanced level of nitrogen is due to the higher alloy content of these steels and, in particular, enhanced chromium contents (Fig. 2.3).³³ In this regard, the beneficial influence of manganese should also be noted. In other grades, with lower Cr and Mn contents, the nitrogen solubility limit can be reached, leading to severe out-gassing or porosity during solidification.

2.2.5 Manganese

Manganese has been quoted^{34,35} as a austenite stabiliser for austenitic steels and yet, for duplex alloys, mixed results have been obtained.^{36,37} The current understanding is that manganese has little effect on duplex phase balance, especially at the levels normally encountered, and is excluded from the Cr_{eq} and Ni_{eq} equations quoted above,⁸ i.e. Eqs 2.1 and 2.2. Nevertheless, it would appear³⁸ that Mn can increase the temperature range and formation rate of detrimental sigma phase.

Manganese additions to stainless steel increase abrasion and wear resistance³⁹ and tensile properties without loss of ductility³⁸. Further, Mn increases the solid solubility of nitrogen and thus allows for increased nitrogen contents to be achieved without risk of out-gassing. However, Mn-additions in excess of 3% and 6%, for nitrogen levels of 0.1% and 0.23% respectively, significantly decrease the critical pitting temperature (CPT), probably due to the increased likelihood of MnS inclusions which can act as initiation sites for pits.⁴⁰ Nevertheless, the combined addition of Mn and N in modern duplex



2.3 Effect of alloying elements on the solubility of nitrogen in liquid Fe-18%Cr-8%Ni alloys at 1600°C at 1 atm N₂ (after reference 33).

alloys improves³⁶ the pitting resistance and counteracts the singular problems associated with Mn.

2.2.6 Copper

Copper additions to high alloy austenitic stainless steel are recognised to reduce the corrosion rate in non-oxidising environments, such as sulphuric acid. In some 25%Cr duplex alloys, 1.5%Cu is added to obtain the optimum corrosion resistance in 70% H₂SO₄ at 60°C,⁴¹ while for boiling HCl, an addition of 0.5%Cu decreases both the active dissolution and crevice corrosion rates. In general, the addition of Cu to duplex stainless steels is limited to about 2%, since higher levels reduce hot ductility and can lead to precipitation hardening (see Section 3.4.8).

Under high velocity conditions where cavitation erosion in H₂S-contaminated sea water prevail, Cu appears⁴² to be beneficial, due to the formation of a Cu-rich layer on the surface during active dissolution.⁴³ Unfortunately, no data from the field supports this mechanism.¹⁵ Further, copper has been found to improve machinability in low oxygen and sulphur materials and can lead to hardening after exposure to the 300–600°C temperature range (Fig. 2.2). This is apparently due to the precipitation of tiny Cu-rich precipitates.³⁹ These precipitates do not significantly reduce corrosion resistance or toughness and have been exploited⁴⁴ for improving abrasion–corrosion resistance in duplex pump castings.

2.2.7 Tungsten

Tungsten additions of up to 2% have been made^{15,45} to duplex steels to improve pitting resistance, i.e. extend the passive potential range and reduce i_{pass} , (Fig. 2.1). Similarly, tungsten increases crevice corrosion resistance in heated chloride solutions.⁴⁶ This is thought⁴⁷ to be due to the adsorption of tungsten into the passive layer without modification of its oxide state. However, in acid chloride solutions tungsten appears to pass from the substrate into the passive film by interaction with water to form insoluble WO₃. In neutral chloride solutions, WO₃ interacts with other oxides increasing their stability and bonding to the substrate.

Tungsten is known to encourage intermetallic formation in the 700 to 1000°C temperature range (Fig. 2.2), and encourages secondary austenite formation in weld metal.⁴⁸ It is believed⁴⁹ to be thermodynamically equivalent, but kinetically non-equivalent, to molybdenum with respect to sigma formation. However, levels between 1% and 3% have been shown to restrict the formation of sigma at the phase boundaries and, instead, precipitation occurs at intragranular sites. This is thought to be due to the large tungsten atom influencing the diffusion of Mo and W at the phase boundaries and thus nucleation of sigma. Notwithstanding this, tungsten alloyed weld metal has been shown to form chi phase more rapidly than otherwise similar deposits without the addition.^{50,51} Nevertheless, a tungsten content of 1% is usually not exceeded in a 4%Mo duplex steel,¹⁵ with 2%W added to steels with about 3%Mo (S39276 in Table 1.1).

2.2.8 Silicon

Silicon is beneficial for concentrated nitric acid service and also enhances the high temperature oxidation resistance.³⁹ High silicon- (3.5–5.5%) bearing duplex stainless steels have been developed with increased pitting resistance (Fig. 2.1) and a claimed¹⁵ immunity to stress corrosion cracking (SCC). Nevertheless, as Si is generally considered to enhance sigma formation (Fig. 2.2), it is generally preferred to limit its addition to the 1% level.

2.2.9 Carbon, sulphur and phosphorus

The carbon content of most wrought duplex stainless steels is limited to 0.02% or 0.03%, primarily to suppress the precipitation of Cr-rich carbides which can act as initiation sites for pitting corrosion and intergranular attack. Similarly, S and P contents are controlled, although not eliminated as the presence of some sulphur is important for weld bead penetration.³⁹ Nowadays, levels of C and S can be controlled by the modern steel making processes, such as AOD and VOD, while phosphorus contents can be reduced using good melting practice (see Section 2.1).

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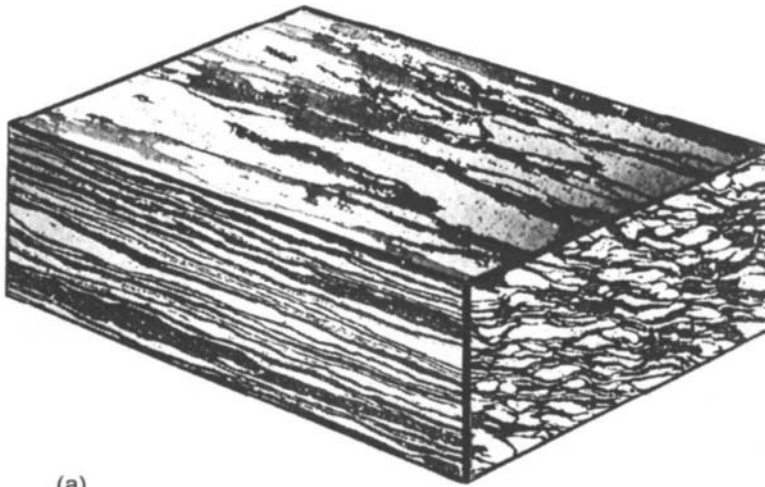
3 Microstructure

3.1 Commercial products

Modern duplex stainless steels are characterised by a two phase structure, which consists of a mixture of about 50% volume FCC austenite islands in BCC ferrite grains. Both cast and wrought products have roughly equivalent volume fractions of ferrite and austenite (see Fig. 3.1), which, in the case of wrought components, contain a rolling texture obtained by hot working, followed by a solution annealing and quench. The optimum phase balance for modern wrought products varies between manufacturers, but overall a range of between 45% and 60% austenite may be expected. The structure is obtained by simultaneous control of the chemical composition and annealing temperature.

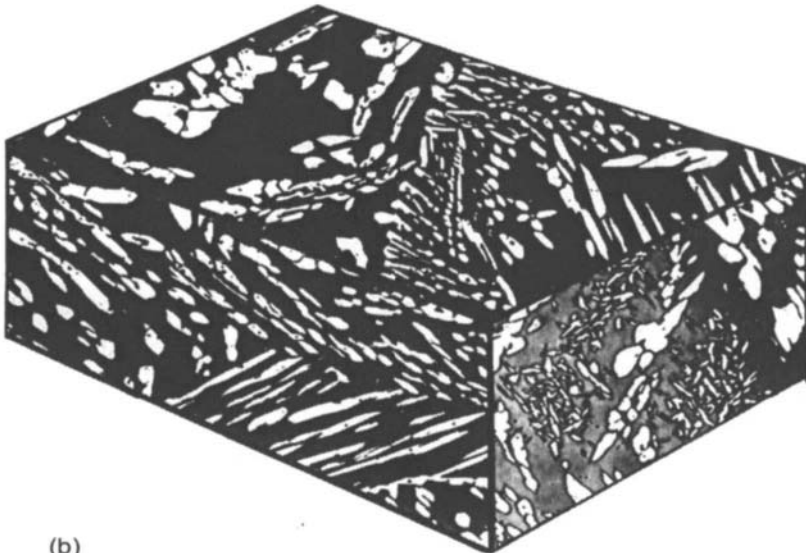
Figure 3.2 shows a schematic section of the Fe-Cr-Ni diagram at the 70%Fe level.¹ The phase proportions and their respective compositions are indicated for a given alloy analysis and annealing temperature, with the high temperature stability of the duplex structure being influenced more by nitrogen content, than by Cr or Mo. As depicted in Fig. 3.3,^{2,3} the addition of 0.25%N to a 25%Cr alloy produces a ferrite volume fraction of about 50% at 1250°C, compared to nearly 80% ferrite with 0.18%N. Nevertheless, it is difficult to predict the microstructure of a duplex alloy from simplified diagrams, due to the effects of other alloying elements, which modify the phase fields.

One approach⁴ has been to produce isothermal ternary sections of Fe-Cr-Ni-Mo-N using a computer program called Thermocalc™ which calculates phase equilibria, over a range of temperatures. This can then be used⁵ to form an isopleth diagram for a given composition (Fig. 3.4). As will be shown later, this approach has been found to be in good agreement with experimental data.



(a)

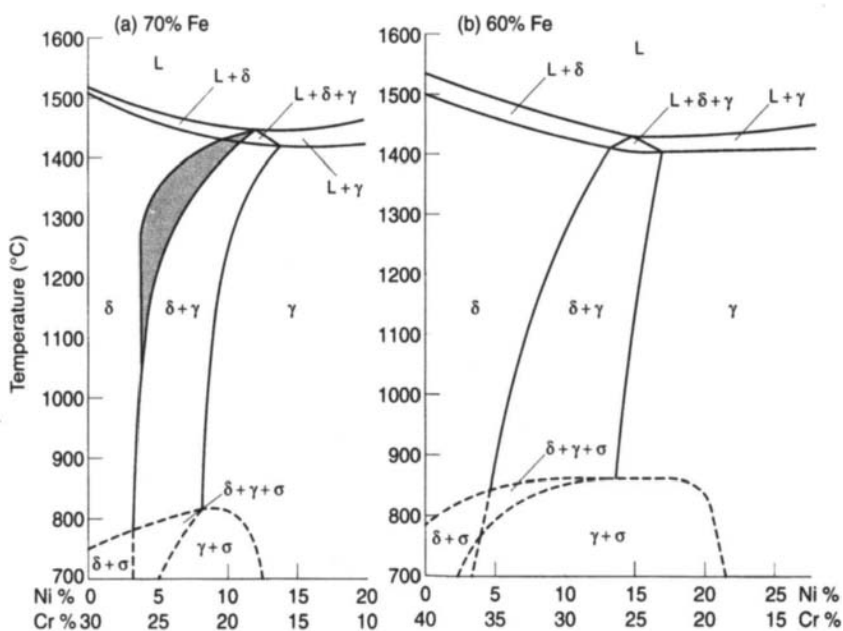
100 μm



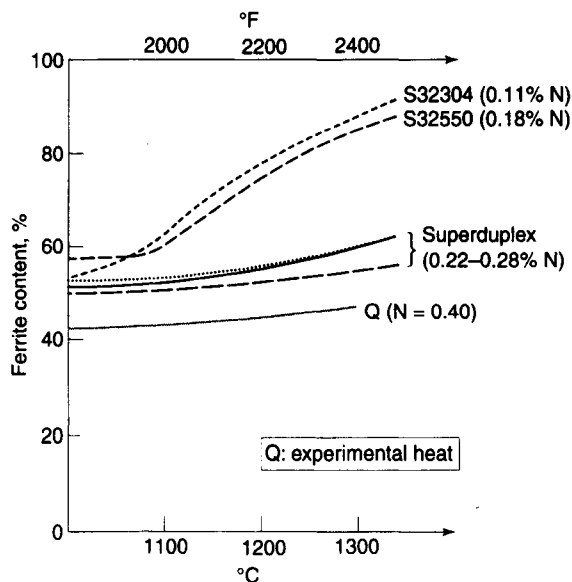
(b)

400 μm

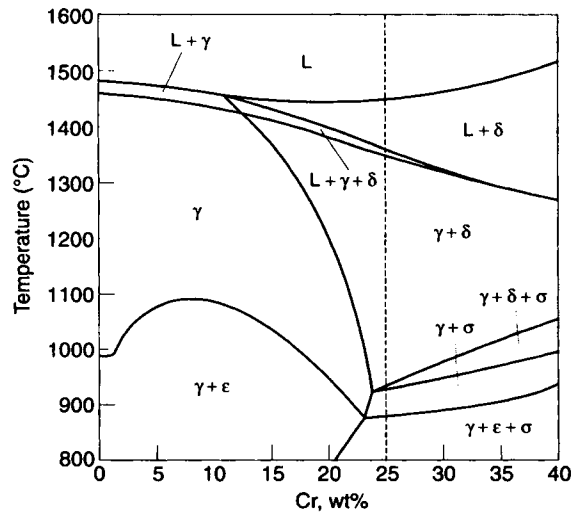
3.1 Typical microstructures of duplex stainless steels: (a) hot rolled plate, $\times 200$; (b) casting, $\times 50$.



3.2 Concentration profiles in the ternary Fe-Cr-Ni constitution diagram at 70% and 60% Fe. The schematic effect of nitrogen additions is shown in 3.2(a) (after references 1 and 2).



3.3 Variation in ferrite content with temperature for several duplex stainless steels (after references 2 and 3).

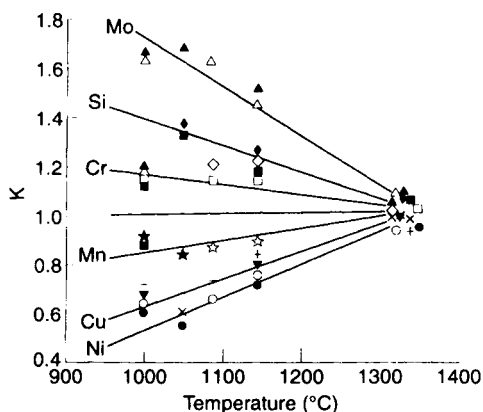


3.4 Computer calculated 'isopleth diagram' with the dotted line indicating the composition of superduplex alloys, e.g. 25%Cr-7%Ni-4%Mo-0.3%N (reference 5).

3.2 Element partitioning

3.2.1 Substitutional elements

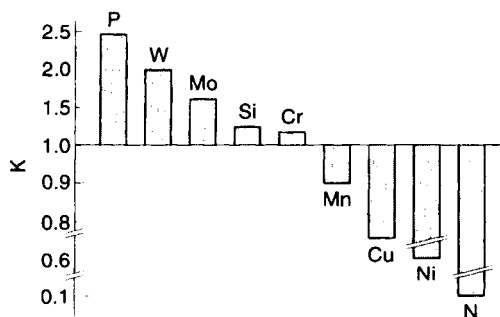
The phase diagram shown in Fig. 3.2 illustrates that the ferrite and austenite will have different compositions depending on the temperature, further illustrated by experimental data⁶ in Fig. 3.5. Several workers⁷⁻¹² have studied the composition of the phases and resultant partition coefficients in solution annealed product and have demonstrated that, with the exception of nitrogen, the partition coefficients for a given element do not vary significantly between alloys, in spite of the wide range of compositions investigated. This is due to the solubility limits for these elements not being exceeded, for the concentrations and annealing temperatures concerned. All agree that the ferrite is enriched in P, W, Mo, Si and Cr and the austenite in N, Ni, Cu and Mn, (Fig. 3.6). However, for the most highly alloyed grades (superduplex steels), it has been proposed⁶ that the partition coefficients tend more towards unity, apparently due to the use of higher solution annealing temperatures (Fig. 3.5).



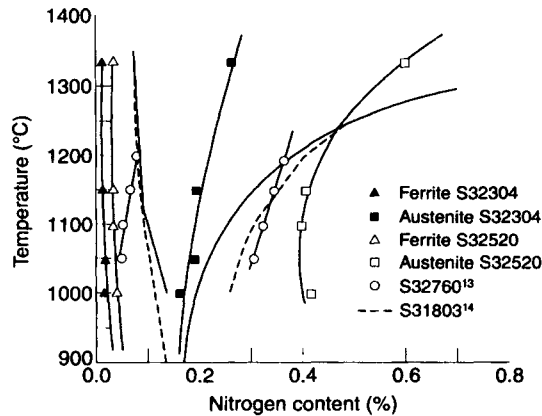
3.5 Temperature dependence of element partitioning coefficients (K = ferrite/austenite) for a range of duplex steels (after reference 6).

3.2.2 Nitrogen

The partition coefficient for nitrogen is seen to vary markedly between alloys and is highly dependent on composition. In particular, Cr and Mn increase nitrogen solubility, (Fig. 2.3), which explains why the superduplex grades can contain higher nitrogen contents than the lower chromium variants (Table 1.1). Nevertheless, the nitrogen partition coefficient is governed also by temperature. During a solution anneal, even though the solubility of nitrogen in ferrite may increase a little, the volume fraction of austenite decreases markedly. This leads to enrichment of nitrogen in the remaining austenite⁶ (Fig. 3.7),

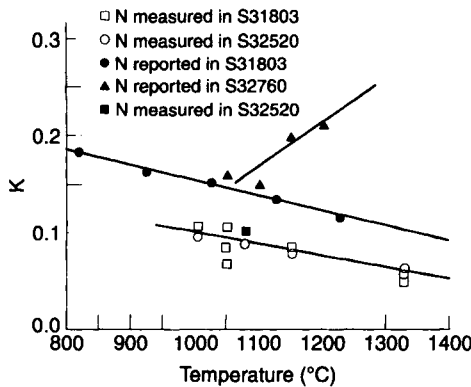


3.6 Typical partition coefficients, K , for solution annealed and water quenched products (reference 6).



3.7 Nitrogen content of ferrite and austenite for different alloys (after references 6, 13 and 14).

and so nitrogen partitioning is increased, i.e. K tends away from unity^{6,13,14} (Fig. 3.8). These figures also show that results generated¹⁴ by ThermocalcTM are in good agreement with the experimental data. Moreover, it has been observed⁶ that the nitrogen content is highest next to the ferrite:austenite interface, just within the austenite, due to phase boundary displacement. However, on cooling, austenite formation occurs and the ferrite becomes rapidly saturated with nitrogen, with the excess nitrogen diffusing into the austenite, with



3.8 Temperature dependence of partition coefficients (K) for different grades (references 6, 13 and 14).

0.03–0.05%N being the equilibrium solubility limit in ferrite at ambient temperatures.¹⁵

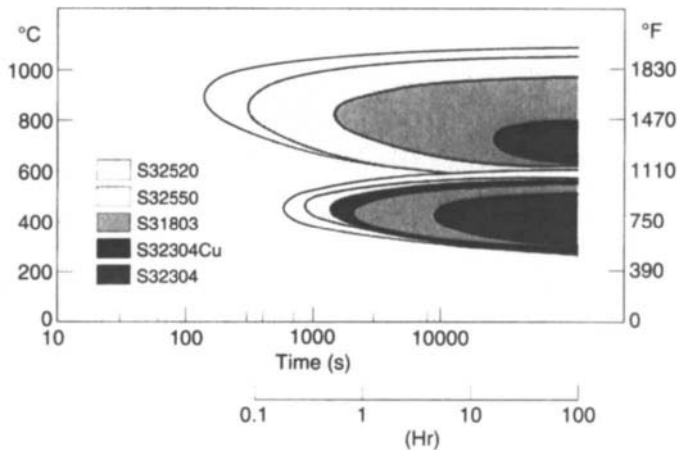
Further additions of nitrogen to the bulk alloy composition, as in the superduplex grades, leads to nitrogen enrichment in the austenite. And, as nitrogen has a significant influence on pitting corrosion resistance, this balances the preferential partitioning of Cr and Mo to the ferrite. In essence, the pitting resistance of the two phases becomes similar.¹⁶

All these data are important in understanding the effect of heat treatment on the microstructure, in particular the formation of secondary phases. For instance, if the heat treatment is undertaken at too high a temperature, then primary austenite dissolves, encouraging secondary austenite on cooling, which has inherently lower N, Mo and Cr contents than primary austenite, with inferior pitting resistance. On the other hand, if the heat treatment temperature is too low, then the substitutional elements can partition and lead to intermetallic phase formation. In fact, these observations are used in the heat treatment of castings (and heavy forgings).^{17,18} In these instances, a double heat treatment may be employed where, first, a solution anneal is undertaken above the σ -solvus to dissolve any precipitates. Second, the temperature is lowered to give the correct phase balance before quenching. The precipitation of secondary phases and their effect on properties will be addressed in the following section.

3.3 Heat treatment

Numerous structural changes can occur in the duplex stainless steels during isothermal or anisothermal heat treatments. Most of these transformations are concerned with the ferrite, as element diffusion rates are approximately 100 times faster than in austenite. This is principally a consequence of the less compact lattice of the BCC crystal structure. Moreover, as already mentioned, the ferrite is enriched in Cr and Mo, which are known to promote the formation of intermetallic phases. Furthermore, element solubility in the ferrite falls with a decrease in temperature, increasing the probability of precipitation during heat treatment.

It should be noted that the current chapter mainly deals with wrought and heat-treated products, which can be considered to be segregation free. In the case of castings or lightly worked products, or in welded joints, it should be remembered that element segregation during cooling will affect² precipitation kinetics and the stability of the phases formed.

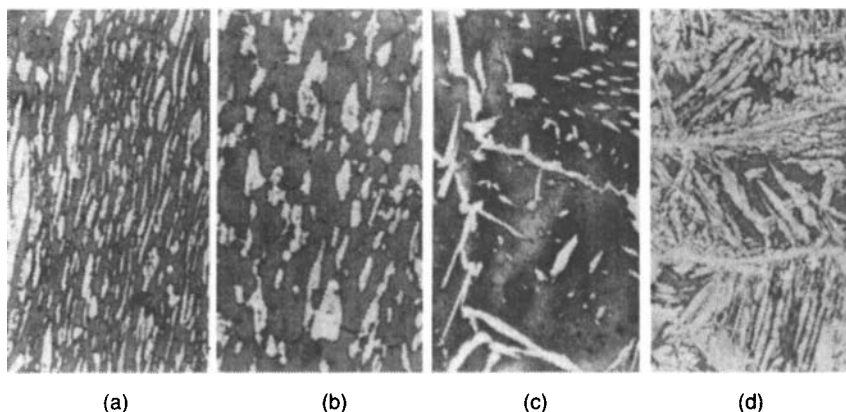


3.9 TTT diagrams of duplex stainless steels derived by optical metallography between 600 and 1050°C and hardness measurements between 300 and 600°C (after reference 2).

Time-temperature transformation (TTT) diagrams, produced by isothermal heat treatment followed by quenching, are often employed to depict the susceptibility of different grades to embrittlement, e.g. Fig. 3.9. In this example, within the 600–1050°C temperature range, the curves are based on optical microscope observations, while in the range 300–600°C, they are determined from hardness measurements. The diagrams are conservative in nature and do not imply that the mechanical properties or corrosion resistance are modified as soon as the boundaries indicated are reached, although an effect on properties may be noticed before the boundaries are reached.

3.3.1 Temperatures above 1050°C

Duplex stainless steels solidify completely in the ferrite field, for standard grades and normal cooling rates. This is followed by solid state transformation to austenite (Fig. 3.2), which is naturally reversible, so that any large increase in temperature, e.g. from 1050°C to 1300°C, leads to an increase in ferrite content (Fig. 3.3). Further, as the temperature increases, there is a reduction in the partitioning of substitutional elements between the phases, i.e. K tends to unity (Fig. 3.5). In addition, the ferrite becomes enriched in interstitial elements such as carbon and nitrogen.



3.10 Effect of heat treatment on the ferrite/austenite microstructure (after reference 2).

Figure 3.3 shows the variation in ferrite content with temperature for different duplex grades. The marked influence of chemical composition on the shape of the curves should be noted. This is particularly true for nitrogen additions, with large concentrations (0.25–0.4%) clearly increasing the stability of the two phase structure. At 1250°C, the volume fractions of ferrite and austenite in these alloys remain roughly equivalent, whereas grades with less than 0.2%N contain 80% to 85% of ferrite. This observation has important repercussions for the structure of the heat affected zones (HAZ) of welds, which will be covered in more detail in Chapter 8.

Heat treatment in the temperature range 1100–1200°C can have a dramatic influence on the microstructure of a wrought product (Fig. 3.10a). The grains can be made equiaxed by prolonged treatment at high temperature, e.g. Fig. 3.10b, or can be rendered acicular, with a Widmannstätten type structure by cooling at intermediate rates, e.g. Fig. 3.10c. A dual structure, consisting of both coarse and fine austenite grains, can be obtained by step quenching, with or without simultaneous mechanical strain, e.g. Fig. 3.10d. These acicular structures are also encountered in weld deposits.

3.3.2 The 600–1050°C nose

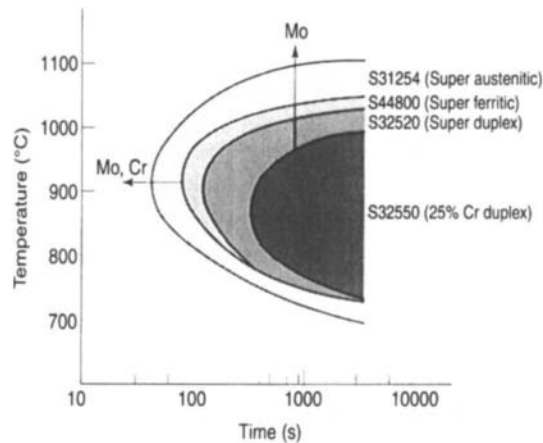
The alloy lean grade S32304 is the least prone to intermetallic phase formation and requires exposure of at least 10 to 20 hours to initiate

precipitation at temperatures below 900°C (Fig. 3.9). For this reason, a solution annealing temperature below 1000°C can be chosen for this material.

Alloy S32205/S31803 is more sensitive to precipitation than grade S32304, due to the molybdenum content. This element not only increases the rate of intermetallic precipitation, but also extends the stability range to higher temperatures. For this reason, higher solution annealing temperatures are necessary, i.e. above 1000°C.

The superduplex grades show the greatest propensity for intermetallic precipitation, due to their higher Cr, Mo and W contents. However, it should be emphasised that the precipitation kinetics in these high alloy grades are, at worst, equivalent to the super-austenitic or superferritic stainless steels^{19–25} (Fig. 3.11). And, as for the last two stainless steels, by taking precautions during heat treatment, including rapid removal from the furnace followed by a water quenching, the superduplex alloys can be used satisfactorily in industrial applications. However, especial care is required for heavy section components, i.e. greater than 60 mm thick,²⁶ during all stages of production. Further consideration should be given to all means that can accelerate the cooling, in particular at the mid-thickness, for instance, the introduction of open bore holes.

Precipitates redissolve during a solution anneal, which for the superduplex grades must be performed at 1050°C or above. A few minutes at 1050–1070°C are sufficient for grades S32550 and S32750, although 1100°C has been recommended for the tungsten bearing



3.11 TTT diagrams for 'super' stainless steels (after reference 3).

grades, such as S32760. Similar high temperatures are required for welds,²⁷ as consumables tend to contain higher Ni, Si and Mn contents than base materials. The higher Ni-content encourages high austenite contents when annealed and results in enrichment of Cr and Mo in the remaining ferrite. This fact, combined with higher Si and Mn levels, increases the stability of intermetallic phases. And yet, lower annealing temperatures (1040°C compared to 1100°C) can be used²⁸ for weldments made with matching consumables.

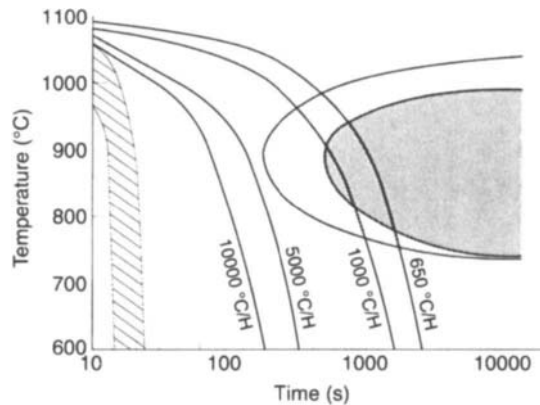
3.3.3 The 300–600°C nose

The alloy lean grade S32304 is the least sensitive to hardening in this temperature range, and a significant effect is not recorded until about three hours exposure to 400°C (Fig. 3.9). A much shorter incubation time is found for grades S32205 and S31803, containing molybdenum, which would appear² to accelerate hardening.

The 25%Cr and superduplex alloys show the widest temperature range for hardening and shortest incubation times. This is the result of both the higher Cr and Mo contents and, if present, copper additions.

3.3.4 Continuous cooling diagrams

For industrial treatments, it is important to remember that, at temperatures near the solvus, the nucleation of precipitates is slow and their growth is fast, whereas the opposite is true at lower temperatures, near the 'nose' of the transformation curve. Therefore, it is difficult to avoid phase transformations, such as sigma precipitation, during the reheating of heavy section products (e.g. ingots, castings, thick plate, etc.), and so a solution treatment should be performed at a sufficiently high temperature to redissolve any such phases. On the other hand, during cooling, the slow nucleation rate at high temperature and the sluggish growth rate at lower temperatures make it relatively easy to avoid the formation of sigma phase, even in the case of air cooling of certain castings or heavy plate.



3.12 Continuous cooling diagram from 1080°C. The hashed area denotes typical HAZ cooling rates, while the two shaded areas depict different sensitivities to intermetallic formation in superduplex alloys (after reference 3).

Figure 3.12 shows a continuous cooling transformation (CCT) diagram for the S32520 grade. A considerable shift in time can be seen in the position of the precipitation 'nose' between the TTT (Fig. 3.9) and CCT (Fig. 3.12) diagrams.^{2,29,30} Cooling rates as low as about 2000°C per hour are possible without precipitation, for solution annealing at 1080°C. However, more rapid cooling is recommended for higher annealing temperatures, since, as will be discussed later, the risk of nitride precipitation is increased. The cooling rates measured in the heat affected zones of welds are generally faster than can be achieved during quenching, which negates intermetallic formation.

3.4 Characteristics and morphology of precipitates

The following sections describe the different precipitates that have been observed in duplex alloys. The character and morphology of these phases vary markedly, as do the time for them to form and their effect on properties (described in more detail in later sections).

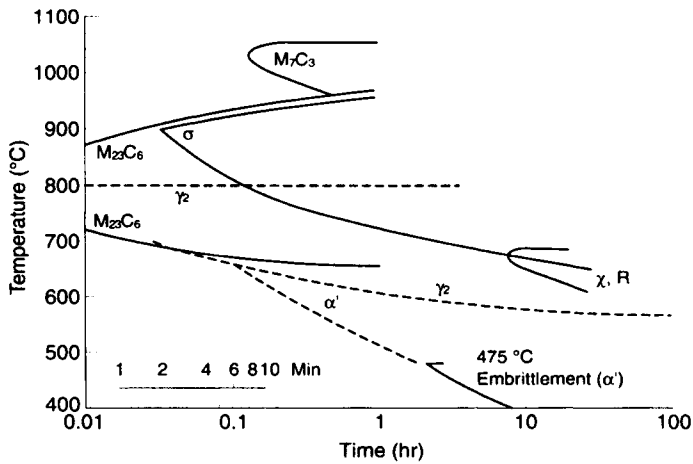
3.4.1 Alpha prime (α') and G-phase

The lowest temperature decomposition within a duplex steel is that of alpha prime (α'), which occurs between 300 and 525°C (Fig. 3.13),

Table 3.1 Crystallographic characteristics of particles observed in duplex stainless steels

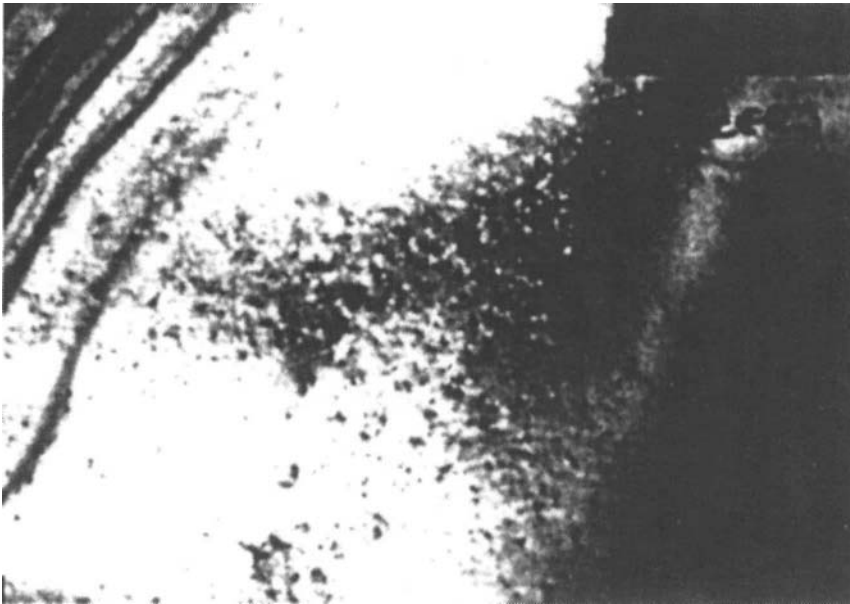
Particle	Chemical formula	Cr	Ni	Mo	Formation range, °C	Lattice type	Space group	Lattice parameter (Å)	Orientation relationship	Preferred location	Reference
ferrite (δ)*	-	27.4	8.7	4.0	-	BCC	Im3m	a = 2.86–2.88		Matrix	-
alpha prime (α')	-~	65	2.5	13	300–525	BCC	Im3m	a = 2.86–2.88	$\langle 001 \rangle$	Intra- δ	31–40
(γ)-phase	$\geq 14\% \text{Si}^S$	25	25	4	300–400						
primary austenite (γ)*	-	26.6	9.6	3.3	<1250	FCC	Fm3m	a = 3.58–3.62	K-S: $(111)_\gamma // (110)_\delta$ $[101]_\gamma // [111]_\delta$	Inter α/γ	42
secondary austenite (γ_2)	Type 1 Type 2 Type 3	same as ferrite 24.3 24.3	11 11	3.4 3.4	<650 650–800 700–900	FCC			<133> δ N-W K-S	Intra- δ δ/γ ; and δ with σ	43 29, 45 46
sigma (σ) #	Fe-Cr-Mo	30	4	7	600–1000	tetragonal	$P4_2/mnm$	a = 8.79, c = 4.54	$\{111\}_\sigma // \{001\}\sigma$ $[110]_\sigma // [110]\sigma$	Inter δ/γ	59
chi (χ) #	$\text{Fe}_{36}\text{Cr}_{12}\text{Mo}_{10}$	25	3	14	700–900	BCC-xMn	I43m	a = 8.92		Inter δ/γ	61, 62
R or Laves ζ	Fe_2Mo	25	6	35	550–650	trigonal	R3	a = 10.903, c = 19.34	$\langle 0001 \rangle_\zeta \langle 111 \rangle_\delta$	δ/γ ; and δ	50, 63
chromium nitrides	Cr_2N ~ CrN	72	6	15	700–950	cubic	P31m Fm3m	a = 4.795, c = 4.469 a = 4.13–4.47	$\langle 0001 \rangle \text{Cr}_2\text{N} \langle 011 \rangle_\delta$	Intra- δ	66 60
Pf (π) ^	$\text{Fe}_7\text{Mo}_{13}\text{N}_4$	35	3	34	550–600	cubic	$P4_332$	a = 6.47	$\langle 001 \rangle \pi \langle 012 \rangle_\delta$	Intra- δ	64, 70
Epsilon (ϵ)	Cu-rich				not defined					Intra- δ	69
Tau (τ)					550–650	orthorhombic	Fmmn	a = 4.05, b = 4.84, c = 2.86			75
Carbides	M_2C_3 M_{12}C_6 , ~				950–1050 650–950		Pnma Fm3m	a = 4.52, b = 6.99, c = 12.11 a = 10.56–10.65	$[111]_\delta \langle 111 \rangle_\delta$	Inter δ/γ Inter δ/γ	72 73

Composition refs: * = 61; # = 61; ^ = 65; ~ = 52; S = 42. K-S = Kurdjumov-Sachs; N-W = Nishiyama-Wasserman



3.13 Time-Temperature Transformation diagram for alloy S32404 (reference 35).

and is the main cause of hardening and '475 embrittlement' in ferritic stainless steels.³¹⁻³³ It is suggested³⁴ that α' -formation is a consequence of the miscibility gap in the Fe-Cr system, whereby



3.14 Bright field TEM micrograph of α' . Steel S32760 after 10 minutes at 500 °C, $\times 66,000$.

ferrite undergoes spinodal decomposition^{35,36} into Fe-rich δ -ferrite (Table 3.1) and a Cr-rich α' (Fig. 3.14), or, just outside the spinodal but still within the gap, classical nucleation and growth of α' occurs.^{37,38} Alpha prime is often associated with the co-precipitation of Cr_2N in the form of subgrain networks of Cr_2N needles interspersed within a film of α' . As a result, there has been conflicting evidence^{35,39,40} in the past as to the nature of '475 embrittlement'.

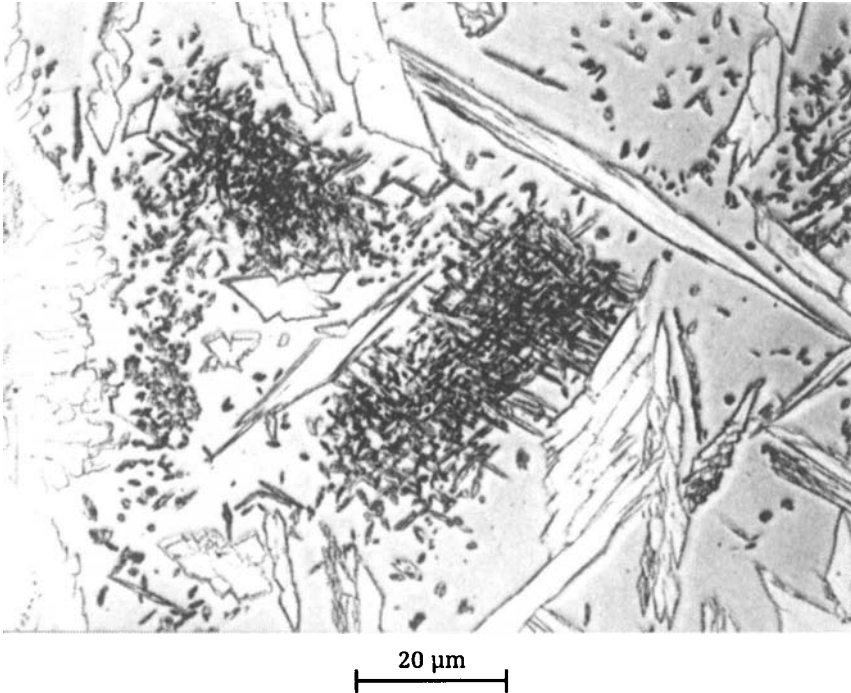
At temperatures below 400°C, the Arrhenius equation is often employed to describe the kinetics of embrittlement. The activation energy characteristic of '475 embrittlement' is similar to Cr-diffusion in ferrite, although other factors influence α' formation, such as Cr, Mo and Cu contents and high ferrite levels.^{9,41} This is illustrated in Fig. 3.9, in which the tendency to α' formation is compared for several duplex stainless steels. Further, G-phase develops at α/α' interfaces between 300 and 400°C after several hours exposure, due to enrichment of Ni and Si at these locations⁴² (Table 3.1).

3.4.2 Secondary austenite (γ_2)

Secondary austenite or γ_2 can form relatively quickly and by different mechanisms depending on the temperature (Table 3.1). Below about 650°C, γ_2 has a similar composition to the surrounding ferrite, suggesting a diffusionless transformation, with characteristics similar to martensite formation.^{43,44}

At temperatures between 650 and 800°C where diffusion is more rapid, many Widmanstätten austenite forms can precipitate^{35,40} (Fig. 3.15). In this temperature range, γ_2 obeys the Kurdjumov–Sachs relationship, its formation involves²⁹ diffusion as it is enriched in Ni compared to the ferrite matrix (Table 3.1). Even though there is some enrichment of nitrogen in γ_2 compared to the ferrite matrix, both Cr and N contents of γ_2 are substantially below that of primary austenite.⁴⁵

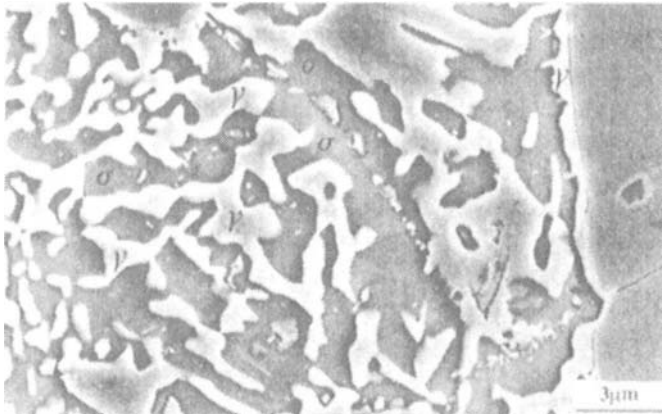
In the 700–900°C temperature range, a eutectoid of $\gamma_2 + \sigma$ can form²⁹ (Fig. 3.16), as γ_2 absorbs Ni and, to some extent, rejects Cr and Mo (Table 3.1), encouraging Cr, Mo-rich precipitates, such as sigma phase. Similarly, one form of γ_2 which forms at δ/γ boundaries is found to be depleted in Cr, especially if it has co-precipitated with Cr_2N .⁴⁶ Either of these diffusion controlled reactions can render the area susceptible to pitting corrosion.



3.15 Optical micrograph of γ_2 in a superduplex weld metal, $\times 1000$. Etch: electrolytic sulphuric acid.

3.4.3 Sigma (σ)

The deleterious Cr, Mo rich σ -phase is a hard embrittling precipitate,

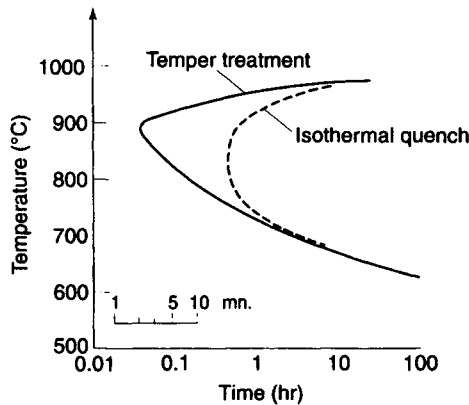


3.16 SEM micrograph of $\gamma_2 + \sigma$ eutectoid. Steel S32750 after 72 hours at 700 °C. (after reference 46).



3.17 Coarse sigma precipitates in superduplex plate after 10 minutes at 1000°C, $\times 800$. Etch: electrolytic sulphuric acid.

which forms between 650 and 1000°C (Fig. 3.13), often associated with a reduction in both impact properties and corrosion resistance. At the peak temperature of around 900°C, ferrite decomposition to sigma may take as little as two minutes in superduplex alloys. The nucleation of σ -phase in austenitic steels has been discussed in the literature with some controversy, mainly concerned with the requirement for pre-existing $M_{23}C_6$ particles.⁴⁷⁻⁴⁹ Certainly, σ -phase has been found^{50,51} to nucleate at temperatures above 750°C in association with such particles in duplex steels, with the following order of preference: δ/γ phase boundaries, austenitised δ/δ sub-grain boundaries and high energy δ/δ grain boundaries (Table 3.1). These nuclei can grow into coarse plates (Fig. 3.17), lamellar eutectoid $\sigma + \gamma_2$ ^{7,52-53} (Fig. 3.16), or $\sigma + \delta$ lamellar aggregates.⁵⁰ In the last case, the interlamellar ferritic region has a high dislocation density probably attributed to the volumetric expansion from δ to σ . Further, in the case of phase boundaries, e.g. when δ transforms to γ or γ_2 , the remaining δ becomes enriched in Cr and Mo, and denuded in Ni, enhancing σ -formation and, for the same reason, growth progresses into the destabilised ferrite.



3.18 C-curves for the beginning of sigma phase formation by a temper treatment or by an isothermal quench (after reference 58).

The elements Cr, Mo, Si and Mn have been noted^{7,52,54} to encourage σ -formation (Fig. 2.2). In addition, nickel has been found also to enhance σ -formation, but reduce the equilibrium volume fraction.⁵⁵ This occurs as nickel induces γ -formation and so concentrates the σ -promoting elements in the remaining ferrite. Finally, 10% plastic strain decreases the time required to form sigma by one order of magnitude⁵⁶ and higher solution annealing temperatures increase δ -content, reduce the concentration of σ -promoting elements, and so retard its formation.²⁹

Comparison of σ formation rates for tempering (reheating from room temperature) and isothermal quenching (cooled from higher temperature) tests, have shown⁵⁷ that the rate is faster when tempering the metal (Fig. 3.18). It is known⁵⁸ that the nucleation rate of a precipitate is low, near its decomposition temperature plateau, which for σ -phase is about 900°C. As the temperature drops to just below the decomposition plateau during an isothermal quench, the structure is devoid of sigma nuclei and formation is governed by the nucleation rate, which is relatively slow. However, in tempering tests, the alloy is brought up through a temperature range where sigma nucleation is rapid. As the temperature is further increased, these nuclei are able to grow quickly.

3.4.4 Chi (χ) phase

Like σ -phase, χ -phase forms between 700 and 900°C, although in much smaller quantities.⁶⁰ However, enrichment of ferrite with



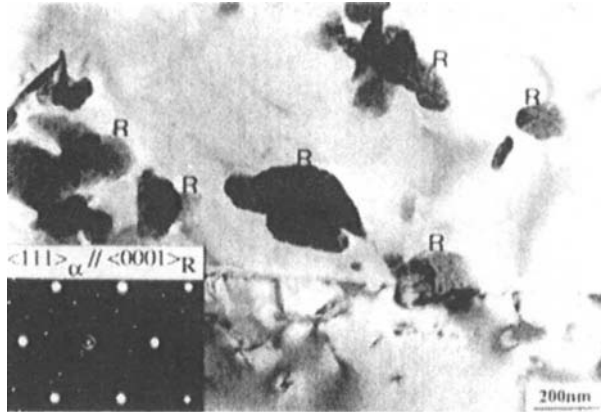
3.19 Backscattered SEM micrograph of grey σ - and white χ -phases. Steel S32750 after 900°C for 10 minutes, $\times 2000$.

intermetallic forming elements during a long exposure to relatively low temperatures, i.e. 700°C, favours the precipitation of χ -phase (Fig. 3.13). Like sigma, χ -phase often forms on the δ/γ interface and grows into the ferrite. However, the cube–cube orientation relationship (Table 3.1) ensures continuity between χ and the δ -matrix. χ -phase has a similar influence on corrosion and toughness properties as σ -phase, but, as the two phases often co-exist, Fig. 3.19, it is difficult to study their effects individually.

Early EDX analyses of χ -phase was performed⁶¹ on a low Mo-bearing steel. More recent work⁶³ on modern duplex steel has shown the composition to be more Mo-rich, and, as χ -phase contains more high atomic number elements than σ -phase, it is easily identified using back scattered electron imaging, e.g. Fig. 3.19.

3.4.5 R, π and τ phases

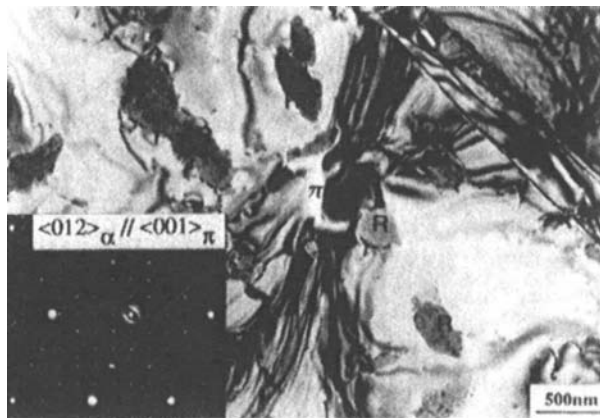
Laves or R phase (Fe_2Mo) precipitates in small quantities between 550 and 650°C after several hours exposure² (Table 3.1). They form at



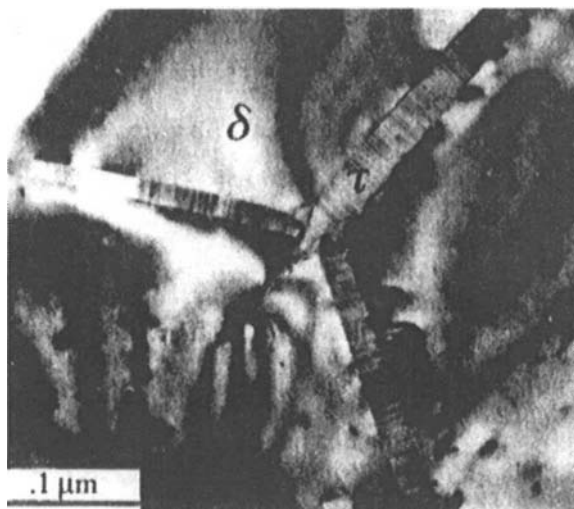
3.20 TEM micrograph of R-phase in a ferrite grain. 22%Cr weld metal after 24 hours at 600°C (after reference 65).

both intra- and intergranular sites^{50,63} (Fig. 3.20), are molybdenum-rich⁶⁴ and reduce pitting corrosion resistance. However, as those that precipitate at intergranular sites contain slightly more molybdenum (40% compared to 35%Mo), their influence on pitting resistance is more marked.

The π -nitride has been identified⁶⁴ at intragranular sites in duplex weld metal after isothermal heat treatment at 600°C for several hours² (Fig. 3.21). It is Cr and Mo rich (Table 3.1) and so has been previously confused with σ -phase.



3.21 TEM micrograph of π -phase in a ferrite grain. 22%Cr weld metal after 24 hours at 600°C (after reference 65).



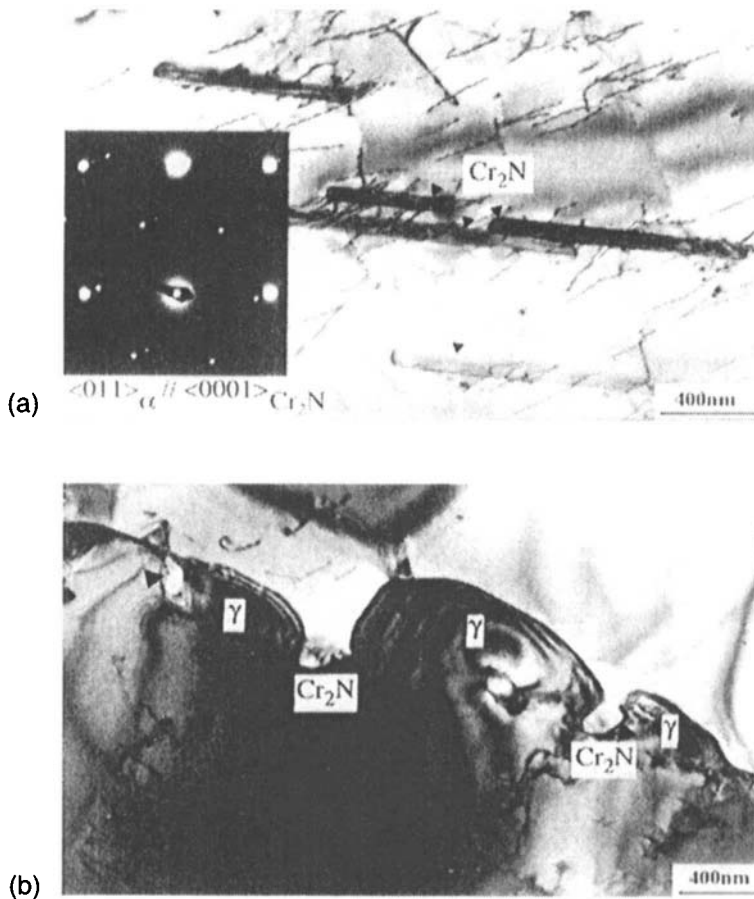
3.22 TEM micrograph of τ -phase at ferrite grain boundaries. Steel S31803 between 550 and 650 °C (after reference 50).

Heat treatment for several hours in the temperature range 550 to 650 °C (Table 3.1) can lead to the formation of the heavily faulted needle-like τ -phase on δ/δ boundaries⁵⁰ (Fig. 3.22).

3.4.6 Nitrides Cr_2N and CrN

Nitrogen is added to duplex alloys to stabilise austenite, and to improve strength and pitting resistance. The solubility of nitrogen is considerably higher in austenite than in ferrite, and has been shown⁶⁵ to partition to the former phase. Above the solution annealing temperature (about 1040 °C), the volume fraction of ferrite increases, until just below the solidus a completely ferritic microstructure can be present (Fig. 3.2), though in the higher alloy grades some austenite may remain. At these temperatures, the nitrogen solubility in ferrite is high, but on cooling the solubility drops and the ferrite becomes supersaturated in nitrogen, leading to the intragranular precipitation of needle-like Cr_2N (Fig. 3.23a). In a similar manner, Cr_2N is more likely to form after higher solution heat treatment temperatures⁵⁴ and forms rapidly even if quenched from such temperatures.⁶⁷ However, welding favours^{68,69} the formation of another nitride in the HAZ: the cubic CrN , Table 3.1.

Isothermal exposure to the 700–950 °C temperature range (Fig. 3.13), produces intergranular Cr_2N at δ/δ grain boundaries as thin



3.23 TEM micrographs of Cr_2N at: (a) intragranular and (b) intergranular sites. (after reference 46). Note the nitrides pin the migrating δ/γ phase boundaries.

plates on subgrain boundaries, triple points, inclusions and along dislocation arrays (Fig. 3.23b). This latter form of Cr_2N has been stated⁶⁰ to affect pitting corrosion.

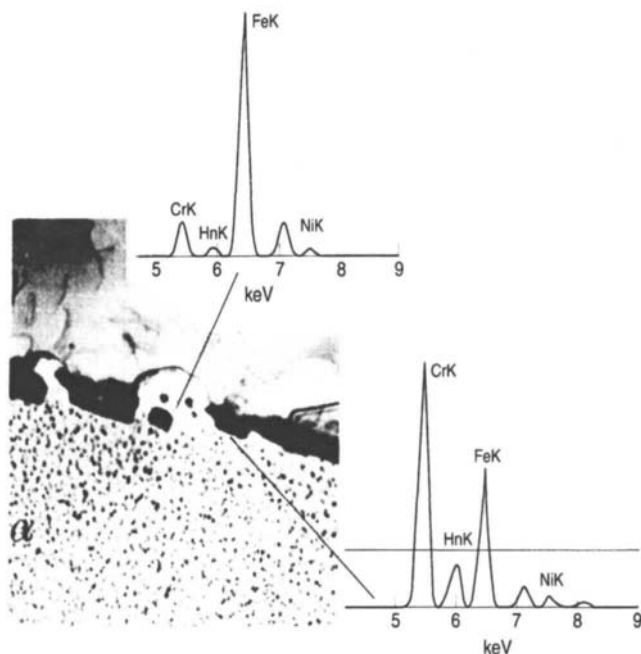
3.4.7 Carbides M_{23}C_6 and M_7C_3

M_7C_3 forms between 950°C and 1050°C (Fig. 3.13) at the δ/γ grain boundaries.^{35,72} However, as its formation takes 10 minutes, it can be avoided by normal quenching techniques. Further, as modern duplex grades contain less than 0.02% C, carbides of either form are rarely if ever seen.⁶⁰

In duplex grades with moderately high carbon levels of about 0.03%, the carbide $M_{23}C_6$ rapidly precipitates between 650 and 950°C (Fig. 3.13), requiring³⁵ less than one minute to form at 800°C. Precipitation predominantly occurs at δ/γ boundaries, where Cr-rich ferrite intersects with carbon rich austenite. However, $M_{23}C_6$ can also be found⁵² at the δ/δ and γ/γ boundaries and to a lesser degree inside the ferrite and austenite grains. Several precipitate morphologies have been recorded including cuboidal and acicular particles, as well as a cellular form,⁷¹ although each type will have an associated Cr depleted zone in its vicinity. This zone has been reported³⁵ as a site for interphase attack, which subsequently propagates into the Cr- and Mo-lean austenite phase.

3.4.8 Cu-rich epsilon (ϵ) phase

In alloys containing copper and/or tungsten, other hardening mechanisms can occur. In the case of copper, the supersaturation of the



3.24 TEM micrograph of ϵ -phase in ferrite grains and $M_{23}C_6$ and Cr_2N on the phase boundaries. Steel S32304Cu at 500°C for 100 hours. Note the Cr-depleted zone between the grain boundary precipitates. (after reference 2).

ferrite due to the decrease in solubility at lower temperatures leads to the precipitation of extremely fine Cu-rich ε -phase particles after 100 hours at 500°C,² which significantly extend the low temperature hardening range of the duplex steels. Figure 3.24 illustrates this type of precipitation seen in grades S32550 and S32304Cu. Although the reported temperature range for their formation varies,⁷⁴ it would seem that they all form in the same temperature regime as γ_2 and have been mistaken for such.

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$(\mathbb{R}_{pO-2})$ and

To David

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Microstructure, properties and applications

Edited by

Robert N Gunn

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Preface

In terms of a common engineering material, modern duplex stainless steels emerged in the early 1980s, developed from cast alloys. Their popularity stems from an attractive combination of properties, including high strength and excellent resistance to chloride stress corrosion cracking. Since this time, many grades have been developed and the production of duplex has increased dramatically. Presently, it is estimated that the world duplex market is about 500,000 T, which equates to about 10% of the world Fe:Cr:Ni stainless steel market, although some have predicted that this could grow to 50% by 2010. However optimistic this percentage might be, duplex stainless steels are established as a viable alternative to many other types of stainless steel and nickel base alloys. This rapid development has led to the production of the following book.

The first dedicated international conference for duplex alloys was held in St Louis, Missouri, USA (1982). At that time, the wrought duplex grade with 22%Cr and 5%Ni was becoming established and some benchmark papers were presented. This conference is still heavily referenced in the literature and fundamental data presented hereafter stems from this time. The second conference was held in The Hague, The Netherlands (1986), when the positive effect of nitrogen on properties was recognised. By the third conference in Beaune, France (1991), the modern duplex family had become established, including the superduplex grades. The fourth conference was held in Glasgow, Scotland (1994). This conference constituted a consolidation of information and allowed for a book on the subject to be written. The next dedicated conference in this series will be held in Maastricht, The Netherlands, in October 1997. Undoubtedly the conferences and learning will continue.

This book is based, to varying extents, on the keynote papers from the Glasgow and Beaune conferences. Contributions by Dr Jacques Charles of Creusot-Loire Industrie and Dr Mats Liljas of Avesta Sheffield AB, are acknowledged for their conference papers, which have acted as the building-blocks for several chapters. Papers by the following authors were inspirational for one or more chapters: J M Nicholls, S Bernhardsson, J-O Nilsson, C I K Sinclair, and

C V Roscoe and K J Gradwell. Recognition especially is paid to Dr Chris Baxter, Dr Trevor Gooch, Kare Johansson, Dr Damian Kotecki, Bela Leffler, Dr Liane Smith and Dr Christoph Wiesner for their valuable comments on earlier drafts. In addition, several colleagues at TWI contributed towards the final text: P H M Hart, Dr R Jones, Dr S Manteghi and C S Punshon. Finally, but not least, the permission of the other keynote authors from the Glasgow conference to employ their papers is acknowledged: V Neubert, J L P Hilkes, M Celant, G H Wagner and J K L Korkhaus.

Abbreviations and glossary

ANSI	American National Standards Institute (USA)
AOD	Argon–oxygen decarburisation
API	American Petroleum Institute (USA)
ASME	The American Society of Mechanical Engineers (USA)
ASTM	American Society for Testing and Materials (USA)
AWS	American Welding Society (USA)
BCC	Body centred cubic (lattice structure)
BS	British Standard (UK)
CCT	Continuous cooling transformation (diagrams, when used in a heat treatment context)
CCT	Critical crevice temperature (when used in a corrosion context)
CEN	European Committee for Standardisation (Europe)
Cr _{eq}	Chromium equivalent ($Cr_{eq} = \%Cr + \%Mo + 0.7 \times \%Nb$)
Cr/Ni	Ratio of Cr _{eq} /Ni _{eq}
CPT	Critical pitting temperature
CTOD	Crack tip opening displacement (fracture toughness)
DBTT	Ductile to brittle transition temperature
FCC	Face centred cubic (lattice structure)
DIN	Deutsches Institut für Normung (Germany)
DdTÜV	Vereinigung der Technischen Überwachungs-Vereine eV (Germany)
EDX	Energy dispersive X-ray analysis
EFC	European Federation of Corrosion
EN	Europäische Norm/Norme Européenne/European Standard (Europe)
E _p	Pitting or breakdown potential
ESW	Electroslag welding
FGD	Flue gas desulphurisation
GMAW	Gas metal arc welding, otherwise known as MIG/MAG (metal inert/active gas)
GTAW	Gas tungsten arc welding, otherwise known as TIG (tungsten inert gas)
HAZ	Heat affected zone (of a weld)
HRC	Rockwell hardness on the C-scale
HTHAZ	High temperature HAZ (adjacent to the weld fusion boundary)
HV	Vickers hardness
IGC	Intergranular corrosion
IIW	International Institute of Welding
i _{max}	Maximum corrosion current
i _{pass}	Corrosion current in the passive range
ISO	International Organisation for Standardisation
K	Element partition coefficient

LTHAZ	Low temperature HAZ (remote from weld fusion boundary)
MTI	Materials Technology Institute of the Chemical Process Industries (USA)
NACE	National Association of Corrosion Engineers (USA)
Ni _{eq}	Nickel equivalent ($\text{Ni}_{\text{eq}} = \% \text{Ni} + 35 \times \% \text{C} + 20 \times \% \text{N} + 0.25 \times \% \text{Cu}$)
PAW	Plasma arc welding
PRE _N	Pitting resistance equivalent number ($\text{PRE}_N = \% \text{Cr} + 3.3 \times \% \text{Mo} + 16 \times \% \text{N}$)
PRE _w	Pitting resistance equivalent number ($\text{PRE}_w = \% \text{Cr} + 3.3 \times (\% \text{Mo} + 0.5\% \text{W}) + 16 \times \% \text{N}$)
PWHT	Postweld heat treatment
REM	Rare earth metals (Lanthanide group of the Periodic Table)
R _m	ISO/EN shorthand for UTS (ultimate tensile strength or stress)
R _{p0.2}	0.2% proof stress (similar to yield stress for BCC steels)
SAE	Society of Automotive Engineers (USA)
SAW	Submerged arc welding
SCC	Stress corrosion cracking (in chloride media)
SCE	Saturated calomel electrode
SEM	Scanning electron microscope
SMAW	Shielded metal arc welding, otherwise known as MMA (manual metal arc)
SSCC	Sulphide stress corrosion cracking (in H ₂ S bearing media)
TEM	Transmission electron microscope
TTT	Time-temperature transformation (diagrams produced by isothermal heat treatment)
UNS	Unified Numbering System (USA)
VARP	Vacuum arc remelting process
VOD	Vacuum oxygen decarburisation
Weldment	Includes weld metal, HT and LT HAZ
WPQ	Weld procedure qualification

Greek letters act as shorthand for the following:

α	Ferrite (see also δ)
α'	Alpha prime phase
χ	Chi phase
δ	Ferrite (see also α)
Δt	Time spent in particular temperature range
ϵ	Epsilon phase
γ	Austenite
γ_2	Secondary austenite
π	Pi-nitride
σ	Sigma
τ	Tau phase