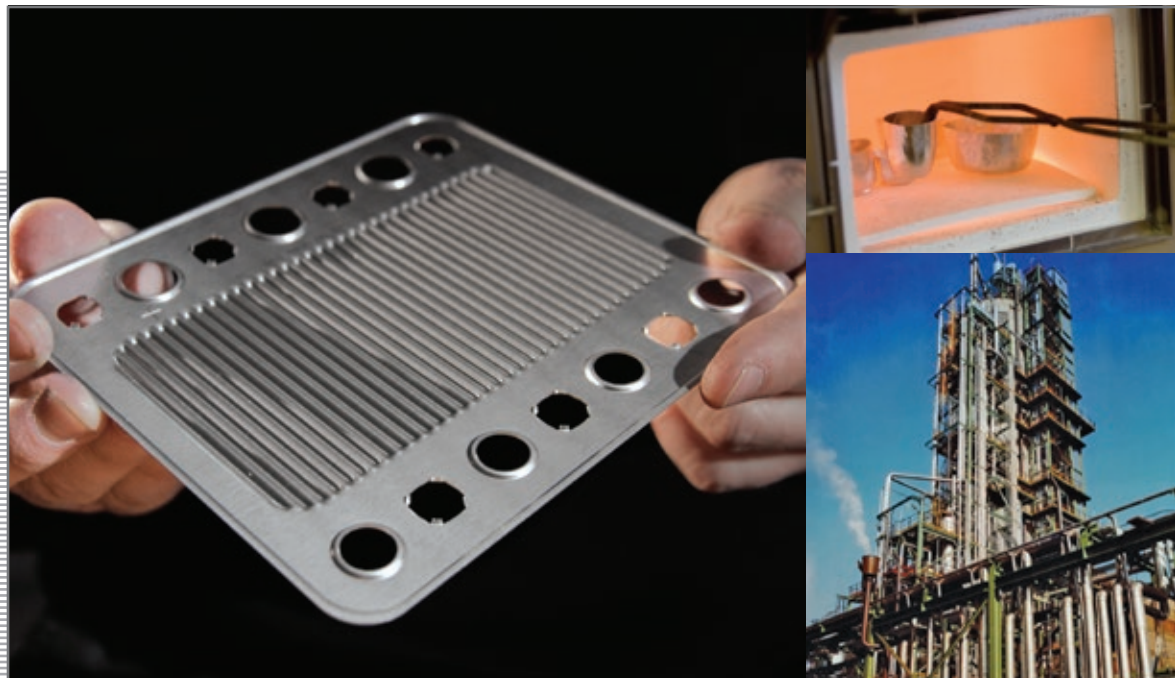


Stainless Steels at High Temperatures



Euro Inox

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Euro Inox
 Diamant Building, Bd. A. Reyers 80
 1030 Brussels, Belgium
 Phone: +32 2 706 82 67
 Fax: +32 2 706 82 69
 E-mail: info@euro-inox.org
 Internet: www.euro-inox.org

Author

Alenka Kosmač, Brussels (B)

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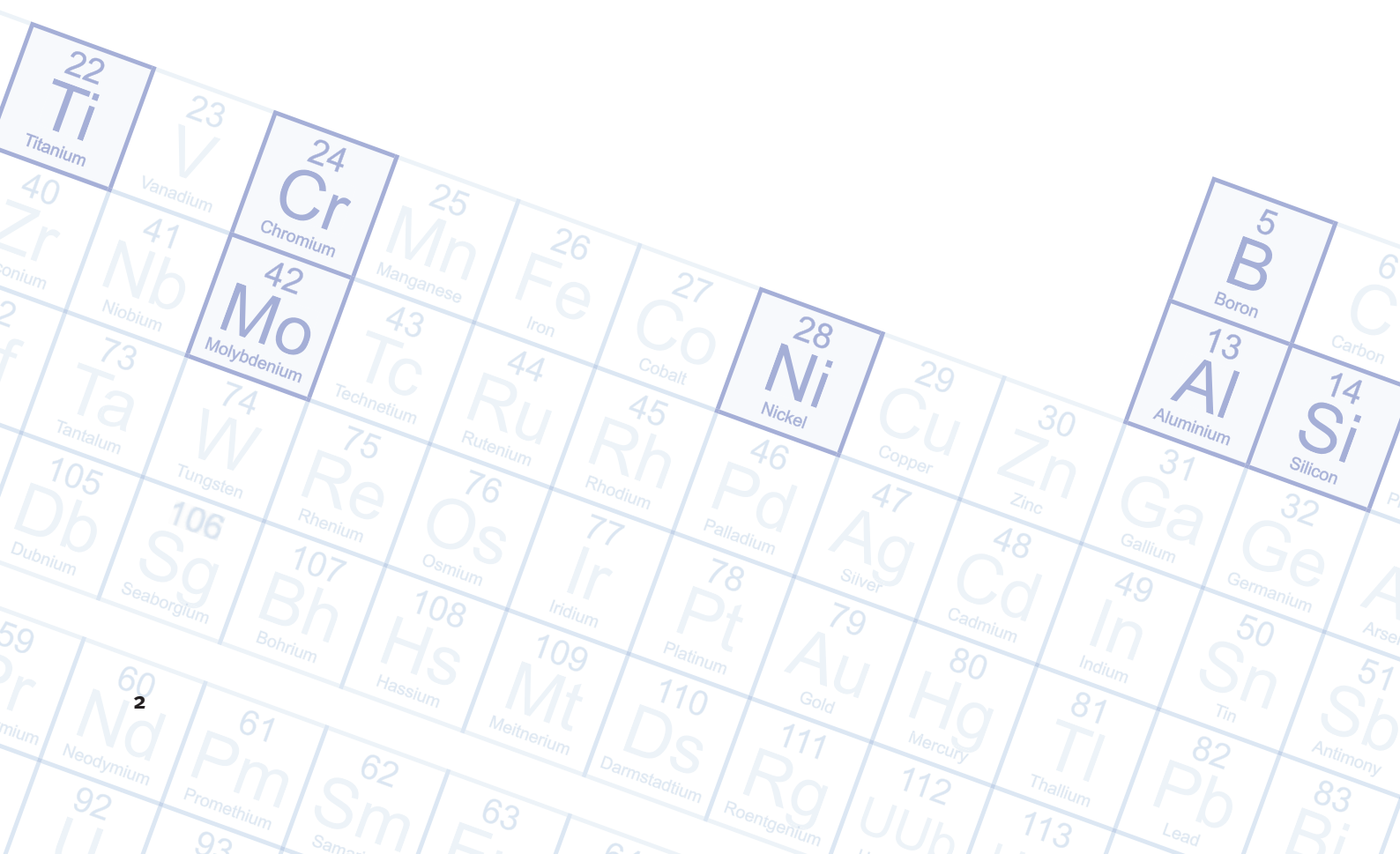
1 Introduction

Stainless steels are mainly used for their resistance to aqueous corrosion but are also widely used at high temperatures when carbon and low-alloyed steels do not provide adequate corrosion resistance and/or strength. They can be found in applications in which high-temperature oxidation resistance or high-temperature strength are required [1]. Construction material is exposed to high temperatures in many industrial, public and domestic applications, sometimes in connection with an aggressive environment.

Depending on the operating conditions, the requirements on material used at high temperatures may be as follows:

- high creep strength (and/or ductility)
- good resistance to oxidation and high-temperature corrosion
- stable microstructure
- good resistance to erosion corrosion

Material selection should be determined by the specific application and operating conditions in each case [2].



2 *The role of alloying elements*

Alloys for high-temperature applications are designed to be able to form protective oxide scales. The only oxides that meet the criteria for protective scales and can form on practical alloys are chromium oxide (Cr_2O_3), aluminium oxide (Al_2O_3) and, possibly, silicon dioxide (SiO_2).

The effect of chromium is particularly evident at temperatures above 500 °C. This element forms a tight, adherent layer of chromium-rich oxide on the surface of the metal, retarding the inward diffusion of oxygen and impeding further reaction [3].

Other elements besides chromium may also be added to stainless steel to increase oxidation resistance. Silicon and aluminium act very similarly to chromium. They oxidise selectively and if present in sufficient amounts can form continuous films of SiO_2 and Al_2O_3 . The adherence of the oxide scale can be greatly improved by small additions of rare earth metals (REM) such as cerium or lanthanum [4]. This is particularly beneficial when the application is subjected to thermal cycling [5].

Nickel increases ductility, high-temperature strength and resistance to both carburisation and nitridation. High-nickel-content alloys should be avoided in reducing sulphidising environments, because of the formation of low-melting-point nickel-sulphur compounds. Nickel counteracts but does not necessarily stop the tendency for an alloy to form sigma phase.

Higher nitrogen and carbon content enhance creep strength.

Molybdenum increases high-temperature creep-rupture strength. It is usually limited to 3.0 %. Higher molybdenum content can cause serious oxidation problems and promote sigma-phase formation, unless counterbalanced by austenite-forming elements such as nickel.

Titanium added in small amounts of about 0.3–0.7 % increases strength in austenitic alloys. The same is true for niobium. Both promote sigma-phase formation.

Boron increases creep-rupture strength and is used at rather low concentrations – typically 0.002 %. This interstitial element tends to concentrate at the grain boundary.



*Chromite, Dyne mine
(New Caledonia),
Photo: Ecole des Mines
de Paris, Paris (F)*

3 The role of microstructure

Microstructure is less important for heat resistance than chemical composition or the appropriate selection of alloying elements but affects suitability for high-temperature service for other reasons. The grades of wrought stainless steels and nickel-based alloys usually used for products where the main requirement is resistance to the effect of hot gases and combustion products at temperatures above 550 °C are specified in European standard EN 10095 – Heat resistant steels and nickel alloys [6]. This standard comprises 6 ferritic grades (see Table 1), 14 austenitic heat-resistant grades (Table 2) and 1 duplex heat-resistant grade (Table 3).

With time and temperature, any metal can be expected to undergo changes in metallurgical structure. In stainless steel, the changes can be softening, carbide precipitation or embrittlement [8].

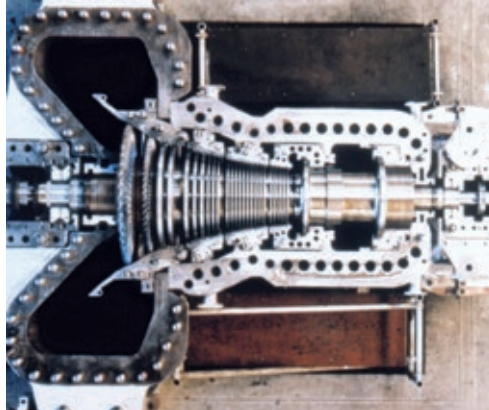
For most **ferritic grades**, long-term service temperature is usually limited to 250 °C, due to 475 °C embrittlement. This does not seem to be a serious problem in low-chromium steel grades with 10.5–12.5 % Cr, where temperatures can at times exceed 575 °C. One reason is that 475 °C embrittlement can be reversed by heat treatment at higher temperatures. The resistance of some ferritic grades to atmospheric corrosion and high-temperature oxidation, and their relatively low cost, explain why these grades have been extensively used in automotive exhaust systems [7]. Other exceptions to the maximum service-temperature limit are high-alloyed chromium steel grades with 23–27 % Cr, which offer outstanding scaling resistance in air at high temperatures, due to their high chromium content. More details on structural stability are provided later in this publication. Minimum operating temperatures (to avoid embrittlement) may be valid in some cases.

Table 1: Chemical composition of heat-resistant ferritic steels [6]

Steel designation			% by mass					
Number	Name	Approximate AISI/ASTM designation	C	Si	Mn max.	Cr	Al	Others
1.4713	X10CrAlSi7	-	max. 0.12	0.5–1.00	1.00	6.00–8.00	0.50–1.00	
1.4724	X10CrAlSi13	-	max. 0.12	0.7–1.40	1.00	12.00–14.00	0.70–1.20	
1.4742	X10CrAlSi18	-	max. 0.12	0.7–1.40	1.00	17.00–19.00	0.70–1.20	
1.4762	X10CrAlSi25	-	max. 0.12	0.7–1.40	1.00	23.00–26.00	1.20–1.70	
1.4749	X18CrN28	446	0.15–0.20	max.1.00	1.00	26.00–29.00		N: 0.15 to 0.25
1.4736	X3CrAlTi8-2	-	max. 0.04	max.1.00	1.00	17.00–18.00	1.70–2.10	$0.2+4\cdot(C+N)\leq Ti\leq 0.80$

Figure 1 gives a broad idea of the hot-strength advantages of stainless steels in comparison with low-carbon unalloyed steels. Ferritic grades are not known for their mechanical strength at high temperature. The high-temperature strength of ferritic and martensitic stainless steels is relatively low compared to that of austenitic grades.

Martensitic stainless steels are listed as creep-resistant steels in European standards EN 10088-1 [9] and EN 10302 [10]. However, due to their low chromium content (12.5 % maximum), they are not primarily specified as heat-resistant grades but are mainly specified when the application requires good tensile strength, creep and fatigue strength, in combination with moderate corrosion resistance and heat resistance up to approximately 650 °C. Low- and medium-carbon martensitic steels are used primarily in steam turbines, jet engines and gas turbines.



Steam turbine half-casing and rotor. The rotor is made of martensitic stainless steel, suitable for use in high temperatures. Photo: Centro Inox, Milan (I)

Austenitic stainless steels provide, next to nickel-based alloys, the best combination of high-temperature corrosion resistance and high-temperature mechanical strength of any alloy group. For this reason, there are a multitude of special heat-resistant austenitic grades listed in EN 10095 and special creep-resistant austenitic grades in EN 10302. Heat-resistant austenitic grades are the preferred metallic material in high-temperature applications.

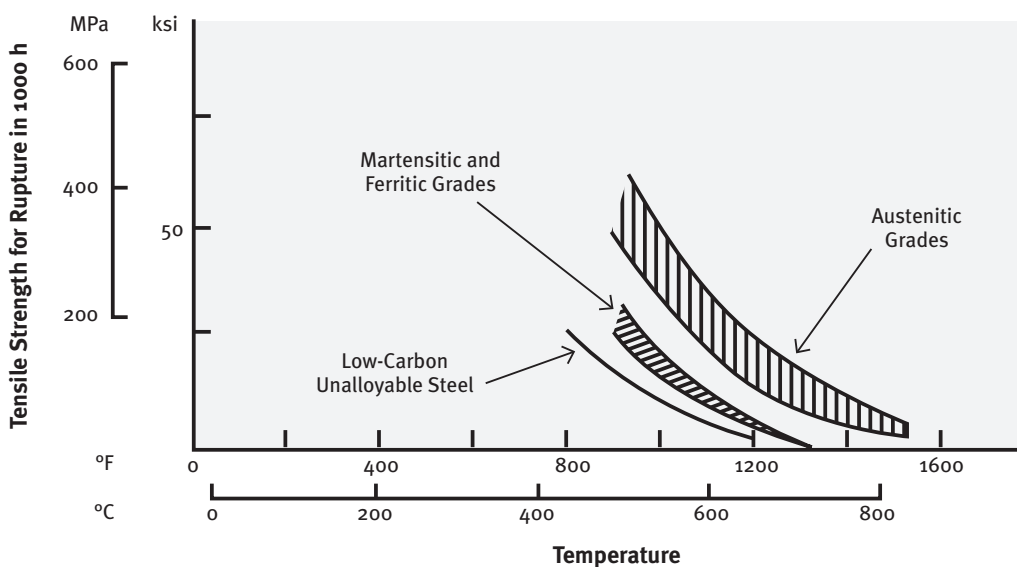


Figure 1: General comparison of the hot-strength characteristics of austenitic, martensitic and ferritic stainless steels with those of low-carbon unalloyed steel [8]

Table 2: Chemical composition of austenitic heat-resistant steels [6]

Steel designation			% by mass					
Number	Name	Approximate AISI/ASTM designation	C	Si	Mn	Cr	Ni	Others
1.4878	X8CrNiTi18-10	321H	max. 0.10	max. 1.00	max. 2.00	17.0–19.00	9.00–12.00	Ti: 5-%C≤Ti≤0.80
1.4828	X15CrNiSi20-12	-	max. 0.20	1.50–2.50	max. 2.00	19.00–21.00	11.00–13.00	
1.4835	X9CrNiSiNce21-11-2	S30815	0.05–0.12	1.40–2.50	max. 1.00	20.00–22.00	10.00–12.00	Ce: 0.03–0.08
1.4833	X12CrNi23-13	309S	max. 0.15	max. 1.00	max. 2.00	22.00–24.00	12.00–14.00	
1.4845	X8CrNi25-21	310S	max. 0.1	max. 1.50	max. 2.00	24.00–26.00	19.00–22.00	
1.4841	X15CrNiSi25-21	314	max. 0.20	1.50–2.50	max. 2.00	24.00–26.00	19.00–22.00	
1.4864	X12NiCrSi35-16	-	max. 0.15	1.00–2.00	max. 2.00	15.00–17.00	33.00–37.00	
1.4876	X10NcrAlTi32-21	-	max. 0.12	max. 1.00	max. 2.00	19.00–23.00	30.00–34.00	Al: 0.15–0.60 Ti: 0.15–0.60
1.4877	X6NiCrNbCe32-27	-	0.04–0.08	max.0.30	max. 1.00	26.00–28.00	31.00–33.00	Al: max. 0.025 Ce: 0.05–0.10 Nb: 0.60–1.00
1.4872	X25CrMnNiN25-9-7	-	0.20–0.30	max.1.00	8.00–10.00	24.00–26.00	6.00–8.00	N: 0.20–0.40
1.4818	X6CrNiSiNce19-10	S30415	0.04–0.08	1.00–2.00	max. 1.00	18.00–20.00	9.00–11.00	Ce: 0.03–0.08
1.4854	X6NiCrSiNce35-25*	S35315	0.04–0.08	1.20–2.00	max. 2.00	24.00–26.00	34.00–36.00	N: 0.12–0.20 Ce: 0.03–0.08
1.4886	X10NiCrSi35-19	No8330	max. 0.15	1.00–2.00	max. 2.00	17.00–20.00	33.00–37.00	
1.4887	X10NiCrSiNb35-22	-	max. 0.15	1.00–2.00	max. 2.00	20.00–23.00	33.00–37.00	Nb: 1.00–1.50

*patented steel grade

Duplex stainless steels have a mixed ferrite and austenite structure. Their yield strength is in the range of 550 MPa to 690 MPa in the annealed condition – significantly higher than that of their austenitic or ferritic counterparts. Despite this relatively high strength at room temperature, duplex grades are subject to embrittlement and loss of mechanical properties, particularly toughness, through prolonged exposure to high temperatures. As a result, duplex stainless steels are generally not recommended for high-temperature applications, their upper temperature limit being generally not higher than approximately 300 °C.

The latest research confirms that duplex grades have somewhat lower strength retention than comparable austenitic grades in the higher-temperature range. However, even in the high-temperature range typical of fire situations, their absolute strength is still similar to that of austenitic grades [11]. The highest temperature therefore depends on mechanical properties (e.g. pressure vessels) and needs to be qualified for the steel concerned.

Table 3: Chemical composition of duplex heat-resistant steel [6]

Steel designation			% by mass				
Number	Name	Approximate AISI/ASTM designation	C	Si	Mn max.	Cr	Ni
1.4821	X15CrNiSi25-4	-	0.10-0.20	0.80-1.50	2.00	24.50-26.50	3.50-5.50

Precipitation-hardening (PH) stainless steels are chromium-nickel grades whose strength can be increased by age hardening. Age hardening is provided by an intermediate-temperature ageing treatment. These steels are of limited use for high-temperature service in the aged condition, since they lose strength rapidly at temperatures above about 425 °C [12]. They will therefore not be discussed further here.

Grades designed for aqueous-corrosion resistance may also be used as heat-resistant steel grades where corrosion resistance is of high importance. These steel grades are listed in EN 10088-1 and EN 10028-7 [13] and shown below in Table 4.

The temperature range in which the above stainless steel grades are used is somewhat lower than that of steel grades specifically designed and listed as heat resistant. It should be borne in mind that maximum service temperature differs depending on whether service is intermittent or continuous.

The embrittlement mechanisms discussed under structural stability should be taken into account, as they also usually set in below the maximum service temperature.

Table 4: Grades from EN 10088-1 and EN 10028-7 which are used in addition to those in EN10095 as heat-resistant steels

Steels from EN 10088-1		Steels from EN 10028-7		Approximate AISI/ASTM designation
Number	Name	Number	Name	
1.4512	X2CrTi12			409
1.4000	X6CrTi13			410S
1.4016	X6Cr17			430
1.4510	X3CrTi17	1.4510	X3CrTi17	439
1.4590	X2CrNbZr17			
1.4509	X2CrTiNb18	1.4509	X2CrTiNb18	
1.4006	X12Cr13			410
1.4301	X5CrNi18-10	1.4301	X5CrNi18-10	304
		1.4948	X6CrNi18-10	304H
1.4541	X6CrNiTi18-19	1.4541	X6CrNiTi18-19	321
		1.4941	X7CrNiTiB18-10	
		1.4950	X6CrNi23-13	
		1.4951	X6CrNi25-20	
1.4362	X2CrNiN23-4	1.4362	X2CrNiN23-4	2304

4 *Mechanical properties at high temperatures*

At high temperatures, metals under stress are subject to slow plastic deformation as well as elastic deformation. Time therefore becomes a critical factor and conventional tensile tests do not furnish values that are useful in design. The data required is that indicating the load which will produce no more than an allowable percentage of elongation at a specified temperature over a given period of time. High-temperature strength properties thus involve factors of time and deformation as well as stress and temperature [14].

The strength of materials at high temperature is not measured in the same way as at room temperature. For room-temperature applications – automobile frames, claw hammers, etc. – the designer needs to know tensile strength, yield strength or hardness, but when the material is exposed to high temperatures, the most important mechanical property is creep or rupture strength [15].

4.1 Creep strength

Metals behave very differently at high temperatures than they do at room temperature. If a metal bar is loaded to just below its yield strength at room temperature, the load can be left there almost indefinitely. It will not fail unless it corrodes or suffers stress-corrosion cracking.

At high temperature, the material begins to stretch, but very slowly. It will keep stretching until it finally breaks [15]. The speed at which the metal stretches, in % per hour, is called its “creep rate”. The high-temperature strength of a material is generally ex-

pressed in terms of “creep strength” – its ability to resist distortion over long-term exposure to a high temperature. Creep occurs in most applications where metal temperatures exceed 480 °C. In time, creep may lead to excessive deformation and even fracture at stresses considerably below those determined in room-temperature and high-temperature short-term tensile tests. It is usually satisfactory if creep does not exceed 1 % deformation in 10,000 hours. This does not mean that this rate of creep can be expected to continue for 10,000 hours without failure in every instance.

Creep values obtained under constant load and temperature conditions are applicable to design. However, safety factors should always be incorporated. The safety factor will depend on the degree to which the application is critical [14]. Of the various types of stainless steel, austenitics provide the highest creep strength.

A design stress figure commonly used for uniformly heated parts not subjected to thermal or mechanical shock is 50 % of the stress to produce 1 % creep in 10,000 hours. However, this should be used carefully and verified with the supplier [16]. A common criterion is for the load to cause failure at 100,000 hours, with an added safety factor of 1.5 (see the ASME code, for example). For guidance, creep properties are given in the Appendix of this publication.

4.2 Stress-rupture properties

Stress-rupture properties determined under constant load at constant temperature are useful in estimating the service life of a material (time to fracture) under specific conditions – and also for comparing alloys. They serve as additional information to creep-strength values in the selection of heat-resistant materials. It should be recognised that long-term creep and stress-rupture values (e.g. 100,000 h) are often extrapolated from shorter-term tests conducted at high stresses. Considerable scatter in test results may be observed, even for a given heat of an alloy, so extrapolated creep- and rupture-strength data can be unreliable. There can typically be a variation of $\pm 20\%$

in stress. Differences can often be traced to differences in, for example, annealing procedures and grain size. Even tests with the longest affordable duration should therefore be interpreted cautiously.

A material's actual behaviour can also be difficult to predict accurately due to the complexity of the actual service stresses as opposed to the idealised, uniaxial loading conditions in standardised tests. Factors such as cyclic loading, temperature fluctuation and metal loss from corrosion may also influence how a material behaves in service [3,17].

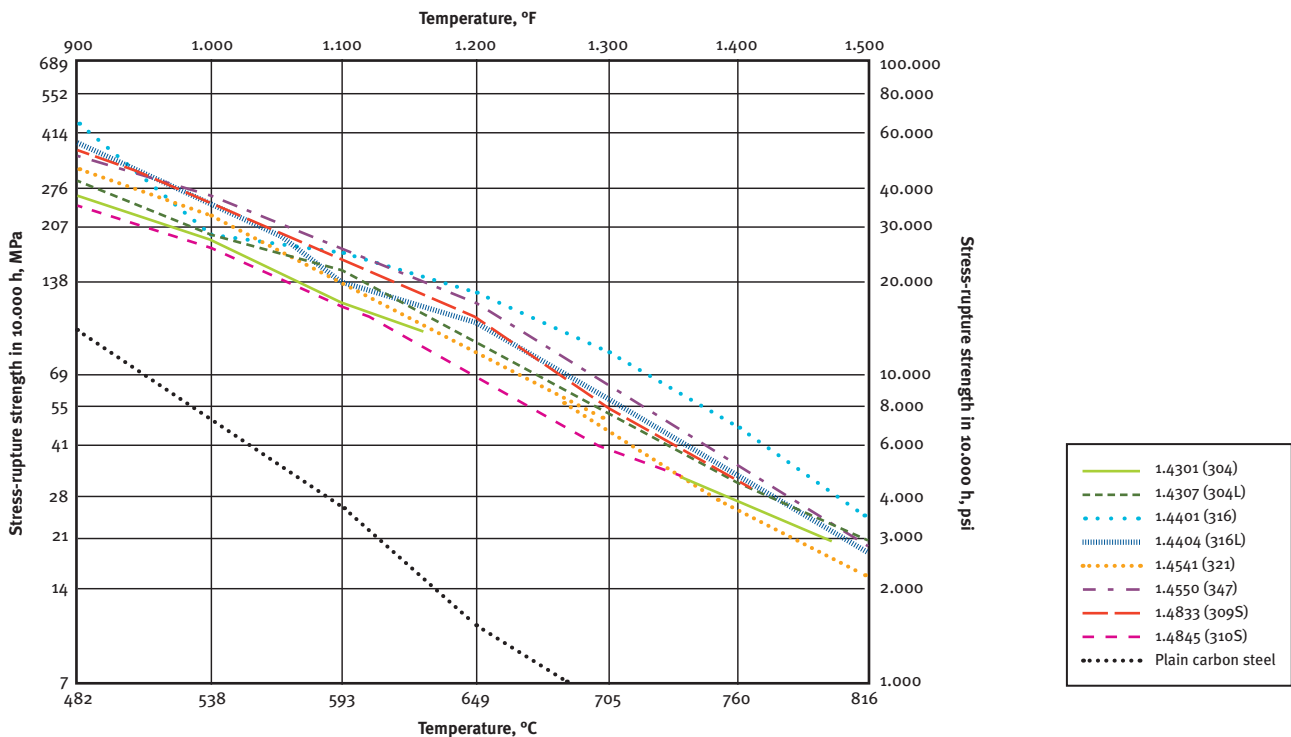


Figure 2: Stress-rupture strength in 10,000 h of different stainless steels grades [25]

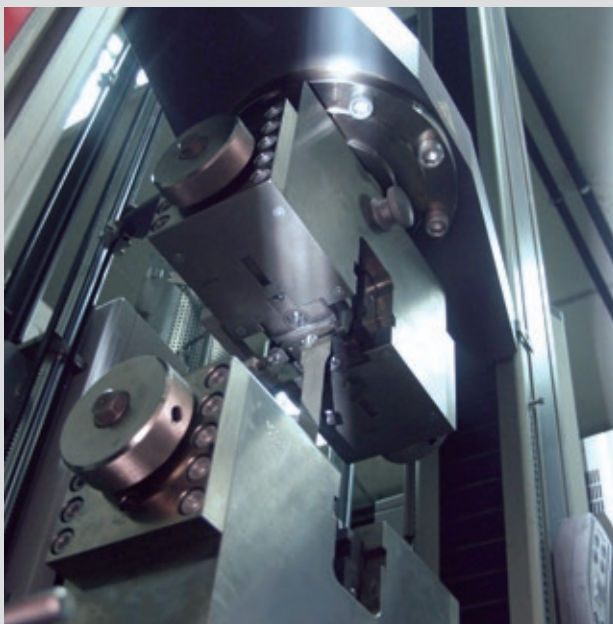
4.3 Short-term tensile strength

Historically, the method used for studying the high-temperature properties of metals and alloys has been short-term tensile testing. While these tests have been largely superseded for design purposes by long-term creep and rupture tests, high-temperature tensile testing nevertheless furnishes useful data for preliminary appraisal.

High-temperature tensile tests are similar to tensile tests at room temperature. Usually, the specimen is surrounded by an electric-resistance furnace, to keep it at a constant selected temperature during application of the load. Rate of testing (or strain rate) is one of the important considerations [3].

The values obtained are as much as five or six times the limiting creep-strength values and therefore greatly over-evaluate load-carrying ability over a long period of time. High-temperature tensile test results can be helpful in evaluating resistance to momentary overloads and are included in some specifications.

Over about 550 °C, tensile and yield strength cannot be used as a basis for design.



Tensile strength (or ultimate strength) is the stress required to pull the specimen until it breaks in two. A tensile test is carried out by mounting a specimen in a machine which pulls on it with a slowly increasing load until it breaks. The strength of the material is reported by its tensile strength in N/mm² or MPa.

*Tensile strength is tested with dedicated equipment.
Photo: Acroni, Jesenice (SI)*

4.4 Ductility

Accurately comparing the hot ductility of heat-resistant materials is difficult, since there is no generally accepted reference test. Total elongation values on both creep- and stress-rupture tests are often used as criteria. Also, elongation in short-term tensile tests is commonly used in specifications as an indication of high-temperature ductility.

In many service conditions, with the combined uncertainties of actual stress, temperature and strength, it may be important that failure does not occur without warning and that the metal retains high ductility throughout its service life. In the oil and chemical industries, for instance, tubing applications under high pressure require high long-term ductility. In these cases, impending rupture will be evident from the bulging of the tubes [3].

4.5 Thermal fatigue

Metal expands when heated and contracts by the same amount when cooled down. This strains both the centre and the outer surface. After a number of these strain cycles the metal cracks. Cracks can start at the surface and grow into the material, as in a carburising environment, or they can start internally (in neutral hardening operations) and give no external sign that anything is wrong until the material suddenly breaks [15]. In many high-temperature applications, intermittent or widely fluctuat-



There are many influencing factors when material is selected for use in industrial environment.

Photo: Centro Inox, Milan (I)

ing temperatures (cyclic heating) are encountered, so the ability to withstand in-service thermal fatigue must be considered.

Very little experimental thermal-fatigue information is available on which comparison of the various alloys can be based and no standard test has as yet been adopted. Field experience indicates that, usually, resistance to thermal fatigue improves with increasing nickel content. As unequal stresses tend to distort or fracture the part, it is helpful in some cases to make parts of a number of small components that are free to expand and contract. Sharp corners and abrupt changes in section are to be avoided [14]¹.

¹ The importance of using sections that are as light as possible should often be considered in design, as less mass means less strained material. A change of dimensions from 12.7 mm to 15.9 mm in diameter for a bar frame basket, for example, could result in halving the lifetime, rather than making the basket stronger. In this case, with increasing diameter the thermal strains were significantly higher. Thermal stress causes more distortion and cracking in heat-resistant alloy equipment than do the mechanical loads imposed on the part [14].

Strength is rarely the only requisite in material selection and frequently is not the major one. More failures are due to brittle fracture from thermal fatigue than from stress rupture or creep. However, high-temperature strength is important where severe thermal cycling is required [16].

4.6 Temperature gradients

Heat-resistant alloys have inherently high coefficients of thermal expansion and low heat conductivity – both properties tending to produce temperature and stress differences between different areas of a part or assembly. Coefficient of thermal expansion is expressed in units of proportional change of length for each degree increase in temperature, usually as $10^{-6} \cdot K^{-1}$. Other units sometimes used are $10^{-6}/^{\circ}C$, $\mu m/m/^{\circ}C$ and $10^{-6}cm/cm/^{\circ}C$. These are identical but are outside the International System of Units².

Increase in length (or diameter, thickness, etc.) can be readily calculated by multiplying the original dimension by the temperature change by the coefficient of thermal expansion. For example, if a 3-meter-long bar of steel grade 1.4301, with a coefficient of thermal expansion of $17.2 \cdot 10^{-6} \cdot K^{-1}$ (or $17.2 \mu m/m/^{\circ}C$), is heated from 20 $^{\circ}C$ to 200 $^{\circ}C$, the length increases by:

$$\Delta L = \alpha \cdot L_0 \cdot \Delta T = 17.2 \cdot 3.00 \cdot 180 = 9288 \mu m = 9.3 \text{ mm}$$

In the equation, α stands for coefficient of thermal expansion, L_0 for original length and ΔT for change in temperature.

Table 5: Coefficient of thermal expansion - average values [18]

	Coefficient of thermal expansion ($\cdot 10^{-6} \cdot K^{-1}$)
Carbon steel	12
Austenitic stainless steel	17
Duplex stainless steel	14
Ferritic stainless steel	10
Martensitic stainless steel	10

Linear-expansion coefficients for specific steel grades are given in the Appendix.

² abbreviated as “SI system” from the French “Système International d’Unités”

4.7 Effect of cold working on properties

The high-temperature strength of heat-resistant austenitic alloys can be increased by cold working processes such as rolling. The increased strength is, however, only retained up to recrystallization temperature.

Figure 3 shows the effect of temperature on the tensile properties of cold-worked 1.4310 (301) stainless steel. In particular, cold-worked products have poor resistance to creep, which generally occurs at temperatures slightly above the recrystallization temperature of the metal. During long-term high-temperature exposure, the benefit



*The microstructure of a steel is checked under high magnification.
Photo: Acroni, Jesenice (SI)*

of cold working is lost and stress-rupture strength may even fall below annealed strength [25].

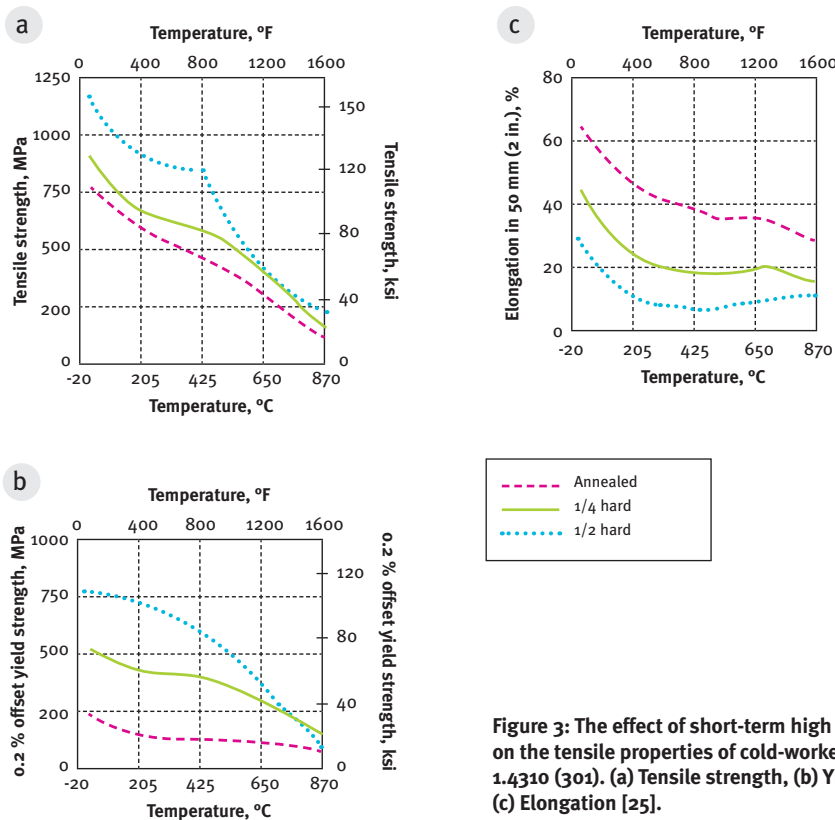


Figure 3: The effect of short-term high temperature on the tensile properties of cold-worked steel grade 1.4310 (301). (a) Tensile strength, (b) Yield strength, (c) Elongation [25].

5 *Microstructure stability*

Some materials change after a few hundred or thousand hours in service. They become brittle instead of remaining tough and ductile. The most common problem is that the alloy forms a hard, brittle, non-magnetic phase, called sigma. Sigma phase forms in the temperature range of 500–980 °C [15]. This microstructural change can occur in austenitic, ferritic or duplex stainless steel, the process being dependent on both time and temperature. Some lower-chromium ferritic grades can form sigma phase at temperatures as low as 480 °C, albeit over extended periods of time. In addition to temperature, the time required to form sigma phase varies considerably depending on composition and processing (the amount of cold working, for example). Embrittlement due to sigma phase starts rapidly if the material has been cold worked.

With a sufficiently high level of nickel, sigma-phase formation can be completely suppressed. If a material is to be used in the sigma-phase-formation range, it is important to evaluate how much embrittlement is likely to occur over the service life of the component and what effect this will have on the component's performance.

Embrittlement is not normally a problem when material is at operating temperature (except when thermal fatigue is involved) but can become serious at ambient temperatures [19]. Generally, such phases are of the most concern when affected parts are cooled down to room temperature. At high temperatures, from a ductility or toughness standpoint, the phases do not appear to be a major problem. Other intermetallic phases very often present besides sigma phase

are Laves and chi (χ) phases. In the case of Laves phase, such intermetallics can even improve high-temperature creep strength.

Intermetallic phase embrittlement is primarily a service problem involving long exposure to high temperatures. These phases can be dissolved by heating to above 1000 °C [12].

At temperatures between 400 °C and 500 °C, ferritic stainless steels tend to split into two separate phases, with respectively high and low chromium contents. The rate of the reaction reaches its maximum at 475 °C and is therefore called 475 °C embrittlement. The 11 % Cr ferritic grades are the least sensitive to this phenomenon, which occurs only to a limited extent in 17 % Cr alloys, whereas 25 % Cr materials, including duplex stainless steels, are highly prone to it [23].

At high temperatures, grain growth may also occur, possibly increasing creep strength somewhat but simultaneously substantially reducing ductility. Even if these microstructural changes lead to impaired material properties, they can be acceptable as long as one is aware of them and considers them during service as well as at maintenance shutdowns [2].

Some austenitic stainless steels can suffer significant ductility loss or embrittlement upon long-term exposure to intermediate temperatures (500–900 °C), due to sigma phase formation [25]. Use of iron-chromium-nickel types should be limited to applications in which temperatures are steady and not within the sigma-forming temperature range [24].

Table 6: Practical considerations of structure stability in use [20,21,22]

	Steel designation			Most suitable temp. range	Max. recommended service temperature in dry air °C	Exposure time ⁽⁴⁾	Embrittlement effect	475 °C embrittlement	Grain boundary carbides	σ-phase	Grain growth		Comments		
	Number	Name	Nearest ASTM/ AISI								°C				
											600-750	600-900		≥ 950	≥ 1050
AUSTENITIC	1.4818	-	S30415	-	1000	Short Long Medium	Low	-	YES	YES	-	YES	-		
	1.4828	X15CrNiSi20-12	-	-	1000	Long Medium	Low	-	-	YES	-	YES	-		
	1.4833	X12CrNi23-13	309S	-	1000	Medium	Medium/strong	-		YES	-	YES	-		
	1.4835	X9CrNiSiNce21-11-2	S30815	850–1100	1100	Long Medium	Low	-	-	YES	-	YES	-		
	1.4841	X15CrNiSi25-21	314	-	1150	-	-	-	-	YES	-	YES	-		
	1.4845	X8CrNi25-21	310S	-	1100	-	-	-	-	YES	-	YES	-		
	1.4854	-	S35315	-	1150	-	-	-	-	YES	-	YES	Risk of reduced room-temperature impact toughness after service below 950 °C		
	1.4878	X8CrNiTi18-10	321H	-	800	Long Medium	Low	-	YES	YES	-	YES	-		
	1.4948	-	304H	-	800	Short Long Medium	Low	-	YES	YES	-	YES	-		
FERRITIC	1.4713	X10CrAl7	-	550–800	800	-	Low	-	-	-	-	-	No brittle phases, but should be exposed to only moderately corrosive atmospheres		
	1.4724	X10CrAl13	-	550–850	850	-	Low	-	-	-	-		No brittle phases		
	1.4742	X10CrAl18	-	550–1000	1000	-	Medium	YES	-	YES (long exposure)	YES	-	-		
	1.4762	X10CrAl24	-	550–1150	1150	-	Medium but higher than 1.4742	YES	-	YES (long exposure)	YES	-	σ-phase after long exposure, but faster than 1.4742 grain growth		

(1) short = seconds-minutes, medium = minutes-hours, long = days-months

6 Resistance to high-temperature corrosion

The term “high-temperature corrosion” is not very accurate. It generally concerns “dry” corrosion, usually by gases, and what is high for one material may be low for another. However, in the case of stainless steels it can often be taken to mean 500 °C and higher. Under these conditions, the surface alteration produced on stainless steel is usually fairly uniform.

At high temperatures, corrosion mechanisms differ significantly depending on the oxygen potential of the atmosphere and the corrosive species present. Atmospheres with high oxygen potential contain species such as oxygen, water vapour, sulphur and its oxides (SO_2 and SO_3), carbon dioxide (CO_2), nitrogen oxides (NO_x), chlorine, etc. Atmospheres with a low oxygen potential are usually dominated by hydrogen, possibly with the presence of hydrogen sulphide (H_2S), carbon monoxide (CO), hydrogen chloride (HCl), hydrocarbons, ammonia, etc. These atmospheres are often loosely termed “oxidising” and “reducing” respectively, which is best interpreted as meaning “with

respect to iron”, since a so-called reducing atmosphere can oxidise elements such as aluminium and silicon and often even chromium [4]. It should be noted that no single alloy will show satisfactory resistance to all high-temperature environments. [14].

6.1 Oxidation

When a material is exposed to an oxidising atmosphere at high temperatures, an oxide layer usually forms on the surface. This layer will retard further oxidation. If the temperature of the material increases, the oxide growth rate will increase and the layer will finally crack and spall off when the scaling temperature is reached, thus losing its protective effect [25]. Chromium-alloyed steels have better resistance to oxidation than carbon steels, due to the presence of chromium and mixed chromium and iron oxides in an oxide layer. Mixed chromium and iron oxides are more protective than a pure iron-oxide layer. When the chromium content (w) is increased from 0 % to 27 %, the maximum service temperature increases from around 500 °C to 1150 °C. At temperatures above 1000 °C, aluminium oxides are more protective than chromium oxides. The amount of aluminium required for the formation of a protective layer will, however, make the alloy rather brittle, making fabrication difficult and costly [26]. Increased nickel minimizes scale spalling when temperature cycling occurs [25].

Heat treatment after hot or cold forming is often part of the fabrication procedure. Photo: Butting, Knesebeck (D)



Water vapour has a specific effect on oxidation. Thus, while oxidation rates in air are generally slightly lower than in pure oxygen, water vapour significantly increases the corrosion rate, particularly in iron-rich alloys. The oxide layer formed tends to be porous and less protective. This is generally attributed to the formation of volatile chromium-oxide and hydroxide species. A cold-worked surface leads to improved behaviour in water vapour compared to an annealed structure, since it promotes the formation of a compact layer of Cr_2O_3 [4]. If elevated water vapour content is present, the maximum recommended service temperature can be reduced by 50–150 °C, depending on steam content [27].

Historically, the oxidation resistance of an alloy has been specified as the “scaling temperature”, i.e. the temperature at which the oxidation rate becomes unacceptably high. Since this temperature is of little technical importance, the concept of “scaling temperature” has been abandoned.

The maximum application temperatures for air are given in EN 10095.

Table 7: Maximum application temperature in air for some heat-resistant stainless steel grades (for guidance only) [6]

Steel designation			Maximum application temperature °C
Number	Name	Approximate AISI/ASTM designation	
Ferritic heat-resistant steels			
1.4713	X10CrAlSi7		800
1.4724	X10CrAlSi13		850
1.4742	X10CrAlSi18		1000
1.4762	X10CrAlSi25		1150
1.4749	X18CrN28		1100
1.4736	X3CrAlTi18-2		1000
Austenitic heat-resistant steels			
1.4878	X8CrNiTi18-10	321H	850
1.4828	X15CrNiSi20-12		1000
1.4835	X9CrNiSiNCE21-11-2	S30815	1150
1.4833	X12CrNi23-13	309S	1000
1.4845	X8CrNi25-21	310S	1050
1.4841	X15CrNiSi25-21	314	1150
1.4818	X6CrNiSiNCE19-10	-	1050
Duplex heat-resistant steel			
1.4821	X15CrNiSi25-4	-	1100

Table 8: Generally accepted maximum service temperatures in air for some standard stainless steel grades (for guidance only) [12]

Steel designation			Maximum service temperature	
Number	Name	Approximate AISI/ASTM designation	Intermittent service °C	Continuous service °C
Ferritic stainless steel				
1.4016	X6Cr17	430	870	815
Martensitic stainless steel				
1.4006	X12Cr13	410	815	705
Austenitic stainless steel				
1.4301	X5CrNi18-10	304	870	925
1.4541	X6CrNiTi18-19	321	870	925

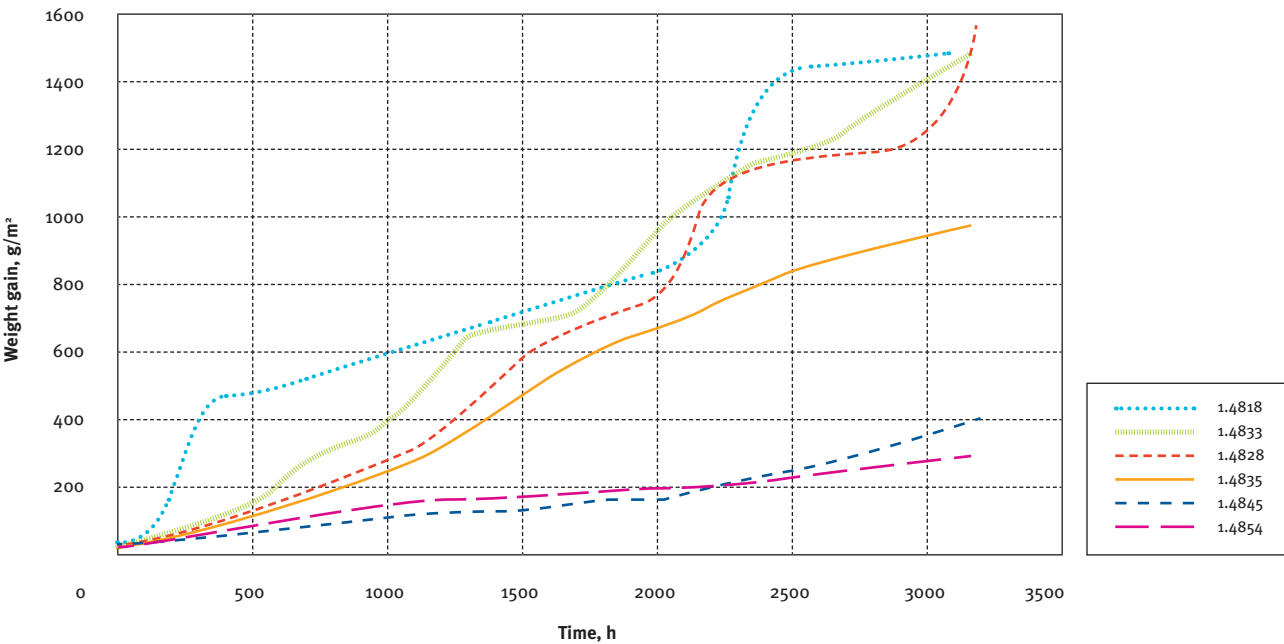


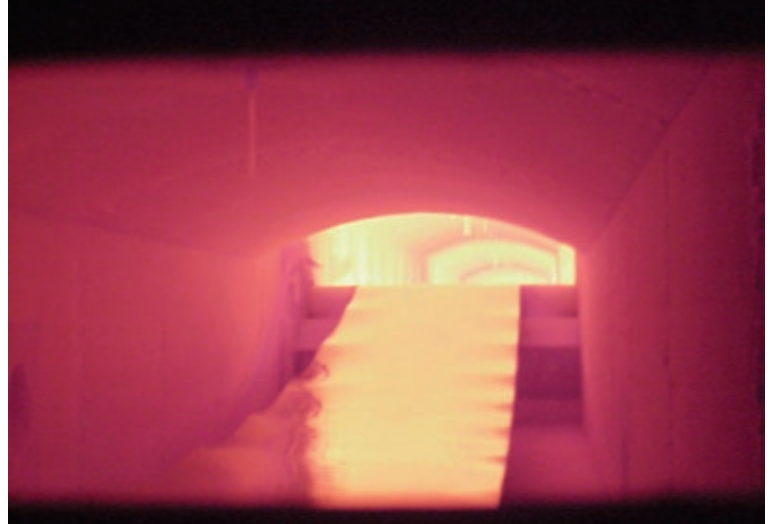
Figure 4: Long-term oxidation at 1100 °C. The specimens were cooled down to room temperature once a week for weighting, 165 h cycles [28].

Catastrophic oxidation is, as its name implies, oxidation that proceeds so rapidly that complete failure of the material occurs in a very short time. Certain elements, such as molybdenum, niobium, vanadium and tungsten, form oxides that are volatile at relatively low temperatures. If these oxides are formed and retained in the scale, they act as fluxes and destroy the protective film. Catastrophic oxidation may be a serious problem under certain operating conditions, i.e. extreme temperatures, stagnant atmosphere or solid deposits [15,29].

6.2 Sulphidation

As with oxidation, resistance to sulphidation relates to chromium content. Unalloyed iron will be converted rather rapidly to iron-sulphide scale, but when iron is alloyed with chromium, sulphidation resistance is enhanced. Alloying elements that provide some protection against sulphidation are silicon, aluminium and titanium.

Various sulphur compounds are often present in flue gases and other process gases. They have a highly detrimental effect on the useful life of exposed components. Due to kinetic factors, non-equilibrium sulphides can form and grow under (nominally) oxidising conditions. Even if initially formed sulphides are later overgrown by oxide or dissolved, their earlier existence has made the oxide layer less protective. In existing oxide layers, attacks can occur in pores and cracks. It is therefore essential that the material is able to form a thin, tough and



adherent oxide layer. This requires high chromium content and preferably also additions of silicon, aluminium and REM.

In addition to the usual factors of time, temperature and concentration, sulphidation depends on the form in which the sulphur exists. Of particular interest are the effects of sulphur dioxide, sulphur vapour, hydrogen sulphide and flue gases. Combustion gases normally contain sulphur compounds. Sulphur dioxide is present as an oxidising gas, along with CO, CO₂, nitrogen and excess oxygen. Protective oxides are generally formed and, depending on the conditions, the corrosion rate may be approximately the same as in air or slightly greater. The resistance of stainless steels to normal combustion gases goes up as chromium content is increased.

Materials may be exposed to extreme conditions. Photo: Drever International, Angleur (Liège) (B)

An old rule-of-thumb says that nickel-containing alloys should be avoided in reducing, sulphidising environments, since the formation of low-melting-point nickel-sulphur compounds may lead to rapid deterioration of the alloy. In practice, however, a “reducing” atmosphere can have a sufficiently high oxygen content (e.g. in the form of SO_2) to enable the formation of a protective oxide layer, provided the chromium content of the alloy is high enough [30].

The low-melting-point nickel/nickel sulphide eutectic may be formed on austenitic stainless steels containing more than 25 % Ni, even in the presence of high chromium levels. The occurrence of molten phases during high-temperature service can lead to catastrophic destruction of an alloy.

Reducing flue gases contain varying amounts of CO, CO_2 , hydrogen, hydrogen sulphide and nitrogen. The corrosion rates encountered in these environments are sensitive to hydrogen sulphide content and temperature. A satisfactory material selection often necessitates service tests. In truly reducing sulphurous atmospheres, any layer of oxide will dissolve rapidly and the bare metal will be exposed to attack. In such circumstances, nickel-free alloys should be used [25,30].

6.3 Carburisation and nitridation

Carburisation of stainless steels can take place in CO, methane (CH_4) and other hydrocarbon gases, such as propane (C_3H_8), at high temperatures. Carburisation can also occur when stainless steels that are contaminated with oil or grease are annealed without sufficient oxygen to burn off the carbon. This can happen during vacuum or inert-gas annealing, as well as during open-air annealing of oily parts whose shapes restrict air access, but is often more of a problem with low-alloy steels than with stainless grades.

Carburisation problems are quite common to heat-treatment equipment used for case hardening of steels by carburising. In the petrochemical industry, carburisation is one of the major modes of high-temperature corrosion for processing equipment [25]. A big increase in carbon pick-up leads to volume changes, which can cause warpage and distortion. The additional carbon also leads to difficulties if repair welding is necessary [14].

When not desired, nitridation is considered a form of corrosion and may be a problem when stainless steels are heated in an environment containing active nitrogen [3]. Nitridation usually happens due to overheating in nitrogen-containing gases or cracking ammonia. In the heat-treating industry, only high-nickel chromium alloys give satisfactory service under nitriding conditions [14].

Table 9: Stability against specific corrosion conditions at high temperatures [32]

Steel designation			Stability against			
Number	Name	Nearest ASTM/AISI	Sulphurated gases		Nitrogenous, poor in oxygen gases	Carburisation
			reducing	oxidising		
Ferritic heat-resistant steels						
1.4713	X10CrAlSi7	-	3	6	2	5
1.4724	X10CrAlSi13	-	3	6	2	3
1.4742	X10CrAlSi18	-	5	6	2	3*
1.4762	X10CrAlSi25	-	5	6	2	3*
Austenitic heat-resistant steels						
1.4878	X8CrNiTi18-10	321H	2	3	5	3
1.4828	X15CrNiSi20-12		2	3	5	2*
1.4835	X9CrNiSiNCE21-11-2	S30815	-	-	-	-
1.4833	X12CrNi23-13	309S	2	2	3	3
1.4845	X8CrNi25-21	310S	2	3	5	1
1.4841	X15CrNiSi25-21	314	1	2	5	2*
Duplex heat-resistant steel						
1.4821	X15CrNiSi25-4	-	3	3	3	3*

1 = very low / 2 = low / 3 = medium / 4 = medium-high / 5 = high / 6 = very high

*at temperatures above 900 °C

The resistance of high-temperature alloys to carbon and nitrogen pick-up rises primarily with increasing nickel content but also with increasing silicon and chromium content. Experience shows that it takes only minor amounts of oxygen in the furnace gas (even in the form of carbon dioxide or steam) to produce a thin, tough oxide layer on steel grade 1.4835, which provides good protection against pick-up of both carbon and nitrogen [31].

A problem in carburising atmospheres is metal dusting, sometimes also called catastrophic carburisation or carbon rot. This occurs at lower temperatures, typically between 430 °C and 650 °C [15] in heat treating, refining and petrochemical processing and other operations [25]. The exact mechanism may be disputed, but the effect is that the metal disappears. Very often the metal literally appears “worm-eaten” on the surface.

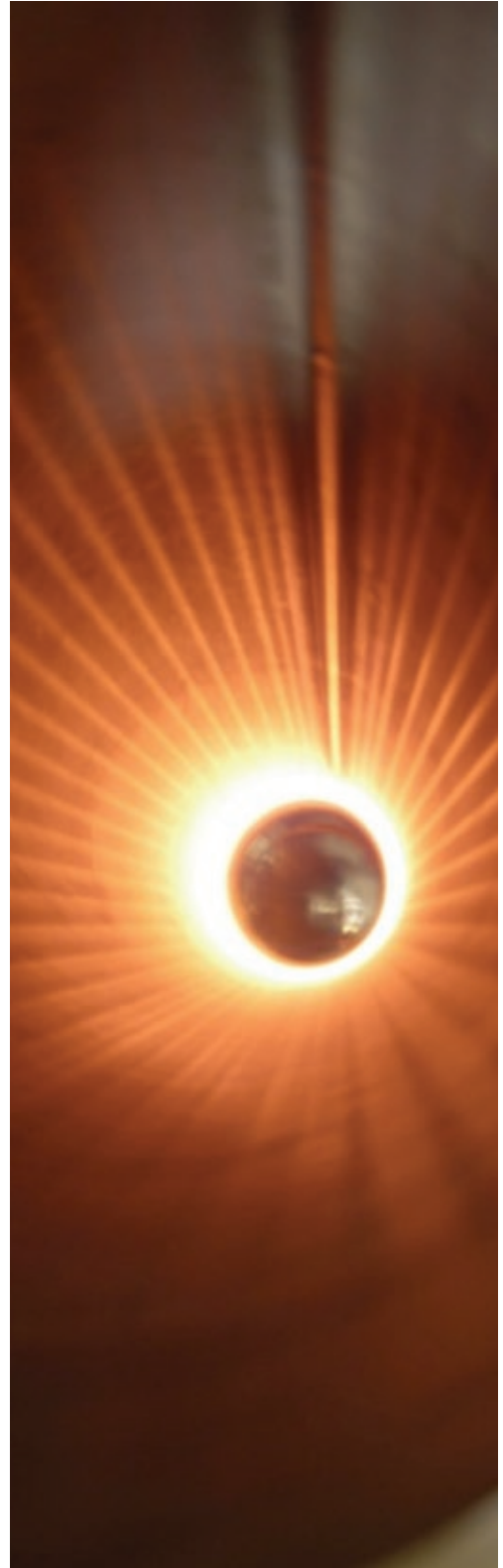
6.4 Halogen-gas corrosion (chlorination)

Halogen-gas corrosion involves reaction between metals and chlorides, fluorides and hydrogen halides such as hydrogen chloride (HCl) and hydrogen fluoride (HF). Halogen and halogen compounds generally attack via the gaseous phase or molten salt compounds. Salts cause slagging and disintegration of the oxide layer and gas-phase halogens penetrate deeply into the material without destroying the oxide layer. Pre-oxidation is therefore of no benefit.

For chloride-bearing environments with no measurable oxygen, iron and carbon steel are very susceptible to chlorination attack. Adding chromium and/or nickel to iron improves the corrosion resistance of the alloy. Thus, ferritic and austenitic stainless steels can better resist chlorination attack at higher temperatures than can cast iron and carbon steels. Nickel and nickel-based alloys are generally even more resistant to chlorination attack than stainless steels.

In oxidising environments containing both chlorine and oxygen, molybdenum and tungsten are detrimental to an alloy's resistance to chlorination attack [25].

Photo: Butting, Knesebeck (D)



7 Formability and weldability

Hot working should be carried out within the temperature ranges given in Table 11. Like other austenitic steels, heat-resistant steels can be formed in cold condition. However, due to their relatively high nitrogen content, the mechanical strength of certain steels is higher and greater deformation forces are consequently required. The relatively high hardness of austenitic steels and their ability to strain-harden must be taken into consideration when machining.

These steels have good or very good weldability and can be welded using the following methods: shielded metal arc welding (SMAW) with covered electrodes, gas shielded welding, e.g. gas tungsten arc welding

(GTAW, also TIG), plasma arc welding (PAW) and gas metal arc welding (GMAW, also MIG), with pure argon used as the shielding gas, and submerged arc welding (SAW).

Heat treatment after hot or cold forming or welding is often not needed if the material is exposed to high temperature during service. However, if that is not sufficient, the best option is solution annealing for austenitic stainless steels and soft annealing for ferritic stainless steels. Suitable temperature ranges are given in Table 11.

Table 10: Weldability and welding filler materials for some selected heat-resistant steels [32]

Steel designation			Weldability		Suitable welding filler materials
Number	Name	Nearest ASTM/AISI	Good, all welding methods	Heating up and electrowelding	
Ferritic heat-resistant steels					
1.4713	X10CrAlSi7	-	-	•	1.4551, 1.4716, 1.4820, 1.4829, 1.4723
1.4724	X10CrAlSi13	-	-	•	1.4502, 1.4723, 1.4773, 1.4820, 1.4829
1.4742	X10CrAlSi18	-	-	(•)	1.4820, 1.4773, 1.4829
1.4762	X10CrAlSi25	-	-	(•)	1.4773, 1.4820, 1.4842
Austenitic heat-resistant steels					
1.4878	X8CrNiTi18-10	321H	•	-	1.4551, 1.4829
1.4828	X15CrNiSi20-12	-	•	-	1.4829
1.4835	X9CrNiSiNce21-11-2	S30815	•	-	-
1.4833	X12CrNi23-13	309S	•	-	1.4842
1.4845	X8CrNi25-21	310S	•	-	1.4842
1.4841	X15CrNiSi25-21	314	•	-	1.4842
Duplex heat-resistant steel					
1.4821	X15CrNiSi25-4	-	-	•	1.4820, 1.4842

• good

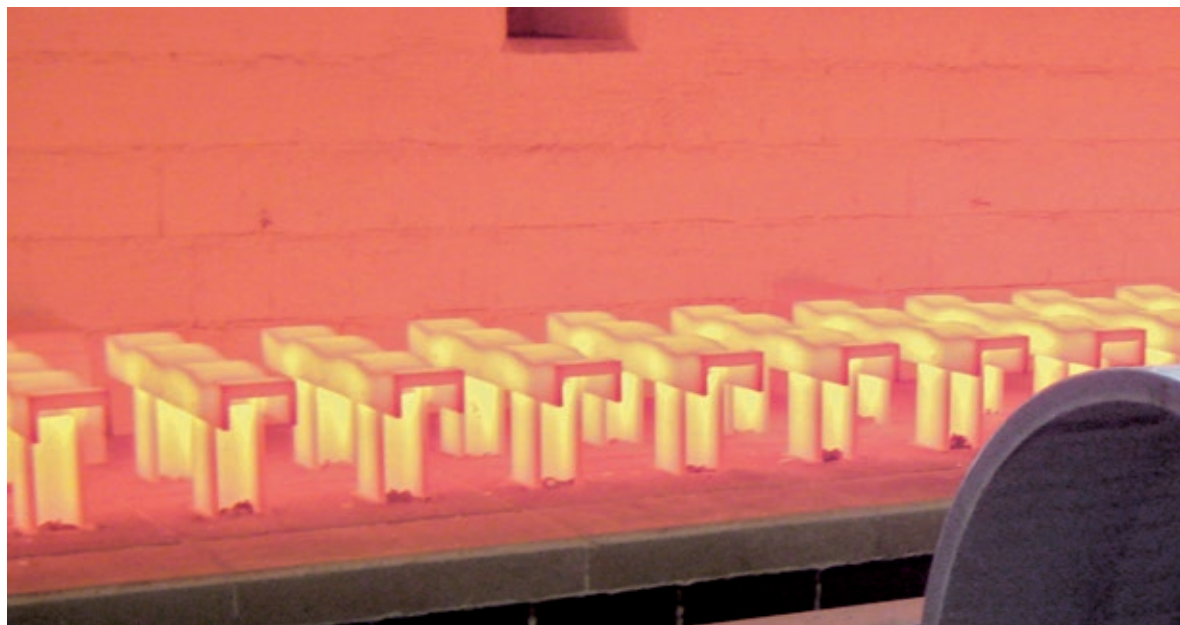
(•) conditional

Table 11: Heat treatment temperatures [6]

Steel designation			Hot working °C	Soft annealing °C*	Solution annealing °C
Name	Number	Nearest ASTM/AISI			
Ferritic heat-resistant steels					
1.4713	X10CrAlSi7	-	1100–800	780–840	-
1.4724	X10CrAlSi13	-	1100–800	800–860	-
1.4742	X10CrAlSi18	-	1100–800	800–860	-
1.4762	X10CrAlSi25	-	1100–800	800–860	-
Austenitic heat-resistant steels					
1.4878	X8CrNiTi18-10	321H	1150–800	-	1020–1120
1.4828	X15CrNiSi20-12		1150–800	-	1050–1150
1.4835	X9CrNiSiNCe21-11-2	S30815	1100–900	-	1020–1120
1.4833	X12CrNi23-13	309S	1100–900	-	1050–1150
1.4845	X8CrNi25-21	310S	1100–900	-	1050–1150
1.4841	X15CrNiSi25-21	314	1150–800	-	1050–1150
Duplex heat-resistant steel					
1.4821	X15CrNiSi25-4	-	1150–800	-	1000–1100

* cooling in calm air

Heat treatment after hot or cold forming is often part of the fabrication procedure. Photo: Butting, Knesebeck (D)



8 *Design for high-temperature applications*

Time-dependent deformation and fracture of structural materials at high temperatures are among the most challenging problems faced by materials engineers. To develop an improved design methodology for machines and equipment operating at high temperatures, several key concepts and their synergism must be understood. These include:

- plastic instability at high temperatures
- deformation mechanisms and strain components associated with creep processes
- stress and temperature dependence
- fracture at high temperatures
- environmental effects

Engineering procedures for the life management of operating components assume that the material is progressively degraded or damaged as creep strain increases and operating time accumulates. However, for the purposes of component-life management – which allows decisions to be made

regarding part replacement, repair or rejuvenation – there is a critical need to quantify the accumulation of damage as a result of operating conditions. There are two basic approaches used for the concept of damage accumulation in life assessment:

- Remaining life is estimated from the known original properties of the construction material, based on detailed knowledge of the operating conditions, including temperature and stress changes,
- Remaining-life estimates are made using post-exposure measurements of microstructural changes, intergranular cavitation or mechanical properties such as hardness, impact energy or stress-rupture life [25].



9 Design for oxidation resistance

Alloys intended for use in high-temperature environments rely on the formation of a continuous, compact, slow-growing oxide layer for oxidation and hot-corrosion resistance. To be protective, this oxide layer must be chemically, thermodynamically and mechanically stable. Successful alloy design for oxidative environments is best achieved by forming adherent scales of either alumina (Al_2O_3), chromia (Cr_2O_3) or silica (SiO_2).

The basic test method for evaluating oxidation resistance is to expose the material, monitor the kinetics and subsequently characterise the oxidation products and substrate material. Exposures are most often performed in air, but can be done in any controlled mix of corrosive gases, such as $\text{H}_2/\text{H}_2\text{S}$, CO/CO_2 or O_2/SO_2 . Oxidation kinetics are usually recorded as weight changes but may also be followed as changes in

scale thickness. Continuous weight change is usually obtained by thermo-gravimetric analysis (TGA). Weight change data provides a very useful measure of the amount of metal converted to oxide and a helpful comparison among alloys. However, the ultimate engineering criterion of the oxidation resistance of a material is retention of mechanical properties after exposure. Creep-rupture data from inert atmosphere tests cannot be used for design purposes when the material will be exposed to conditions of severe oxidation [25].



Austenitic stainless steels are used in environments in which a combination of high-temperature corrosion resistance and mechanical strength is required. Photo: Stappert Spezial-Stahl Handel, Düsseldorf (D)

10 *Selecting the alloy*

Technical data illustrating the properties of heat-resistant alloys is a very helpful guide in selecting a suitable alloy for an application. However, long-term exposure to different environments and temperatures can neither be completely documented nor described by laboratory tests. Experiences obtained from many actual installations are most helpful. One must develop the judgement needed to determine which of the many factors involved are the most important.

10.1 Temperature

Temperature is often the first and sometimes the only data point given in alloy selection, but a successful material selection cannot be based on temperature alone. A simple first guide to alloy selection, however, is to know the maximum temperature at which a given alloy may have useful long-term engineering properties. Thin sheet material will have a lower limiting temperature, due to proportionally greater losses to oxidation.

10.2 Atmosphere and combustion gases

Vacuum – Since metal loss from oxidation can obviously not occur, rather lean alloys may be used to an extreme temperature, if their mechanical properties are suitable.

Air – Those alloys useful in plain hot air are also suitable for the oxidising combustion products of natural gas and even coal. Generally, oxidation and strength are the only issues. “Oxidation” usually refers to metal wastage, but concern about product contamination from scale is an occasional issue [15].

The combustion of fossil fuels, biofuels or waste produces combustion gases containing various aggressive impurities. The least contaminated fuel is natural gas, the combustion products of which are mainly carbon monoxide, carbon dioxide and water. It may contain minor amounts of sulphur. The reduction in maximum service temperature compared to pure-air exposure is modest, at around 50–100 °C. Sulphur is more abundant in coal and oil. In addition, coal contains chlorine, while rather high levels of vanadium can be found in oil. Impurity levels vary according to the grade and origin of the fuel and can lead to more than 500 °C of reduction in maximum service temperature compared to service in air (see also Table 7 and Table 8). High-nickel alloys are preferred in high-chlorine or fluorine atmospheres [26].

11 Applications

A partial list of typical applications can be divided into two categories. The first consists of parts that go through the furnaces and are therefore subjected to thermal and/or mechanical shock. These include trays, fixtures, conveyor chains and belts and quenching fixtures. The second comprises parts that remain in the furnace with less thermal or mechanical shock. These include support beams, hearth plates, combustion tubes, radiant tubes, burners, thermowells, roller and skid rails, conveyor rolls, walking beams, rotary retorts, pit-type retorts, muffles, recuperators, fans and drive and idler drums. In addition, there are applications such as boilers, reaction vessels, exhaust systems and gas turbines that require strength and oxidation resistance and where heat-resistant stainless steels are also used to advantage.

Steel grades designed for aqueous corrosion resistance are used also as heat-resistant grades [3,22,32,33].

Austenitic

1.4301 (304) has good resistance to atmospheric corrosion and oxidation.

1.4401 (316) has better mechanical properties than steel grades 1.4301 (304) and 1.4541 (321) and is more resistant to corrosion in some media, such as fatty acids at high temperatures and mild sulphuric-acid solutions.

1.4541 (321) and 1.4550 (347) can be used where solution treatment after welding is not feasible, such as in steam lines, superheater tubes and exhaust systems in reciprocating engines and gas turbines that operate at temperatures from 425 °C to 850 °C.

1.4948 (304H) is a creep-resistant variant of 1.4301, with a standardised minimum carbon content for service at temperatures up to 800 °C in dry air. It is used for sodium-cooled fast aggregates, pipelines and pressure vessels.

1.4878 (321H) is a heat-resistant variant of 1.4541 (321) with a slightly higher maximum carbon content. The recommended maximum service temperature for this steel in dry air is 800 °C. There is also a creep-resistant variant of 1.4541, i.e. 1.4941, which is included in EN 10028-7 and in ASTM A 240. Applications for steel grade 1.4878 are annealing bells and muffles, cementation and hardening

boxes; and for grade 1.4941, pressure vessels and steam boilers.

1.4828 is used for service at temperatures up to 950–1000 °C in dry air. Utilisation in the 600–900 °C temperature range can lead to embrittlement of the material. This grade is used for parts exposed to both high temperatures and high mechanical loads. Typical examples include supporting elements and pipes in furnaces, annealing bells, cementation and hardening boxes and annealing pots.

1.4833 (309S) and 1.4845 (310S) rank higher because of their higher nickel and chromium content. Steel grade 1.4845 (310S) is useful where intermittent heating and cooling are encountered, because it forms a more adherent scale than type 1.4833 (309 S). Both grades are used for parts such as firebox sheets, furnace linings, boiler baffles, thermocouple wells, aircraft-cabin heaters and jet-engine burner liners.

1.4835 is very often used for hydrogen and/or nitrogen atmospheres but should not be used in carburising environments. The most suitable temperature range is 850–1100 °C. When used at temperatures between 600 °C and 850 °C, reduced room-temperature impact toughness might occur. It is used in furnace construction and petroleum installations.

1.4841 is a variant of 1.4845 with increased silicon content for increased resistance to oxidation. More susceptible to embrittlement than 1.4845, it is often used for superheater suspensions, annealing pots and enamelling grates.

1.4845 is used at temperatures up to 1100 °C in dry air. This steel is also prone to embrittlement when used in the 600–900 °C temperature range. There is also a creep-resistant variant of 1.4845, i.e. 1.4951, which is included in EN 10028-7 and in ASTM A 240. Applications can be found in industrial furnaces, steam boilers and petroleum processing plants.

1.4854. The maximum service temperature in air is 1150 °C, but after service at temperatures below approximately 950 °C, there is a risk of reduced room-temperature impact toughness.

Ferritic

1.4512 (409) is used extensively due to its good fabricating characteristics, including weldability and formability, and its availability. Its best-known high-temperature applications are in automotive exhaust systems where metal temperatures in catalytic converters exceed 550 °C. It is also used for exhaust ducting and silencers in gas turbines.

1.4016 (430) and **1.4510 (439)** are used for heat exchangers, hot-water tanks, condensers and furnace parts.

1.4749 (446) is used in industrial ovens, blowers, exhaust systems, furnace equipment, annealing boxes, kiln liners and pyrometer tubes.

1.4713 is best suited to service temperatures between 550–800 °C. It does not form brittle phases but should only be exposed to moderately corrosive atmospheres, owing to its low chromium content. It will withstand oxidising sulphur attacks. Most common applications are superheater suspensions, annealing bells, pyrometer sheath tubes.

1.4724 is a truly stainless high-temperature grade with 13 % chromium. It is applicable in oxidising sulphur-containing atmospheres. It is not critical in terms of embrittlement. It

is used for rocker bars, rails, grates and thermocouple sheath tubes.

1.4742 shows better scaling resistance than 1.4724 and can be subjected to reducing sulphur environments without risk. It is subject to 475 °C embrittlement and grain coarsening at temperatures above 950 °C. Sigma phase may form after long-term exposure to temperatures around 650 °C. This steel grade is mostly used for furnace fittings, transport elements, bolts, annealing tubes and pots in the 700–1000 °C temperature range.

1.4762 has the highest chromium content and is therefore the most resistant to reducing sulphurous gases. It is susceptible to the same embrittlement phenomena as 1.4742, whilst sigma phase forms during long exposures in the 600–800 °C range. Possible applications are coal burners and conductor strips for steam-boiler superheaters, within the 800–1150 °C temperature range.

Martensitic

1.4006 (410) is general-purpose stainless steel used for steam valves, pump shafts, bolts and miscellaneous parts requiring corrosion resistance and moderate strength up to 500 °C.

12 *Cost considerations*

Some of the factors affecting the service life, not necessarily in order of importance, are alloy selection, design, maintenance procedures, furnace and temperature control, atmosphere, contamination of atmosphere or workload, accidents, number of shifts operated, thermal cycles and overloading. High-alloyed parts may last from a few months to many years, depending on operating conditions. In selecting a heat-resistant steel for a given application, all properties should be considered in relation to the operating requirements, to obtain the most economical life.

Life expectancy is best measured in cycles rather than hours, particularly if the parts are quenched. It may be cheaper to replace all trays after a certain number of cycles, to avoid expensive shutdowns caused by wrecks in the furnace. Chains or belts that cycle from room temperature to operating temperature several times a shift will not last as long as stationary parts that do not fluctuate in temperature. Parts for carburising furnaces will not last as long as those used for straight annealing [16].

From a competitive standpoint, alloy selection must be based on expected cost-effectiveness. The best choice is usually the lowest-cost material able to meet design criteria. However, a higher-cost material offering greater reliability may be justified for certain components in a system that is critical and/or expensive to shut down for maintenance. Knowledge of alloy capabilities can be helpful in making a wise decision [25].

Heat-resistant alloys are supplied in either wrought or cast forms. In some situations, they may be a combination of the two. The properties and costs of the two forms vary, even though their chemical compositions are similar.

13 Summary

It should be apparent that the intelligent selection of an alloy for high-temperature service is a complex business and should not be lightly or inexpertly undertaken. It should also be evident that choice will never be easy, since the ideal alloy that satisfactorily fills all of every designer's requirements will never be discovered [3].

The very complex nature of high-temperature corrosion and the lack of standardised testing practices make it virtually impossible or at least not meaningful to present corrosion data in tables.

Corrosion-resistance requirements depend on the processes and constructions involved. In some plants, components can be maintained, repaired, or replaced with little if any interference to normal service while in other applications maintenance

and repair must be carefully planned and can only be performed during annual or semi-annual shutdowns. Obviously, a more careful choice of material must be made in those cases.

Choosing material for high-temperature applications requires an extensive knowledge of existing or expected service conditions, such as gas temperature and composition and material temperature. Knowledge of previously used materials, their service performance and the cause(s) of previous failures is usually of great help when trying to identify an optimum grade [26].



14 Appendix

The values in the tables are given for guidance only [6].

Table 12: Creep properties. Estimated average value of strength for rupture at high temperature^(a)

Number	Nearest AISI/ ASTM	Creep-rupture strength R _m (N/mm²) 1,000 h						Creep-rupture strength R _m (N/mm²) 10,000 h						Creep-rupture strength R _m (N/mm²) 100,000 h					
		Temperature °C						Temperature °C						Temperature °C					
		500	600	700	800	900	1000	500	600	700	800	900	1000	500	600	700	800	900	1000
Ferritic heat-resistant steels																			
1.4713	-	160	55	17	7.5	3.6	-	100	35	9.5	43	1.9	-	55	20	5	2.3	1.0	-
1.4724	-																		
1.4742	-																		
1.4762	-																		
1.4749	446																		
1.4736	-																		
Austenitic heat-resistant steels																			
1.4878	321H	-	200	88	30	-	-	-	142	48	15	-	-	-	65	22	10	-	-
1.4828	-	-	190	75	35	15	-	-	120	36	18	8.5	-	-	65	16	7.5	3	-
1.4835	S30815	-	238	105	50	24	(12)	-	157	63	27	13	(7)	-	88	35	15	8	(4)
1.4833	309S	-	190	75	35	15	-	-	120	36	18	8.5	-	-	65	16	7.5	3	-
1.4845	310S	-	170	80	35	15	-	-	130	40	18	8.5	-	-	80	18	7	3	-
1.4841	314	-	170	90	40	20	5	-	130	40	20	10	-	-	80	18	7	3	-
1.4864	-	-	180	75	35	15	-	-	125	45	20	8	-	-	75	25	7	3	1.5
1.4876	-	-	200	90	45	20	-	-	152	68	30	10	-	-	114	48	21	8	-
1.4877	-	-	-	-	-	-	-	-	175	80	24	10	(3.5)	-	140	52	16	5	(1.5)
1.4872	-	-	-	80	26	11	-	-	-	45	12	5	-	-	-	-	-	-	-
1.4818	S30415	-	238	105	46	18	(7)	-	157	63	25	10	(4)	-	88	35	14	5	(1.5)
1.4854	S35315	-	200	84	41	22	12	-	127	56	28	15	8	-	80	36	18	9.2	4.8
1.4886	No8330	-	190	80	43	22	-	-	130	55	26	13	-	-	-	-	-	-	-
1.4887	-	-	190	80	43	22	-	-	130	55	26	13	-	-	-	-	-	-	-
Duplex heat-resistant steel																			
1.4821	-	160	55	17	7.5	3.6	-	100	35	9.5	4.3	1.9	-	-	-	-	-	-	-

^(a) Values in parentheses involve time and/or stress extrapolation

Table 13: Creep properties. Estimated average value of strength for 1 % elongation at high temperature⁽⁴⁾

Number	Nearest AISI/ ASTM	Elongation 1 % in 1,000 h (Strength in N/mm ²)						Elongation 1 % in 10,000 h (Strength in N/mm ²)						Elongation 1 % in 100,000 h (Strength in N/mm ²)					
		Temperature °C						Temperature °C						Temperature °C					
		500	600	700	800	900	1000	500	600	700	800	900	1000	500	600	700	800	900	1000
Ferritic heat-resistant steels																			
1.4713	-	80	27.5	8.5	3.7	1.8	-	50	17.5	4.7	2.1	1.0	-	-	-	-	-	-	-
1.4724	-																		
1.4742	-																		
1.4762	-																		
1.4749	446																		
1.4736	-																		
Austenitic heat-resistant steels																			
1.4878	321H	-	110	45	15	-	-	-	85	30	10	-	-	-	-	-	-	-	-
1.4828	-	-	120	50	20	8	-	-	80	25	10	4	-	-	-	-	-	-	-
1.4835	S30815	-	170	66	31	15.5	(8)	-	126	45	19	10	(5)	-	80	26	11	6	(3)
1.4833	309S	-	100	40	18	8	-	-	70	25	10	5	-	-	-	-	-	-	-
1.4845	310S	-	100	45	18	10	-	-	90	30	10	4	-	-	-	-	-	-	-
1.4841	314	-	105	50	23	10	3	-	95	35	10	4	-	-	-	-	-	-	-
1.4864	-	-	105	50	25	12	-	-	80	35	15	5	-	-	-	-	-	-	-
1.4876	-	-	130	70	30	13	-	-	90	40	15	5	-	-	40	14	4	1.5	-
1.4877	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.4872	-	-	-	55	15	4	-	-	-	34	8	2	-	-	-	-	-	-	-
1.4818	S30415	-	147	61	25	9	(2.5)	-	126	42	15	5	(1.7)	-	80	26	9	3	(1.0)
1.4854	S35315	-	150	60	26	12.5	6.5	-	88	34	15	8	4.5	-	52	21	9.7	5.1	3.0
1.4886	No8330	-	110	60	25	12	-	-	60	35	20	10	(4)	-	-	-	-	-	-
1.4887	-	-	110	60	25	12	-	-	60	35	20	10	(4)	-	-	-	-	-	-
Duplex heat-resistant steel																			
1.4821	-	80	27.5	8.5	3.7	1.8	-	50	17.5	4.7	2.1	1.0	-	-	-	-	-	-	-

⁽⁴⁾ Values in parentheses involve time and/or stress extrapolation

Table 14: Physical properties for heat-resistant steels

Number	Nearest AISI/ ASTM	Density kg/dm³	Linear expansion coefficient 10 ⁻⁶ K ⁻¹ between 20 °C and					Thermal conductivity W/(m·K)		Specific heat capacity kJ/kg·K at 20 °C	Electrical resistivity Ω mm²/m at 20 °C	Magnetis- ability
			Temperature °C					at 20 °C	at 500 °C			
			200	400	600	800	1000					
Ferritic heat-resistant steels												
1.4713	-	7.7	11.5	12.0	12.5	13.0	-	32	25	0.45	0.70	yes
1.4724	-	7.7	10.5	11.5	12.0	12.5	-	21	23	0.50	0.75	yes
1.4742	-	7.7	10.5	11.5	12.0	12.5	13.5	19	25	0.50	0.93	yes
1.4762	-	7.7	10.5	11.5	12.0	12.0	13.5	17	23	0.50	1.1	yes
1.4749	446	7.7	10.0	11.0	11.5	12.0	13.0	17	23	0.50	0.70	yes
1.4736	-	7.7	10.5	10.8	12.0	12.5	13.0	21	23	0.50	0.60	yes
Austenitic heat-resistant steels												
1.4878	321H	7.9	17.0	18.0	18.5	19.0	-	15	-	0.50	0.73	no ⁽ⁱ⁾
1.4828		7.9	16.5	17.5	18.0	18.5	19.5	15	21	0.50	0.85	no ⁽ⁱ⁾
1.4835	S30815	7.8	17.0	18.0	18.5	19.0	19.5	15	21	0.50	0.85	no ⁽ⁱ⁾
1.4833	309S	7.9	16.0	17.5	18.0	18.5	19.5	15	19	0.50	0.78	no ⁽ⁱ⁾
1.4845	310S	7.9	15.5	17.0	17.5	18.5	19.0	15	19	0.50	0.85	no ⁽ⁱ⁾
1.4841	314	7.9	15.5	17.0	17.5	18.0	19.0	15	19	0.50	0.90	no ⁽ⁱ⁾
1.4864	-	8.0	15.0	16.0	17.0	17.5	18.5	12.5	17	0.55	1.0	no ⁽ⁱ⁾
1.4876	-	8.0	15.0	16.0	17.0	17.5	18.5	12	17	0.55	1.0	no ⁽ⁱ⁾
1.4877	-	8.0	15.5	16.5	16.5	17.7	18.4	12	20	0.45	0.96	no ⁽ⁱ⁾
1.4872	-	7.8	16.5	18.0	18.5	19.0	19.5	14.5	20	0.50	0.75	no ⁽ⁱ⁾
1.4818	S30415	7.8	16.5	18.0	18.5	19.0	20.0	15	21	0.50	0.85	no ⁽ⁱ⁾
1.4854	S35315	7.9	15.5	16.5	17.0	17.5	18.0	11	18.5	0.45	1.0	no ⁽ⁱ⁾
1.4886	No8330	8.0	15.5	16.0	17.0	17.7	18.0	12	19.5	0.46	1.0	no ⁽ⁱ⁾
1.4887	-	8.0	15.5	16.0	17.0	17.7	18.0	12	19.5	0.46	1.0	no ⁽ⁱ⁾
Duplex heat-resistant steel												
1.4821	-	7.7	13.0	13.5	14.0	14.5	15.0	17	23	0.50	0.90	yes

⁽ⁱ⁾ slightly magnetic when cold worked

15 References

- [1] *Stainless Steel - High Temperature Resistance*; available at <http://www.azom.com/article.aspx?ArticleID=1175>
- [2] Outokumpu, *High Temperature Stainless Steel Properties*, available at <http://www.outokumpu.com/en/Products/Grades/stainless-properties/high-temperature-grades/Pages/default.aspx>
- [3] ASM International, *Stainless Steels at High Temperatures*, Course 18, 1994
- [4] Cunat, P.-J., *The Euro Inox Handbook of Stainless Steel*, Materials and Application Series, Volume 1, 2002
- [5] Itoh, I., et al., *Development of Ferritic Stainless Steel Foil as Metal Support for Automotive Catalytic Converter*, Nippon Steel Technical Report No.64, 1995
- [6] *EN 10095: Heat resisting steels and nickel alloys*, CEN – European Committee for Standardization, 1999
- [7] *Our offer for automotive exhaust: a range of tailored solutions*; retrieved in June 2012 from http://www.aperam.com/uploads/stainlesseurope/Brochures/200807_Exhaustoffer_GB_241ko.pdf
- [8] *High Temperature Properties*; available at <http://www.ssina.com/composition/temperature.html>
- [9] EN 10088-1:2005 – *Stainless steels – Part 1: List of stainless steels*
- [10] EN 10302:2008 – *Creep resisting steels, nickel and cobalt alloys*
- [11] Schedin, E., Ivarsson, B., Andersson, M., Lindstrom, R., *Duplex stainless steel in fire*, Proceedings of Stainless Steel Science and Market 2011 Conference, Como, Italy
- [12] *ASM Specialty Handbook, Stainless Steels*, edited by J.R. Davis, ASM International, 1994
- [13] EN 10028-7:2007 - *Flat products made of steels for pressure purposes - Part 7: Stainless steels*
- [14] Nickel Institute, Publication Nr. 266, *Heat and corrosion resistant castings: Their engineering properties and applications*
- [15] *Rolled Alloys, Heat Resistant Alloys Handbook*, available at <http://www.rolledalloys.fr/trcdocs/heatresist/handbook.pdf>
- [16] Lai, G.Y., *Heat-Resistant Materials for Furnace Parts, Trays and Fixtures, Heat Treating, Vol.4*, ASM Handbook, ASM International, 1991, p.510-518
- [17] ThyssenKrupp Nirosta, *Corrosion of Stainless Steels*, available at <http://www.nirosta.de/fileadmin/media/produkte/werkstoff-PDF/Verarbeitung-NIROSTA-Werkstoffe-gb.pdf>
- [18] Atlas Steels, *The Atlas Steels Technical Handbook of Stainless Steels*, available at http://www.atlassteels.com.au/documents/Atlas_Technical_Handbook_rev_July_2010.pdf
- [19] Nickel Institute, *Better high temperature strength than other grades*, Stainless Steel Focus, July, 2009, p.30-33
- [20] ThyssenKrupp Nirosta, *Thermax Heat-Resistant Steels*, available at http://www.thyssenkrupp-nirosta.de/fileadmin/media/PDF/thermax_en.pdf

- [21] Outokumpu, *Microstructural Stability*, available at
<http://www.outokumpu.com/en/Products/Grades/stainless-properties/high-temperature-grades/structural-stability/Pages/default.aspx>
- [22] Outokumpu, *High Temperature Austenitic Stainless Steel*, available at
http://www.outokumpu.com/SiteCollectionDocuments/Austenitic_High_Temperature_Grades_Datasheet.pdf
- [23] Cunat, P-J, *Working with stainless steels*, Euro Inox, 2nd edition, 2009
- [24] *ASM Handbook, Heat Treating, Vol. 4*, ASM International, 1991
- [25] *ASM Specialty Handbook, Heat-Resistant Materials*, edited by J.R. Davis, 1997
- [26] *Outokumpu Corrosion Handbook*, Tenth Edition, Outokumpu Oyj, 2009
- [27] Outokumpu, *Resistance to Oxidation*, available at
<http://www.outokumpu.com/en/Products/Grades/stainless-properties/high-temperature-grades/oxidation/Pages/default.aspx>
- [28] Outokumpu, *High Temperature Stainless Steel*, available at http://www.outokumpu.com/SiteCollectionDocuments/Austenitic_High_Temperature_Grades_Datasheet.pdf
- [29] Leffler, B., *Stainless – Stainless Steels and Their Properties*, available at
http://static.gest.unipd.it/esercizi/IIP_pmmi/acciai_inox.pdf
- [30] Outokumpu, *Sulphur Attack*, available at
<http://www.outokumpu.com/en/Products/Grades/stainless-properties/high-temperature-grades/sulphur-attack/Pages/default.aspx>
- [31] Outokumpu, *Carburization and Nitridation*, available at
<http://www.outokumpu.com/en/Products/Grades/stainless-properties/high-temperature-grades/c-n-pickup/Pages/default.aspx>
- [32] Wegst, C., Wegst, M., *Stahlschlüssel*, Verlag Stahlschlüssel Wegst, 2004
- [33] Outokumpu, *High Temperature Ferritic Stainless Steel*, available at
http://www.outokumpu.com/SiteCollectionDocuments/High_temperature_ferritic_grades_Datasheet.pdf

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