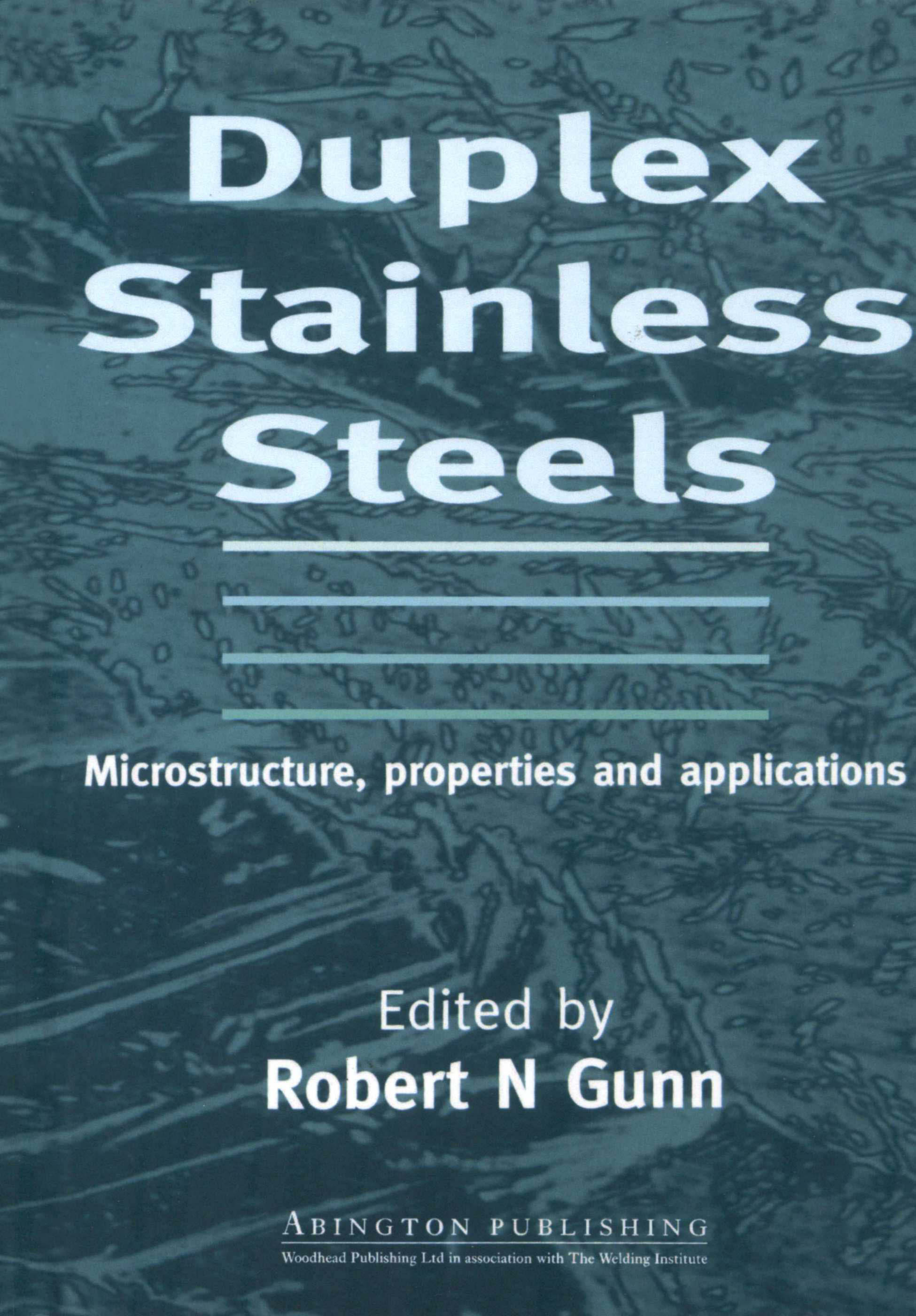

Duplex Stainless Steels

Microstructure, properties and applications

Edited by

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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 Griffith[1] 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 1929[2] 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 analysis[3] 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 made[15] 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%**										
	C	S	P	Si	Mn	Ni	Cr	Mo	Cu	W	N
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	–	0.05–0.60	–	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%, designed[16] to

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

UNS	Element, wt%										
	C	S	P	Si	Mn	Ni	Cr	Mo	Cu	N	Other
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 (Escoloy)	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 puposes 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]

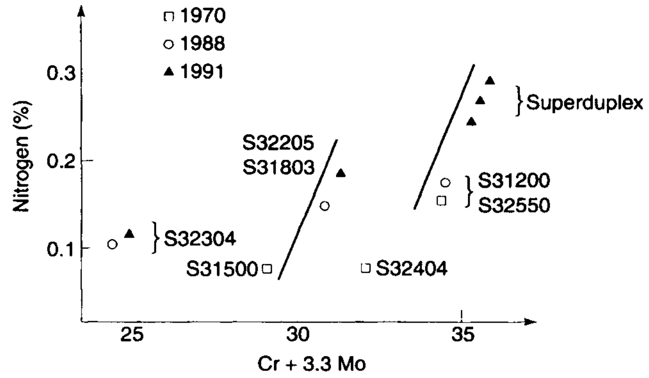
Even though grades such as S31500 were a breakthrough in alloy design and can be described as the second generation of duplex stainless steel, they were still susceptible to IGC under certain conditions.[20–22] This was believed[23] to be due to a high Cr/Ni equivalent ratio which led to an almost fully 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 patent[24] 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 nitrogen[12] (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:

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

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:

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

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

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
[2] Creusot–Loire Industries (Usinor Group)
[3] Valinox
[4] Sumitomo Metal Industries
[5] Weir Materials Ltd
[6] Alloy Casting Institute
[7] Krupp Stahl
[8] Böhler Edelstahl
[9] Mannesmann

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	Y			Forged flanges, fittings
A240		Y		Y	(Y)	Y	Y	Y	Y	Y	Y	Y			Plate and sheet
A268									Y						Tubing
A276				Y	(Y)							Y			Bars and shapes
A314										Y		Y			Forging stock
A473				Y	(Y)					Y		Y			Forgings
A479				Y	(Y)			Y		Y	Y				Bars and shapes
A789	Y	Y		Y	(Y)	Y	Y	Y	Y	Y	Y		Y		Pipe and tube
A790	Y	Y		Y	(Y)	Y	Y	Y	Y		Y	Y	Y		Pipe and tube
A815				Y	(Y)					Y		Y	Y		Fittings
EN															
pr10028		Y		Y	(Y)			Y			Y	Y			Flat products
10088		Y		Y	(Y)			Y	Y		Y	Y			General
pr10250		Y		Y	(Y)			Y	Y		Y	Y			Forgings
pr10272			Y	Y	(Y)			Y			Y	Y			Bars
NACE															
MR0175			Y	Y	(Y)		Y	Y			Y	Y	Y	Y	Sour service

Table 1.6 Cast duplex grades covered in national standards

UNS	J93183	J93345	J93370	J93380	J93404
EN	1.4462	–	1.4517	1.4508	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.
A949/949M–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 Assocation 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

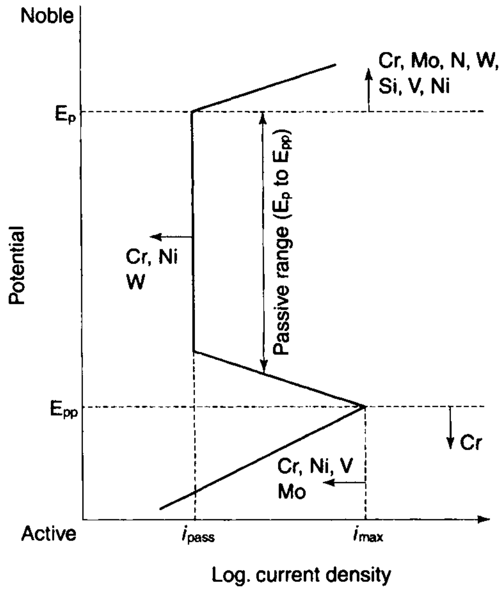
The melt for a duplex alloy can be produced using either high purity material in a conventional induction furnace, or high alloyed scrap in an electric arc furnace (EAF) followed by AOD, VOD or VARP converters.[1] Although both these methods produce high quality materials, the latter method favours lower 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).

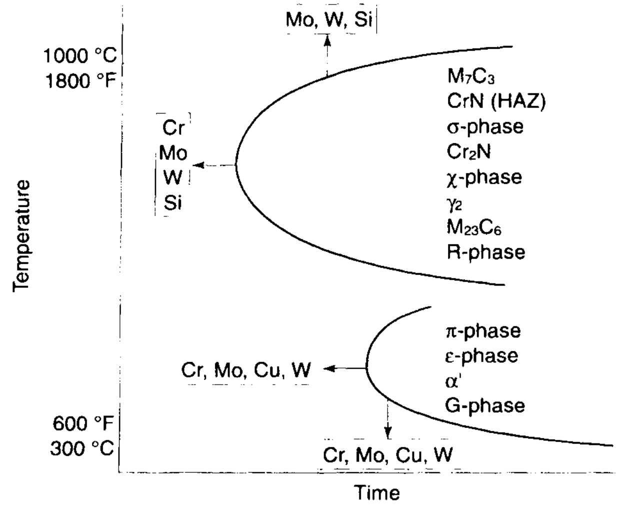
of ever higher levels is negated by the enhanced precipitation of intermetallic phases (Fig. 2.2),[7] such as sigma. These phases often lead to reduction in ductility, toughness and corrosion properties, and are covered in Section 8.3.4.

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:

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

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 recommended[14] to prevent crevice corrosion, while an upper limit of about 4%Mo has been quoted.[15] This limit stems[16] 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:

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

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 enhanced[16] 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 phase[21] 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/cm^2. 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 reported[30] 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.

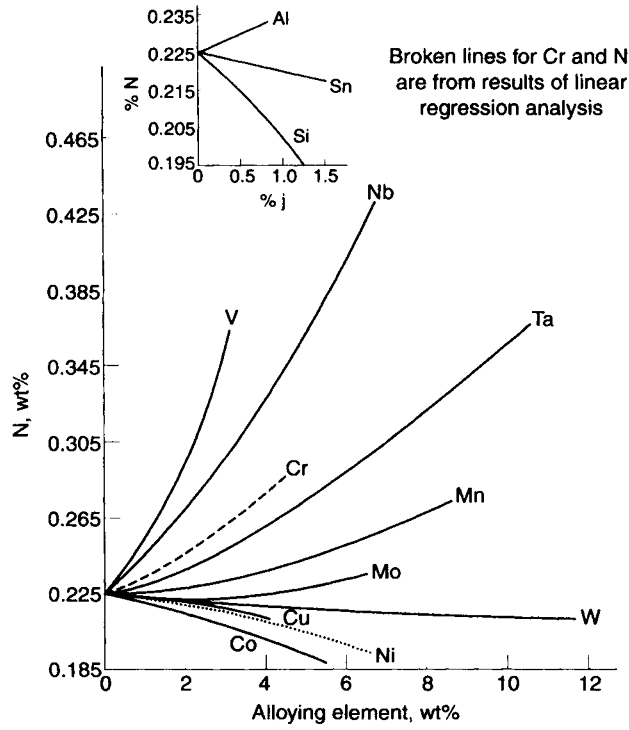
The addition of C and N strengthens both ferrite and austenite by dissolving at interstitial sites in the solid solution.[31,32] And yet, as carbon is undesirable in stainless steel, due to the risk of sensitisation, the addition of nitrogen is preferred. Further, as nitrogen is a strong austenite stabiliser 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 appear[38] that Mn can increase the temperature range and formation rate of detrimental sigma phase.

Manganese additions to stainless steel increase abrasion and wear resistance[39] and tensile properties without loss of ductility[38]. 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 N_2 (after reference 33).

alloys improves[36] 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% H_2SO_4 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 H_2S-contaminated sea water prevail, Cu appears[42] 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 exploited[44] 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 thought[47] 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 WO_3. In neutral chloride solutions, WO_3 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 believed[49] 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 claimed[15] 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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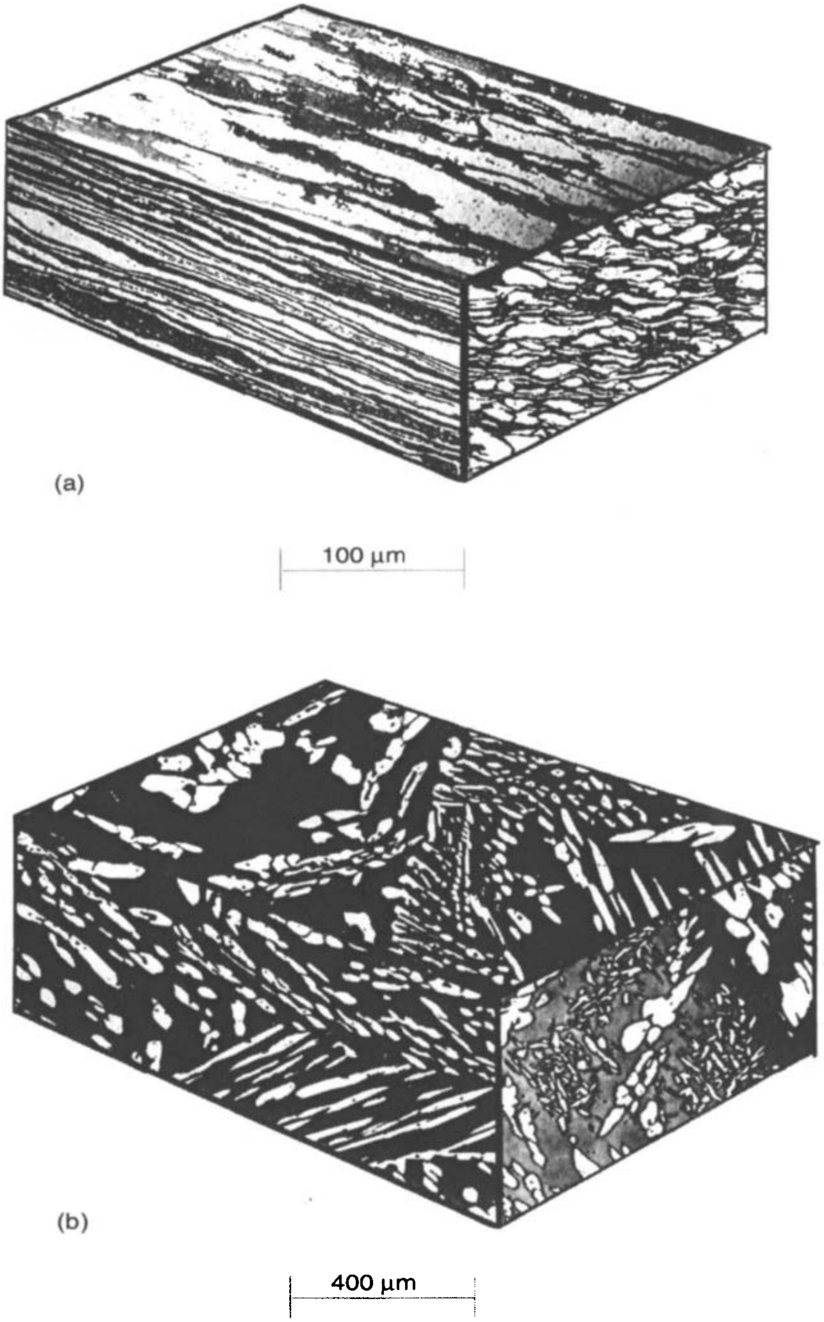
3 Microstructure

3.1 Commercial products

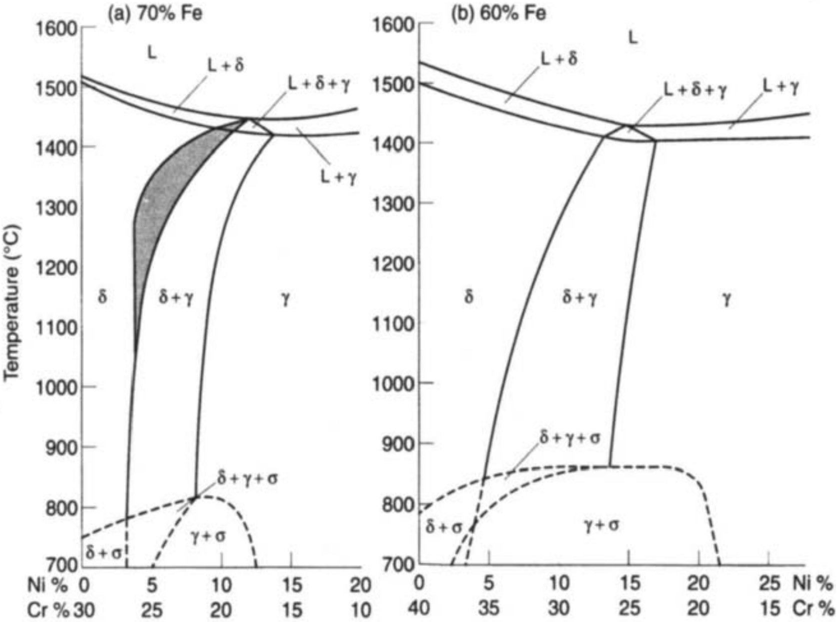
Modern duplex stainless steels are characterised by a two phase structure, which consists of a mixture of about 50% volume FCC austenite islands in BCC ferrite grains. Both cast and wrought products have roughly equivalent volume fractions of ferrite and austenite (see Fig. 3.1), which, in the case of 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.

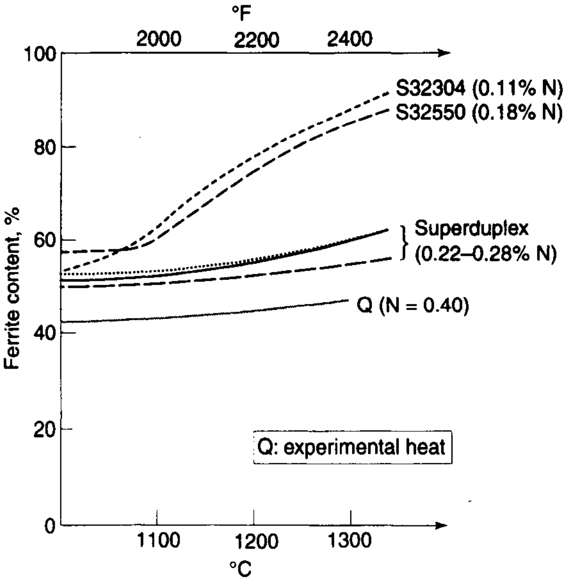
One approach[4] has been to produce isothermal ternary sections of Fe-Cr-Ni-Mo-N using a computer program called Thermocalc™ which calculates phase equilibria, over a range of temperatures. This can then be used[5] to form an isopleth diagram for a given composition (Fig. 3.4). As will be shown later, this approach has been found to be in good agreement with experimental data.



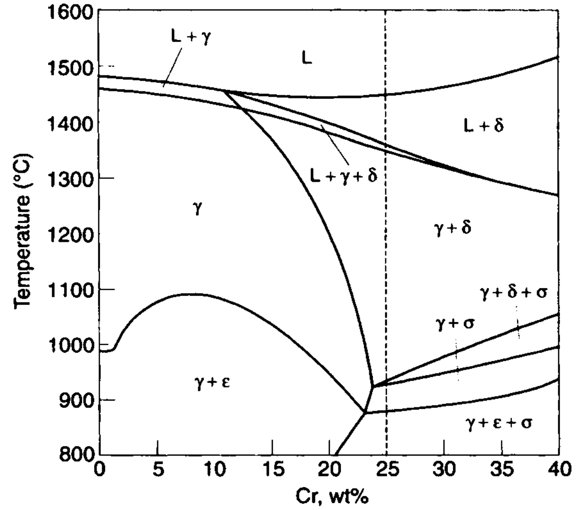
3.1 Typical microstructures of duplex stainless steels: (a) hot rolled plate, × 200; (b) casting, × 50.



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).

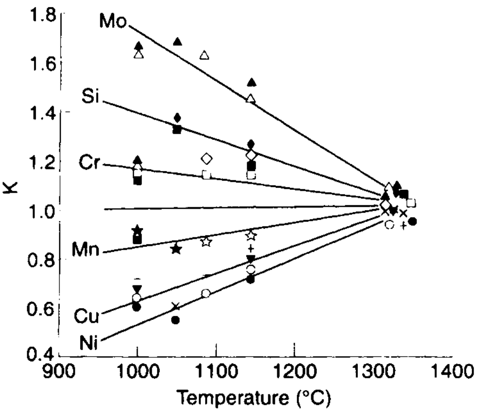


3.4 Computer calculated 'isopleth diagram' with the dotted line indicating the composition of superduplex alloys, e.g. 25%Cr-7%Ni-4%Mo-0.3%N (reference 5).

3.2 Element partitioning

3.2.1 Substitutional elements

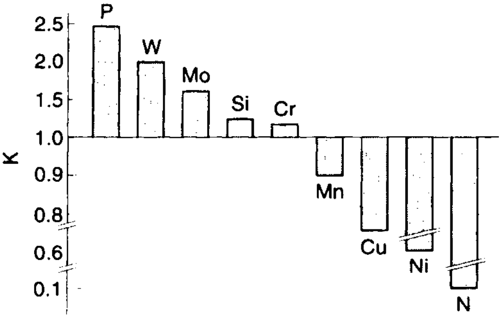
The phase diagram shown in Fig. 3.2 illustrates that the ferrite and austenite will have different compositions depending on the temperature, further illustrated by experimental data[6] in Fig. 3.5. Several workers[7-12] have studied the composition of the phases and resultant partition coefficients 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 proposed[6] that the partition coefficients tend more towards unity, apparently due to the use of higher solution annealing temperatures (Fig. 3.5).



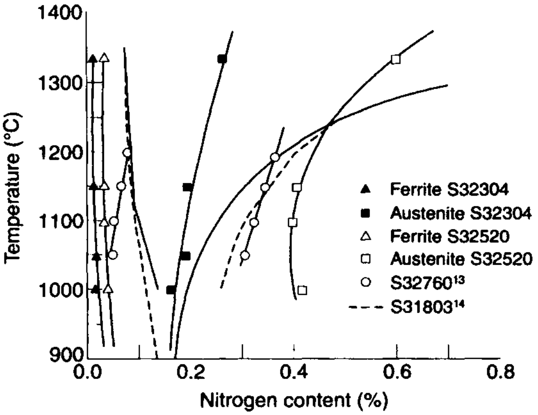
3.5 Temperature dependence of element partitioning coefficients (K = ferrite/austenite) for a range of duplex steels (after reference 6).

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 austenite[6] (Fig. 3.7),

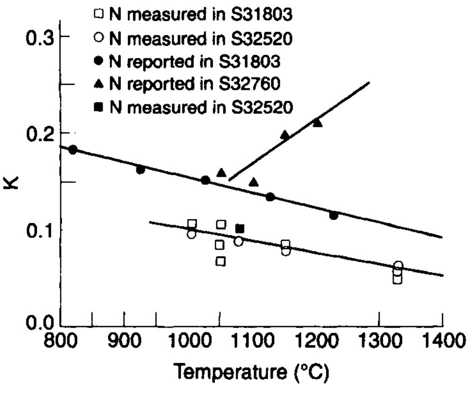


3.6 Typical partition coefficients, K, for solution annealed and water quenched products (reference 6).



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 generated[14] by Thermocalc™ are in good agreement with the experimental data. Moreover, it has been observed[6] 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]

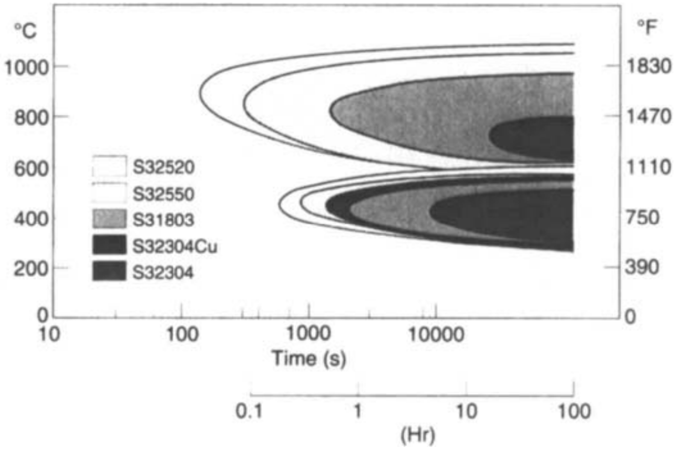
Further additions of nitrogen to the bulk alloy composition, as in the superduplex grades, leads to nitrogen enrichment in the austenite. And, as nitrogen has a significant influence on pitting corrosion resistance, this balances the preferential partitioning of Cr and Mo to the ferrite. In essence, 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 affect[2] precipitation kinetics and the stability of the phases formed.

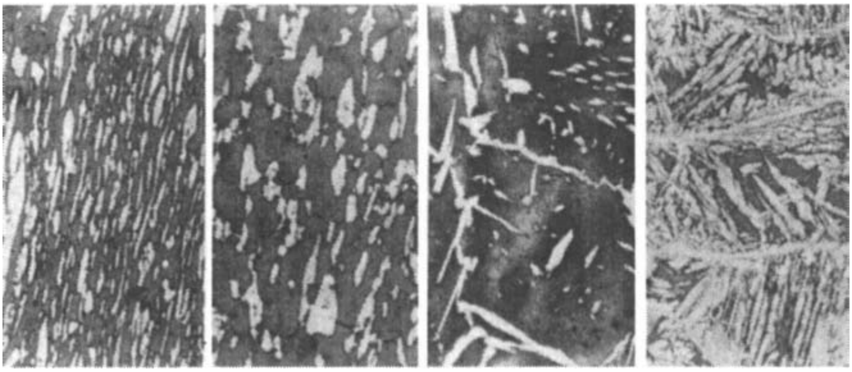


3.9 TTT diagrams of duplex stainless steels derived by optical metallography between 600 and 1050°C and hardness measurements between 300 and 600°C (after reference 2).

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.



(a) (b) (c) (d)

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.

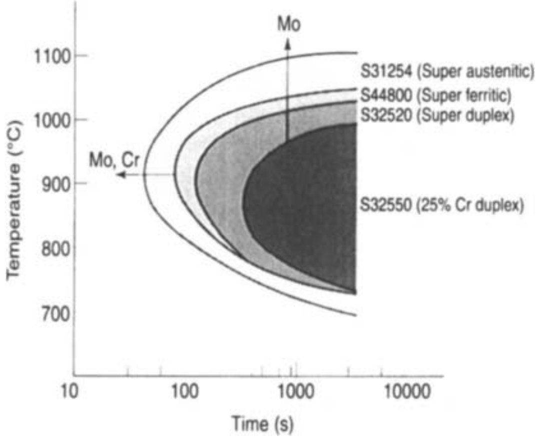
3.3.2 The 600–1050°C nose

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 superaustenitic 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 used[28] for weldments made with matching consumables.

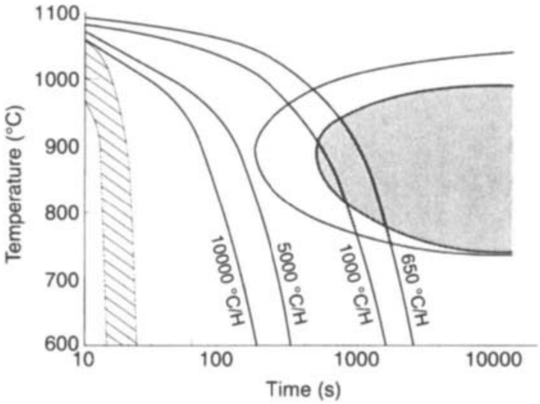
3.3.3 The 300–600°C nose

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 appear[2] 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).

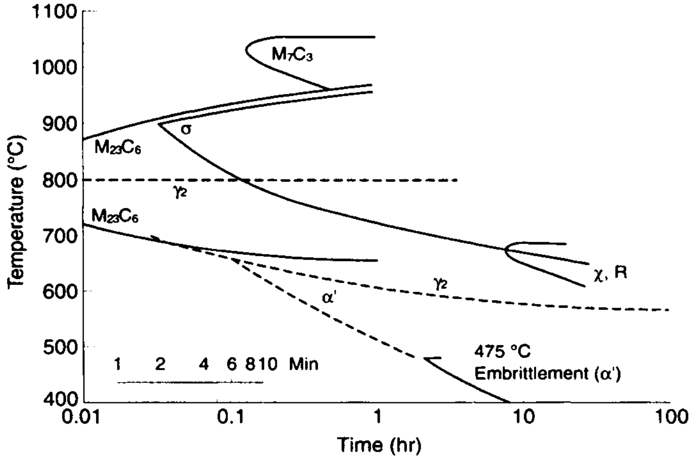
3.4.1 Alpha prime (α') and G-phase

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

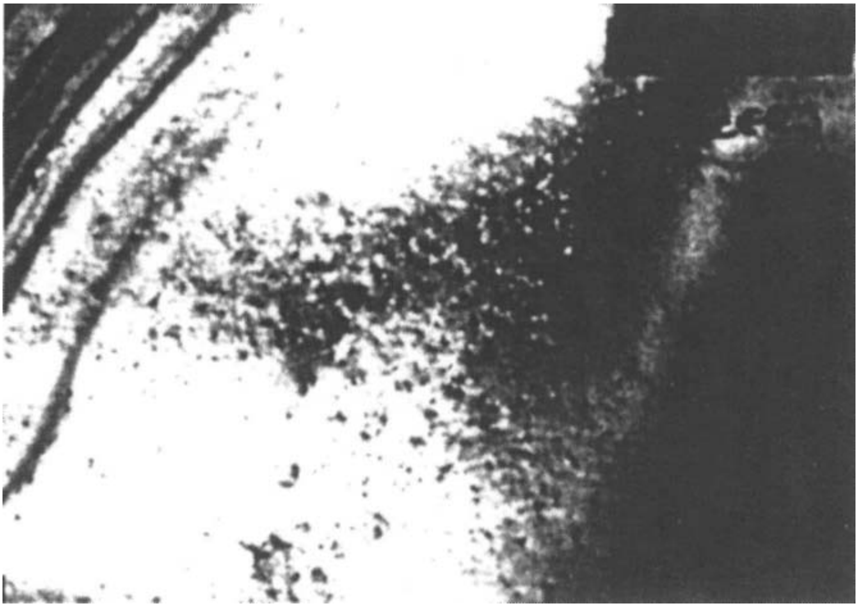
Particle	Chemical formula	Cr	Ni	Mo	Formation range, C	Lattice type	Space group	Lattice parameter (A)	Orientation relationship	Preferred location	Reference
ferrite (δ)*	–	27.4	8.7	4.0	–	BCC	Im3m	a = 2.86–2.88		Matrix	–
alpha prime (α')	–~	65	2.5	13	300–525	BCC	Im3m	a = 2.86–2.88	⟨001⟩	Intra-δ	31–40
G-phase	$\geq$14%Si^S	25	25	4	300–400					Inter α/α'	42
primary austenite (γ)*	–	26.6	9.6	3.3	<1250	FCC	Fm3m	a = 3.58–3.62	K–S: $(111)_\gamma//(110)_\delta$ $[101]_\gamma//[111]_\delta$	Intra-δ	–
secondary austenite (γ_2)	Type 1	same as ferrite			<650	FCC			<133>δN–W	Intra-δ	43
	Type 2	24.3	11	3.4	650–800				K–S	δ/γ and δ	29, 45
	Type 3				700–900					with σ	46
sigma (σ) #	Fe-Cr-Mo	30	4	7	600–1000	tetragonal	$P4_2/mnm$	a = 8.79, c = 4.54	$\{111\}_\gamma // (001)_\sigma$ $[110]_\gamma // [110]_\sigma$	Inter δ/γ	59
chi (χ) #	$Fe_{36}Cr_{12}Mo_{10}$	25	3	14	700–900	BCC-αMn	I43m	a = 8.92		Inter δ/γ	61, 62
R or Laves ^	Fe_2Mo	25	6	35	550–650	trigonal	R3	a = 10.903, c = 19.34	$\langle 0001\rangle_R\langle 111\rangle_\delta$	δ/γ and δ	50, 63
chromium nitrides	Cr_2N ~	72	6	15	700–950		P31m	a = 4.795, c = 4.469	$\langle 0001\rangle Cr_2N\langle 011\rangle_\delta$	Intra-δ	66
	CrN					cubic	Fm3m	a = 4.13–4.47			60
Pi (π) ^	$Fe_7Mo_{13}N_4$	35	3	34	550–600	cubic	$P4_132$	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	Fmmm	a = 4.05, b = 4.84, c = 2.86			75
Carbides	M_7C_3				950–1050		Pnma	a = 4.52, b = 6.99, c = 12.11	$\{111\}_\delta\langle 111\rangle_\delta$	Inter δ/γ	72
	$M_{23}C_6$ ~	58	2.5	12	650–950	FCC	Fm3m	a = 10.56–10.65		Inter δ/γ	73

Composition refs: * = 61; # = 2; ^ = 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 suggested[34] 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, × 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'.

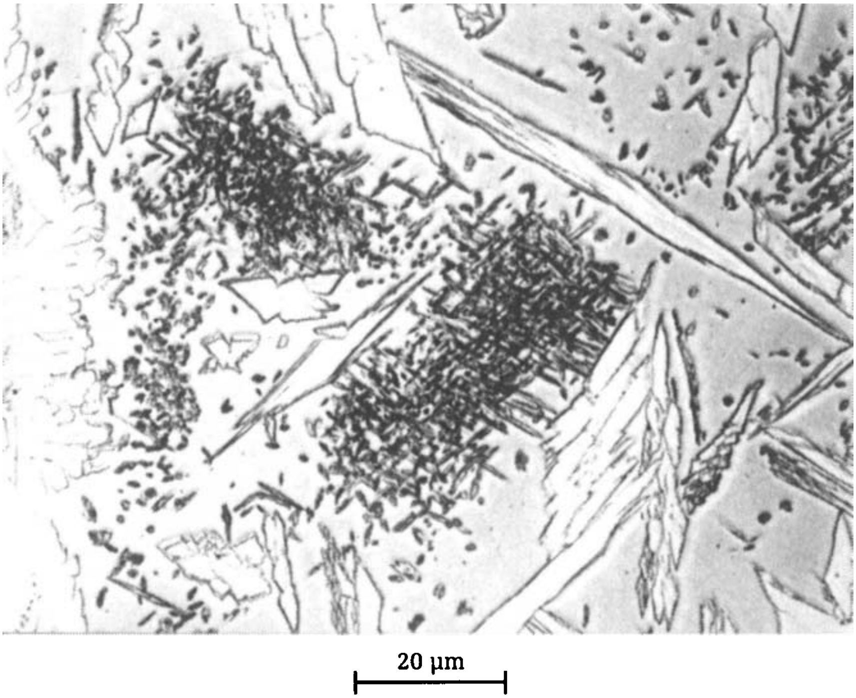
At temperatures below 400°C, the Arrhenius equation is often employed to describe the kinetics of embrittlement. The activation energy characteristic of '475 embrittlement' is similar to Cr-diffusion in ferrite, although other factors influence α′ formation, such as Cr, Mo and Cu contents and high ferrite 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 locations[42] (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 involves[29] 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]

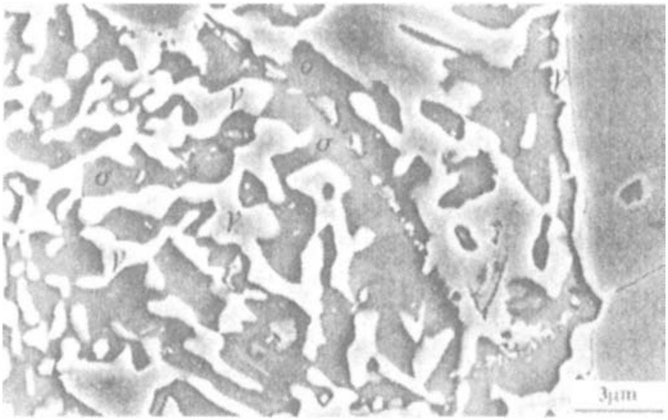
In the 700–900°C temperature range, a eutectoid of $\gamma_2 + \sigma$ can form[29] (Fig. 3.16), as γ_2 absorbs Ni and, to some extent, rejects Cr and Mo (Table 3.1), encouraging Cr, Mo-rich precipitates, such as sigma phase. Similarly, one form of γ_2 which forms at δ/γ boundaries is found to be depleted 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, × 1000. Etch: electrolytic sulphuric acid.

3.4.3 Sigma (σ)

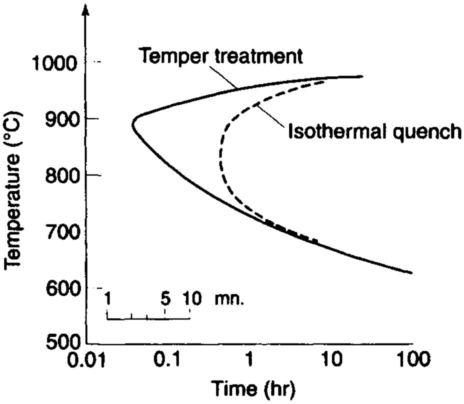
The deleterious Cr, Mo rich σ-phase is a hard embrittling precipitate,



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, × 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.



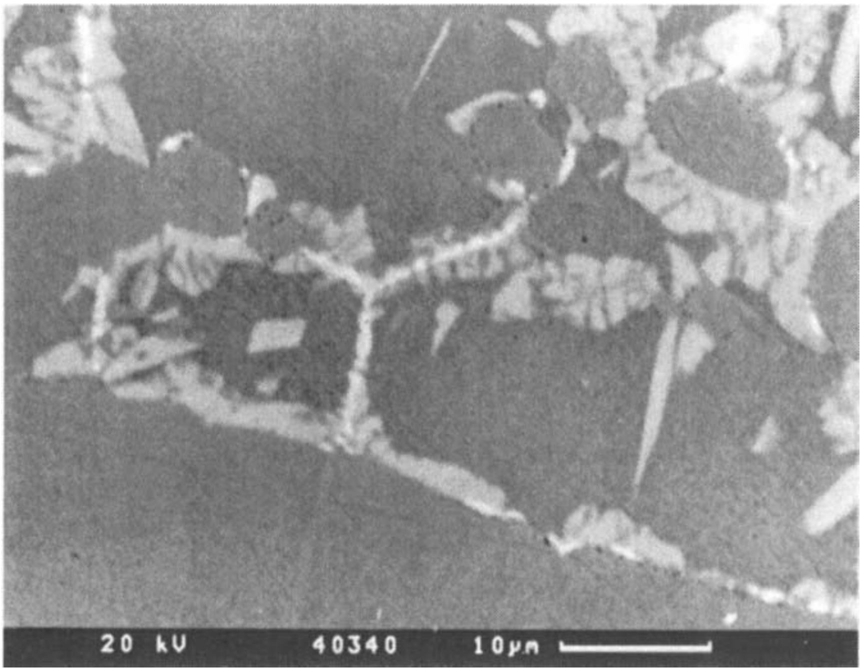
3.18 C-curves for the beginning of sigma phase formation by a temper treatment or by an isothermal quench (after reference 58).

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 magnitude[56] 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 shown[57] that the rate is faster when tempering the metal (Fig. 3.18). It is known[58] 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



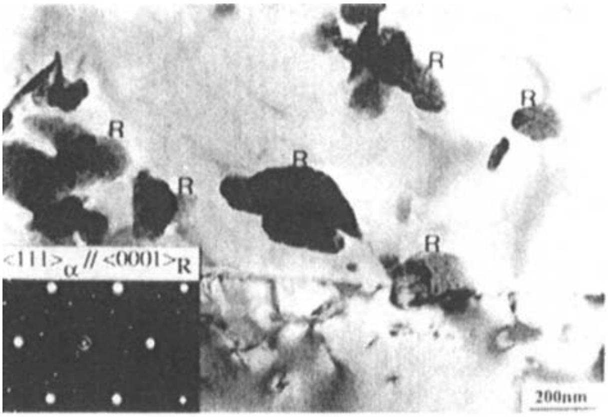
3.19 Backscattered SEM micrograph of grey σ- and white χ-phases. Steel S32750 after 900°C for 10 minutes, × 2000.

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 performed[61] on a low Mo-bearing steel. More recent work[63] 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

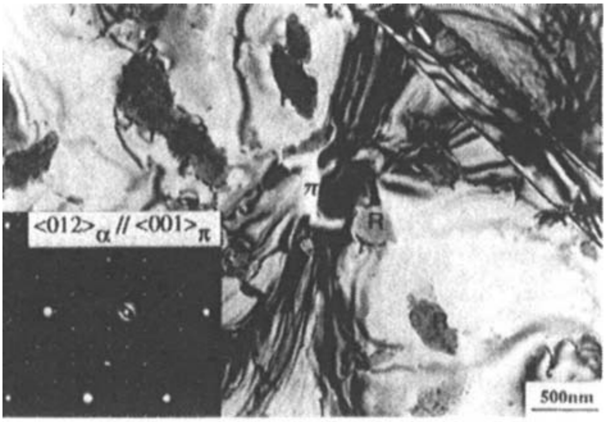
Laves or R phase (Fe_2Mo) precipita in small quantities between 550 and 650°C after several hours exposure[2] (Table 3.1). They form at



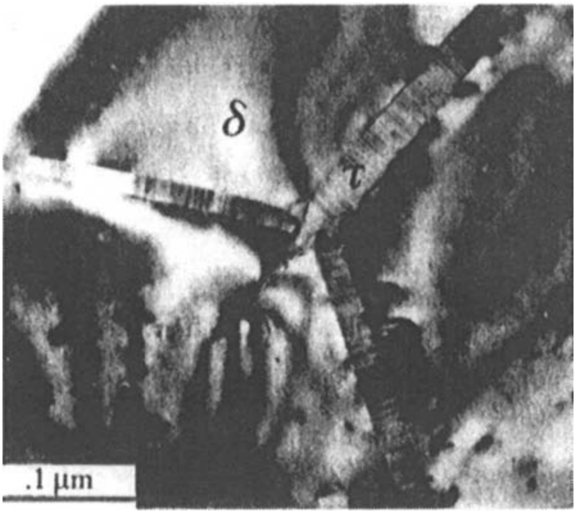
3.20 TEM micrograph of R-phase in a ferrite grain. 22%Cr weld metal after 24 hours at 600°C (after reference 65).

both intra- and intergranular sites[50,63] (Fig. 3.20), are molybdenum-rich[64] 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 identified[64] at intragranular sites in duplex weld metal after isothermal heat treatment at 600°C for several hours[2] (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).



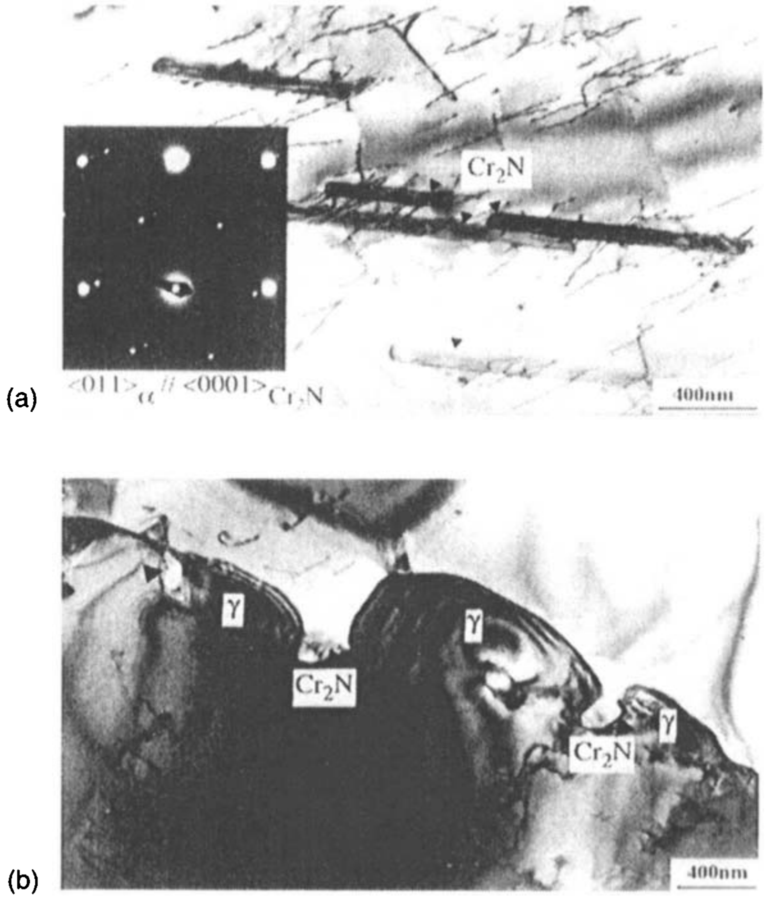
3.22 TEM micrograph of τ-phase at ferrite grain boundaries. Steel S31803 between 550 and 650°C (after reference 50).

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 boundaries[50] (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 shown[65] 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 temperatures[54] 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 stated[60] to affect pitting corrosion.

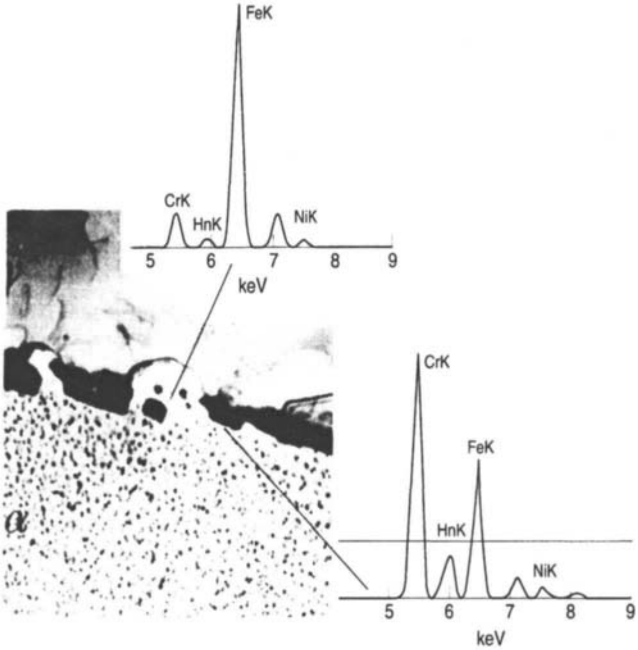
3.4.7 Carbides $M_{23}C_6$ and M_7C_3

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), requiring[35] 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 found[52] 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 reported[35] 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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4 Forming and machining

4.1 Cold forming

Duplex stainless steels have higher mechanical strength and lower ductility compared to the austenitic grades. Table 4.1 shows some cold bending and cupping values determined on annealed and quenched thick sheets.[1] The behaviour appears to be very similar to that of high Mo and N austenitic steels. Consequently, high forming pressures are required, greater than those for the 304 grade, and it must be ensured that this extra power is available. Furthermore, local strains, e.g. at the surface during bending, of up to 60% can be tolerated in the base metal, but the maximum permissible value is much lower in welds, particularly when the ductility of the weld metal has not been optimised by controlling the oxygen and hydrogen contents and by ensuring the absence of intermetallic phases.[2]

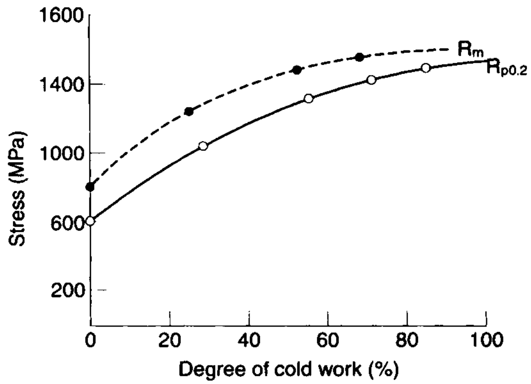
Table 4.1 Cold forming of duplex and austenitic plates (7 mm thick) (after reference 1)

Material type	Calculated strain, max %	Ratio, i.e. $\frac{\text{Disc diameter}}{\text{inside diameter}}$	Results
Austenitic*	71	2.03	Success
	79	2.20	Critical
	86	2.37	Rupture
Duplex^	67	1.95	Sucess
	71	2.03	Success
	75	2.12	Rupture

Grades: * = 317LMN, ^ = S32550

It is common practice to specify an intermediate heat treatment wherever the real strain exceeds 30%. Industrial experience has shown that, by taking a number of precautions similar to those used for high molybdenum and nitrogen austenitic alloys, cold drawing of the duplex grades can be performed without major difficulty.

The increase in tensile strength of duplex steels is often utilised in cold worked products.[3] Figure 4.1 illustrates that proof ($R_{p0.2}$) and



4.1 Ultimate tensile (R_m) and proof stress ($R_{p0.2}$) of a duplex alloy as a function of cold drawing (after reference 1).

ultimate tensile (R_m) strengths can approach 1400 MPa, although a commensurate drop in ductility should be noted.

4.2 Hot forming and superplasticity

Because of their two phase structure, with 50% ferrite, the duplex steels can be readily hot formed above 950 °C. Indeed, they deform so easily at high temperatures that precautions are necessary to avoid creep during heat treatment. One way to overcome this problem, in the case of tubes, is to use induction heating, which prevents loss of shape, due to its rapidity and local nature. Superplastic behaviour (elongation of several 100% before failure) has even been shown[4,5] to be possible in duplex steels deformed above 900 °C. This phenomenon requires low strain rates (a few mm/min), a temperature of at least 0.6 Tm (where Tm is the absolute melting temperature) and a very fine structure (grain size ~1 μm). Such superplastic microduplex structures can be obtained in the following ways:

1. Formation of an almost completely ferritic structure by high temperature annealing above 1200 °C and a low nitrogen content, followed by cooling to room temperature; cold working; then reheating to about 900 °C and isothermally deforming at this temperature. The uniform precipitation of γ_2 phase, and subsequent sigma precipitation, produces the required fine structure.

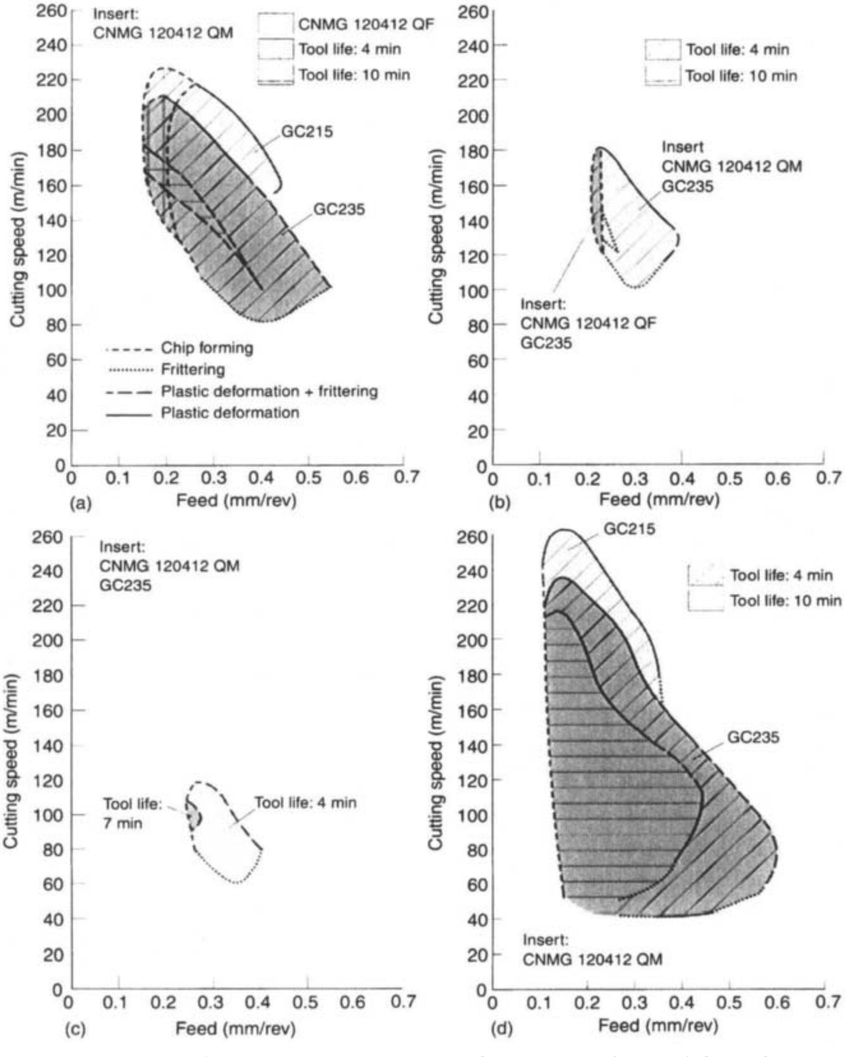
2. In a process similar to item 1 above, except that the mechanical work is begun immediately following the initial heating phase (formation of a single phase ferritic structure), with anisothermal deformation producing the required fine γ_2 precipitation.

Elongations of 600–800% have been obtained in this way for an alloy containing 26%Cr, 7%Ni and 0.2%Ti, with or without molybdenum, and with very low nitrogen levels. Until now, very few industrial applications have taken advantage of this exceptional hot formability. However, in the future, it is possible that this aptitude for 'controlled creep' will be used for forming sheet components, or for the production of complex parts by isothermal forging, as is already the case for certain titanium base alloys.[6]

4.3 Machinability

The term 'machinability' covers many operations including turning, drilling, cutting and threading. The lower alloyed duplex grades, such as S32304, are comparatively easy to machine[7] and behave in a similar manner to austenitic grades, such as 316 or 317 for machining with high speed steel (HSS) tools and with 317LN and 317LMN for machining with cemented carbide tools. In general, the modern duplex grades tend to be more difficult to machine than the older grades, by virtue of the higher austenite and nitrogen contents. With increasing alloy content, especially nitrogen and molybdenum, the machinability decreases rapidly. Thus the superduplex grades are the most difficult to machine, but present the fabricator with the same problems as superaustenitic alloys. The basic influence of alloying content seems to be the same for duplex and austenitic grades, even if the machining profiles seem different. Comparison of duplex and austenitic alloys with similar levels of alloying addition reveals that for some machining operations, such as end milling with HSS tools, the duplex grades are easier to machine. On the other hand, intermittent cutting operations are more difficult for duplex than for austenitic alloys.

The differences in machinability between austenitic and duplex alloys are, in part, a function of the higher strength of duplex alloys and, in particular, the high temperature tensile strength.[8] But other factors, such as the low volume fraction of non-metallic inclusions and the low carbon content, also contribute. At fast cutting speeds, plastic deformation of the tool takes place, in combination with flaking of the insert coating and frittering. Chip hammering can also



4.2 Machinability diagrams with recommended cutting conditions (after reference 9). (a) S32750. The diagram for four minutes has three limiting mechanisms: 1. plastic deformation at high speed; 2. frittering at high feed and low speed; 3. chip breaking at low feed. 10 minute tool life could not be reached. The only possible insert grade was GC235^{TM}. (b) S31803. The diagram has four limiting mechanisms at four minutes tool life: 1. plastic deformation at high speed; 2. plastic deformation and frittering at high feed; 3. frittering at low feed and low speed; 4. chip breaking at low feed. For 10 minute tool life, frittering is the main limiting mechanism around the entire area. The insert grade was GC235^{TM} with QM-geometry. With GF-geometry, the feed could be decreased by only 0.02 mm/rev. (c) S32304. The same as for S31803, but plastic deformation is more important at high speed and low feed. This means that a harder insert could be used, GC215^{TM} for high speed and low feed. With QF-geometry, the feed could be decreased by 0.04 mm/rev. (d) S32900. Principally the same behaviour as S32304 but the area is larger. As for S32304, there is an area where GC215^{TM} gives better tool life than GC235^{TM}, but in contrast to S32304, QF-geometry did not give any better chip-breaking than QM-geometry.

be a problem under these conditions, although improved chip-breaking properties can be obtained using an insert with a smaller tip radius. At low cutting speeds, built-up edges (BUE) causing flaking and frittering seem to be the limiting factor. Overall, the higher the strength of the alloy, especially the high temperature strength, the greater the cutting force required. This leads to an enhanced risk of plastic deformation.

Improved machinability can be achieved by introducing non-metallic inclusions, such as sulphides. Nevertheless, high sulphur grades will be sensitive to weld metal (solidification) cracking and have a lower resistance to pitting corrosion.[9] Thus they should only be selected where welding is not envisaged and corrosion resistance is not paramount. Notwithstanding this, other free-machining duplex grades have additions other than S or Se and can produce comparable corrosion resistance and weldability to similar grades without such additions.[10]

The diagrams presented in Fig. 4.2 provide comparison of the machinability of different duplex grades during turning with cemented carbide tools.[8] The areas given in these diagrams represent comparative tool life limitation mechanism charts. Unfortunately, these diagrams cannot be used to determine the optimum machining conditions for a specific application, as they were developed with some machining parameters fixed. Nevertheless, the behaviour of different grades will hold for similar operations and the diagrams can act as a guide for initial machining set-up. It should be noted that for milling operations, which are generally more difficult to perform than turning, entirely different behaviour is to be expected and other tools should prove more appropriate.

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5 Physical and mechanical properties

5.1 Physical properties

Duplex stainless steels have low thermal expansion coefficients, similar to carbon steels (Table 5.1).[1-3]. This reduces the requirement for expansion joints and renders duplex alloys suitable for thermal cycling conditions.[1] Further, the thermal conductivity is higher than for austenitic grades and this, combined with the higher mechanical strength, allows for thinner walled components in many applications, such as pressure vessels and tubing. Finally, as duplex stainless steels contain about 50% ferrite, they show a degree of magnetism, but at an insufficient level to avoid mechanical clamping during machining.

Table 5.1 Typical physical properties of different stainless steels (after references 1–3)

Grades		Temperature		Young's modulus	Thermal expansion coefficient	Specific heat capacity	Thermal conductivity
		C	F	GPa	$10^{-6}K^{-1}$	$J\,kg^{-1}\,K^{-1}$	$Wm^{-1}\,K^{-1}$
Ferritic	A516*	20	68	205	12.5	450	60
	S43000	20	68	205	10	480	22
	S44700	20	68	205	10	480	21
Austenitic	S30400	20	68	205	16	520	16
	N08904	20	68	205	16	544	15
Duplex	S31803	20	68	200	–	470	14
		100	212	190	13	500	15
		200	392	180	14	530	17
		300	572	170	14.5	560	18
	S32304	20	68	200	13	470	16
Superduplex	S32750	20	68	200	13	470	14
	S32760	20	68	190	12.8	482	12.9
	S32520	20	68	205	13.5	450	17
		100	212	195	14	500	18
		200	392	185	14.5	530	19

* = carbon steel

5.2 Tensile characteristics

Table 5.2 lists minimum tensile properties for duplex steel plate, sheet and strip listed in ASTM A240[4] and demonstrates that duplex alloys have higher R_p and R_m values than most ferritic and austenitic grades. Like all other metals and alloys, the mechanical properties depend on factors such as the grain size, texture and degree of segregation.[5,6] Caution should be taken when extrapolating these data to other product forms, such as thin section products (e.g. cold-rolled sheet), forgings or castings.

Table 5.2 Minimum room temperature tensile properties and maximum hardness of wrought solution annealed stainless steels (after reference 4)

	Grades	$R_{p0.2}$ MPa	R_m MPa	A_5 %	Hardness HB	Hardness HRC
Ferritic	S40900	205	380	20	179	–
	S44700	415	550	20	223	20
Austenitic	S31603	170	485	40	217	–
	S31254	300	650	35	223	–
Duplex	S31200	450	690	25	293	31
	S31260	485	690	20	290	–
	S31803	450	620	25	293	31
	S32304	400	600	25	290	32
	S32550	550	760	15	302	32
	S32750	550	795	15	310	32
	S32760	550	750	25	270	–
	S32900	485	620	15	269	28
	S32950	485	690	15	293	32

The major characteristic of the duplex stainless steels is their extremely high proof strength at room temperature, twice that of comparable austenitic grades. The ultimate tensile strength is also high, while the elongation is greater than 25%. This combination of properties allow for duplex steels to be used as thinner sections than austenitic grades (Table 5.3),[7] which can lead to considerable savings in weight and capital investment. However, the opportunity to take advantage of these potential savings depends on the code adopted. For instance, those codes which are based on both R_m and R_p have significantly lower permissible stresses than those based solely on R_p. This is a consequence of the latter codes being developed for austenitic steels where the differences between R_m and R_p are more marked than for duplex alloys.

Table 5.3 Design stresses at room temperature for different pressure vessel codes (after reference 7)

Code	Allowed stress	Allowed stress at 20°C (68°F) in MPa			
		S31603	S32304	S31803	Superduplex*
ASME VIII	min $\{R_m/4;\ R_{p0.2}/1.6\}$	115	150	155	188
BS 5500	$R_{p0.2}/1.4$	129	285	321	393
CODAP	min $\{R_m/3;\ R_{p0.2}/1.6\}$	128	200	226	343
AD Merkblatt W2	$R_{p0/2}/1.5$	128	266	300	366

* e.g. S32520

The high proof (R_p) and tensile (R_m) strengths are the result of several simultaneous mechanisms:

- Interstitial solid solution hardening (C, N).
- Substitutional solid solution hardening (Cr, Mo, Ni, etc.).
- Strengthening by grain refinement due to the presence of two phases.
- Possible hardening due to the formation of γ_2 phase.
- Strengthening due to ferrite, since, for a similar composition, this phase is harder than the austenitic structure.
- Strain induced by differential contraction of the two phases on cooling from annealing temperatures.

The equations below were derived[8] from regression analysis and agree well with experimental data.[9]

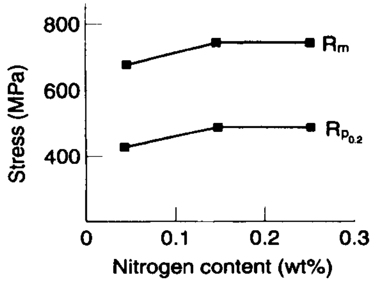
$$R_{p0.2} = 120 + 210\sqrt{N + 0.02} + 2(Mn + Cr) + 14Mo + 10Cu + (6.15 - 0.054\delta)\delta + (7 + 35\,(N + 0.02))\,d^{-1/2} \qquad [5.1]$$

$$R_{p1.0} - R_{p0.2} = 40 \pm 9 \text{ MPa} \qquad [5.2]$$

$$R_m = 470 + 600(N + 0.02) + 14Mo + 1.5\delta + 8d^{-1/2} \text{ MPa} \qquad [5.3]$$

where δ is the ferrite content in % and d is the lamellar spacing in mm.

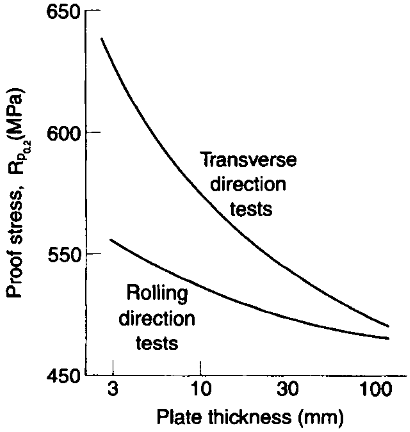
The combination of these different mechanisms explains the remarkable mechanical properties of the duplex stainless steels. However, it is important to emphasise the particular role of nitrogen. In effect, raising the nitrogen content preferentially strengthens the austenite by interstitial solid solution hardening, to the point where it becomes stronger than the ferrite.[10] Indeed, for low nitrogen contents (<0.1%), the austenite has the lower R_p, while at higher levels (>0.2%) the ferrite becomes the weaker phase. This explains why macroscopic hardening is most pronounced for small nitrogen additions, becoming less marked beyond a certain level, i.e. 0.12%



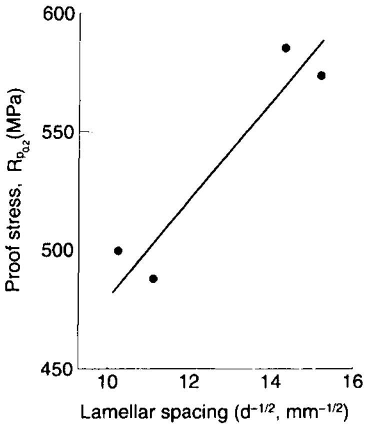
5.1 Effect of nitrogen additions on the 0.2% proof ($R_{p0.2}$) and ultimate tensile (R_m) strength of S31803-type alloys (after reference 10).

for grade S31803 (Fig. 5.1), where only moderate hardening occurs. A similar effect has been found in the superaustenitic grades, as no significant increase in R_p is obtained when the nitrogen content rises from 0.20% to 0.28%. Moreover, this point is important with respect to the stress corrosion resistance and the fatigue strength, since, depending on the compositional balance, either the austenite or the ferrite can be the first to yield.

The tensile properties of duplex grades are influenced by plate thickness, becoming increasingly anisotropic with reduction in thickness,[6] (Fig. 5.2). The anisotropy, and concomitant strengthening, are due to refinement of the structure, with the ferrite/austenite structure being elongated parallel to the principal strain axis (Fig. 5.3). There is no 'fibre-strengthening' effect, since the two

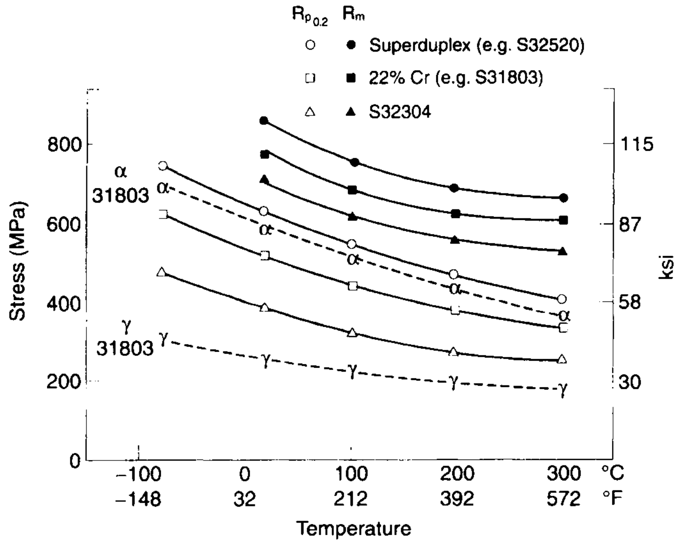


5.2 Representative proof stress in the rolling and transverse directions, as function of plate thickness (after reference 6).

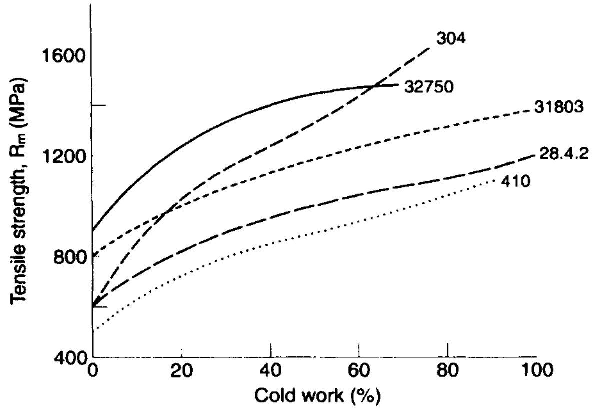


5.3 Petch plot relating proof stress (average of 0° and 90° tests) to lamellar spacing (d) (after reference 6).

phases have similar hardness levels. However, a marked and unusual texture is observed for the two phases, with a major orientation of the type (100)[011] to (211)[011] for the ferrite fibres and (110)[223] for the austenite fibres.

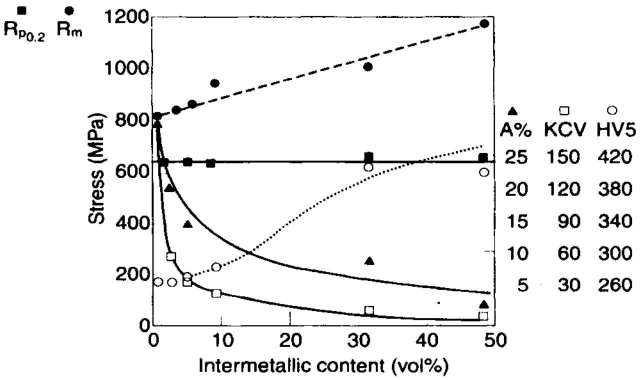


5.4 Temperature dependence of mechanical properties of several stainless steels (after reference 1).

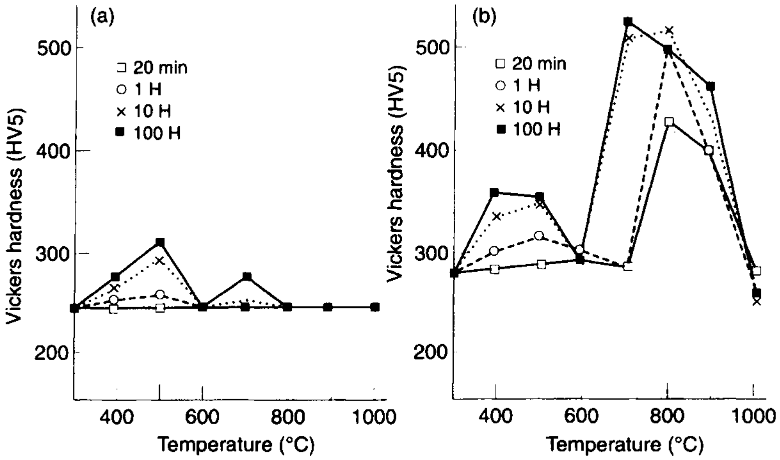


5.5 Tensile strength of different stainless steels a a function of cold work by wire drawing (after references 11 and 12).

The influence of temperature on the tensile properties of various duplex grades is shown in Fig. 5.4, together with austenitic and ferritic alloys with similar composition. The variation in mechanical strength for duplex alloys can be seen to be controlled essentially by the ferrite. Strengthening is accentuated at low temperatures, with some drop over the temperature range 20–300°C. This drop can be significant, as an increase in wall thickness may prove necessary when operating at 100°C, as compared to 20°C.

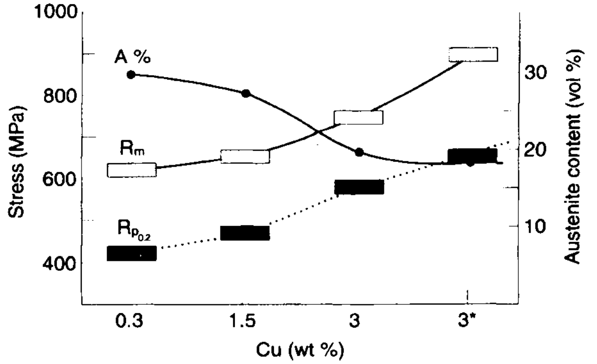


5.6 Mechanical properties of S32550 duplex alloy as a function of sigma phase precipitation by thermal ageing (after references 13 to 15). Note second y-axis: A% = austenite content; KCV = Absorbed energy, J/cm^2; HV5 = Vickers hardness 5 kg load.



5.7 Effect of thermal ageing on Vickers hardness (HV5) of (a) S32304 and (b) S32550 alloys (after references 13 to 15).

Figure 5.5 illustrates the effect of cold work on the tensile properties of a number of duplex alloys.[11,12] The work hardening rate is similar to other types of stainless steel. Only the 304 grade shows a higher work hardening rate, as this alloy undergoes a strain-induced martensite transformation: a phenomenon which may also occur in the low alloy S32304 grade. The capacity to work harden duplex alloys up to tensile strengths (R_m) of 1200 MPa or above is exploited in the manufacture of wirelines, surgical prostheses, etc.



5.8 Effect of copper additions and 400°C ageing on the mechanical properties of alloy S32304 (after reference 1). *400°C for 5 hours.

Figures 5.6 and 5.7 show the influence of structural transformations during heat treatment on the tensile properties and hardness.[13–15] Sigma and chi phases, which form in the range 700–950°C, clearly have a marked effect on ductility. Further, the addition of copper enables considerable hardening to be obtained, without excessive loss of ductility,[1] Figs 5.7 and 5.8, provided that the heat treatment has been optimised. Therefore it is not surprising that the use of copper is particularly appreciated for applications requiring both abrasion and corrosion resistance, e.g. in pumps or FGD units, involving two phase fluid flows.

5.3 Hardness

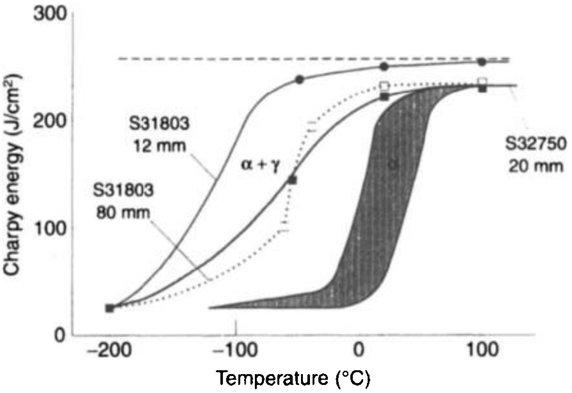
The hardness of duplex parent materials has received attention, especially due to the NACE MR-01-75 requirements for sour service.[16] In this standard, the hardness requirement varies between 28 and 34 Rockwell C (HRC) depending on the alloy type. As shown in Table 5.2, the hardness of solution annealed duplex and superduplex alloys is generally below these limits, unless subject to cold work or precipitation of intermetallic phases, e.g. Fig. 5.6. Thus, as far as meeting the NACE requirements for solution annealed products are concerned, duplex stainless steels should not pose a problem. This situation is different for weldments, as will be discussed in Section 10.2.

5.4 Impact strength

Duplex stainless steels are included in some national and international pressure vessel codes, although the approach and requirements of respective codes differ. For instance, most codes are concerned with the properties of weldments (Section 10.3), while ASTM VIII considers Charpy impact requirements of base material,[17] dependent on wall thickness (Table 5.4).

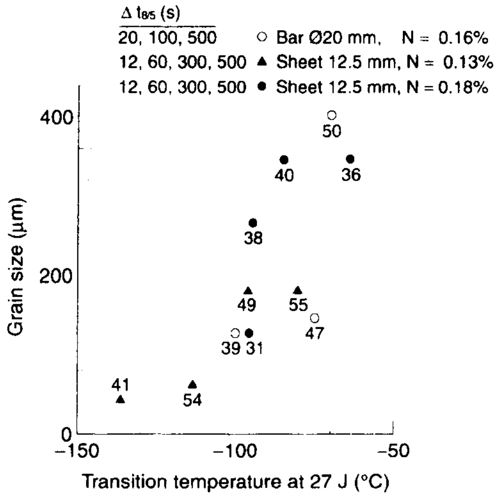
Table 5.4 Toughness requirements in ASME VIII (after reference 17)

Thickness range		Charpy requirement		Comment
mm	inch	J	ft lb	
16–32	$\frac{5}{8}$ to $1\frac{1}{4}$	28	20	Single requirement
32–50	$1\frac{1}{4}$ to 2	28 to 37	20 to 27	Linear increase of J/ft lb with thickness



5.9 Normalised Charpy energy versus temperature measured for several stainless steels (after reference 1).

The low temperature toughness behaviour of duplex stainless steels is between that of ferritic and austenitic steels (Fig. 5.9). High impact energies can be achieved in duplex alloys, e.g. 100 J, at temperatures as low as −100°C, in the solution annealed and unwelded condition. As with all materials, marked scatter in the toughness values should be expected dependent on the alloy composition and thermomechanical history, which in turn influence the microstructure and texture,[18] (Fig. 5.10). In addition, residual

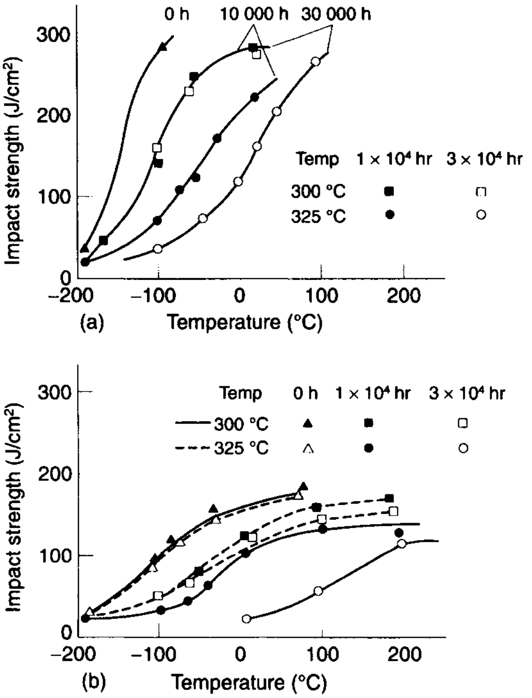


5.10 Relation between grain size (HAZ) and impact transition temperature (27J) for S31803 with austenite content given in the graph (after reference 18).

elements play an important role. Indeed, the impact strength can be improved by reducing the oxygen content, and by controlling the aluminium level[19–23] to avoid the formation of AlN.

There are a number of other factors[24–29] that affect the toughness of wrought duplex alloys. Any precipitation of intermetallic phases, such as sigma, chi etc., leads to a sharp decrease in toughness, e.g. Fig. 5.6. This phenomenon is particularly important in the superduplex grades, in which the transformations are the most rapid. Care should be taken throughout the total thermomechanical process, including the correct solution anneal (see Section 3.3), with attention paid[30] to the thickness of the component and quench rate.

In alloys containing copper, it is possible to undertake low temperature heat treatment to obtain appreciable hardening and wear resistance, while maintaining satisfactory toughness, e.g. a few hours at 400–500°C. And yet, for most grades, prolonged exposure in the 280–350°C temperature range can produce a marked decrease in room temperature toughness, while the ductile to brittle transition

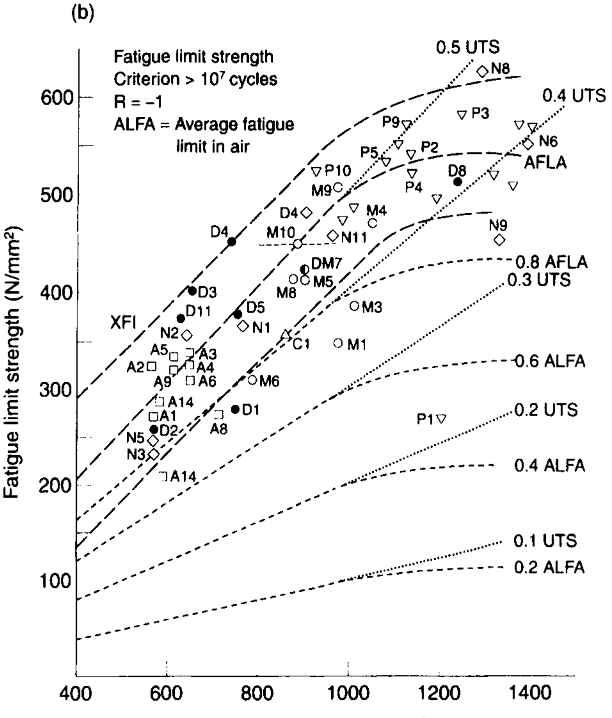


5.11 Impact energy curves for alloys aged at 300°C or 325°C: (a) quench annealed S32750; (b) 45% cold worked S31803. (after reference 1).

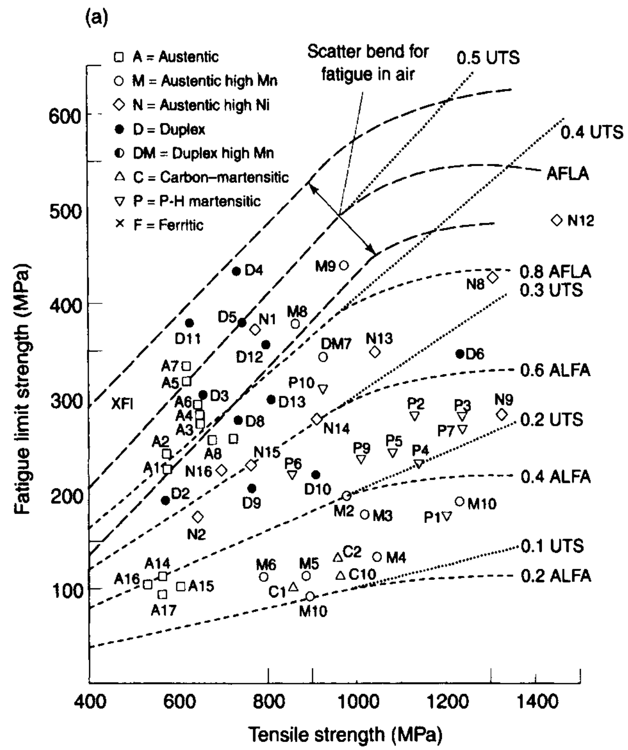
is shifted to higher temperatures[24–29] (Fig. 5.11a). Nevertheless, even in superduplex alloys, respectable impact toughness may remain after such exposures.

Cold work reduces the room temperature impact strength of the duplex steels and increases the ductile to brittle transition temperature. The combination of cold work and ageing in the range 300–400°C leads to an even greater drop in the room temperature impact strength, and in some batches of grade S31803, it has been reported[31] that the ductile to brittle transition can be raised above ambient temperature (Fig. 5.11b).

Given the current understanding, duplex steels should not be used beyond 300°C, unless specific toughness evaluations are made. Furthermore, particular attention must be paid to welds, where the initial impact strength should be sufficiently high to accommodate the drop which occurs after service ageing. Indeed, a limit of 250°C has been propounded for welded structures.[32,33]



5.12 (a) Un-notched rotating bend fatigue strength limits versus tensile strength (UTS) for various types of stainless steel and higher nickel alloys: in air (after reference 34).

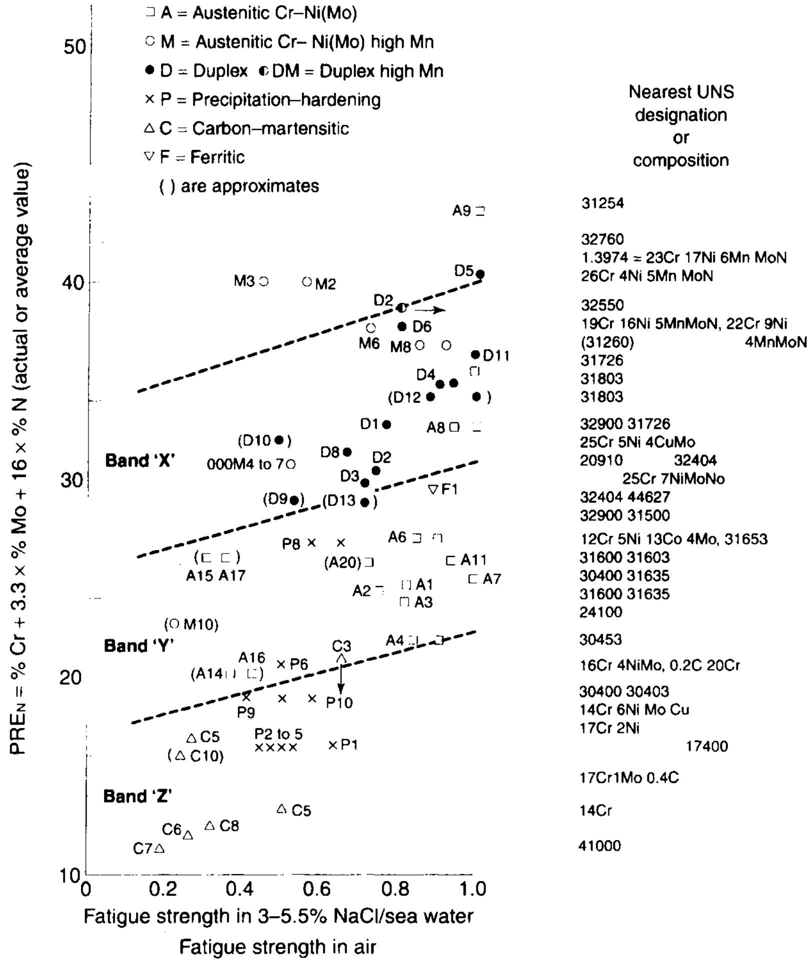


5.12 (b) Un-notched rotating bend fatigue strength limits versus tensile strength (UTS) for various types of stainless steel and higher nickel alloys: in 3–3.5%NaCl or sea water-type solutions (after reference 34).

5.5 Fatigue properties

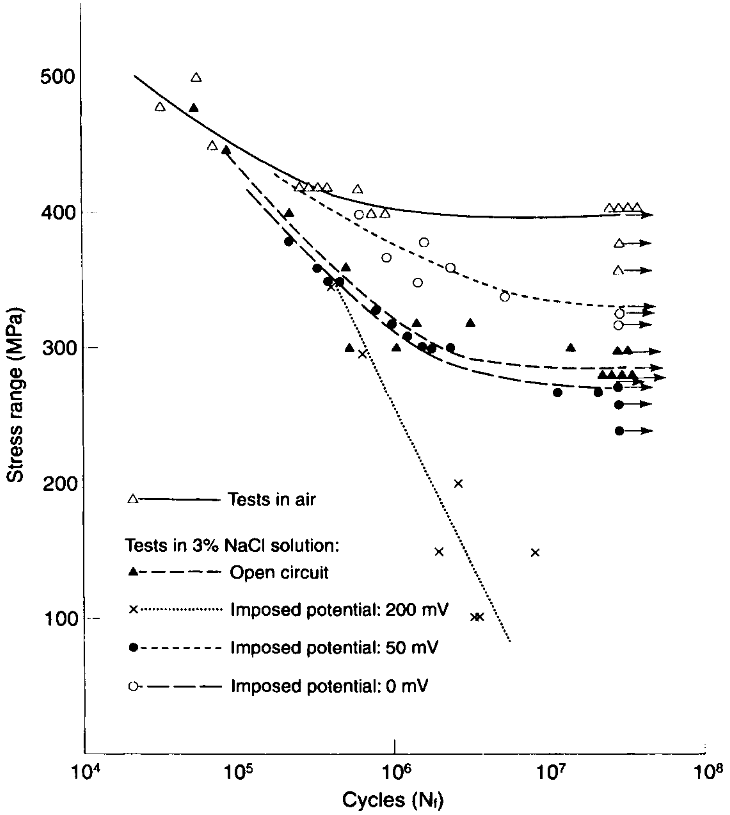
The results of rotational bending tests in air on smooth specimens indicate[34–37] a fatigue limit for all types of stainless steel, at about 50% R_m (Fig. 5.12a). However, for materials with R_m greater than 1000 MPa, the value is generally found to be less than 50%. Similar results obtained in sea water-type environments appear to show marked scatter[34–40] (Fig. 5.12b), with some duplex and austenitic steels giving corrosion fatigue limits (CFLs) close to the average fatigue limit in air (AFLA), whereas others hardly attain values equivalent to 0.4 × AFLA (or 0.2 × R_m).

The drop in fatigue strength in a corrosive environment is clearly linked to the intrinsic resistance of the materials to the corrosion mechanisms encountered in the test medium employed. Thus, for



5.13 PRE$_N$ versus the ratio of un-notched fatigue strength in sea water-type solutions to that in air, for various stainless steels (ambient to 40°C). Values in parentheses have been estimated (after reference 34).

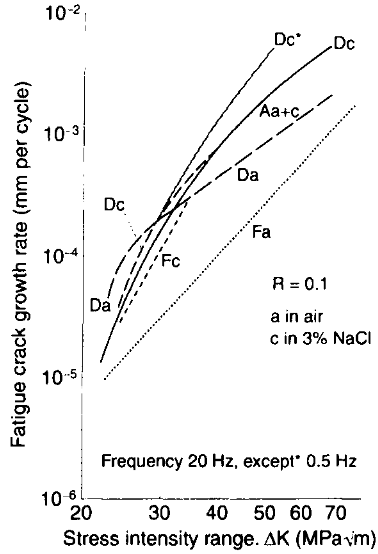
sea water, the ratio between the fatigue limit in the corrosive medium and the fatigue limit in air can be correlated with the pitting resistance. In part, this explains the scatter in Fig. 5.12b. In Fig. 5.13, the ratio of fatigue limits in sea water to air are plotted against PRE$_N$.[34–35,38–40]. Alloys in Band X indicate that a PRE$_N$ greater than 40 is necessary to ensure minimum risk of fatigue strength reduction in sea water (ratio = 1), while a PRE$_N$ of around 32 is desirable to minimise the reduction in fatigue strength. The value of 1 represents



5.14 Corrosion–Fatigue test results on alloy S32404 in 3%NaCl under applied potentials (AP) (after reference 41).

the limiting conditions for resistance to pitting corrosion in sea water. It is quite normal that the fatigue limit in the corrosive environment should be reduced when the passive film is damaged by pitting

The effect of an imposed potential on the fatigue–corrosion properties is demonstrated[41] in Fig. 5.14. The fatigue life is reduced by increasing anodic polarisation, particularly at low stress ranges and high numbers of cycles. The fatigue crack growth rates of duplex and other stainless steels are shown[41] in Fig. 5.15. For the alloys tested, the growth rates of duplex and austenitic alloys are similar and somewhat higher than for ferritic stainless steels. There is also an effect of frequency for duplex properties at $\Delta k > 30$ MPa$\sqrt{m}$. This may be due to the interactive effects of corrosion, or more specifically the conditions at the crack tip (composition of the



5.15 Fatigue crack growth rates in air and 3%NaCl for stainless steels: austenitic grades S31600 and S31635 (A), duplex S32404 (D) and ferritic S44627 (F) (after reference 41).

solution and oxidation/reduction potential), which can be markedly different from those at the free surfaces. This can affect transport of ionic species and the possibility of repassivation.

In conclusion, the fatigue and fatigue–corrosion behaviour of the duplex stainless steel parent materials is at least equivalent to that of the austenitic grades in the majority of applications. Nevertheless, care must be taken to choose an alloy with sufficient corrosion resistance in the intended environment, particularly in cases where the high ferrite content of the duplex steels could lead to accelerated crack propagation (e.g. conditions causing hydrogen pick-up). However, such conditions are rare, and in the majority of cases, duplex stainless steels have excellent fatigue and corrosion-fatigue properties. For further information about the performance of welded joints and service failures, the reader should consult Sections 10.4 and 13.8.

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6 Corrosion

6.1 Introduction

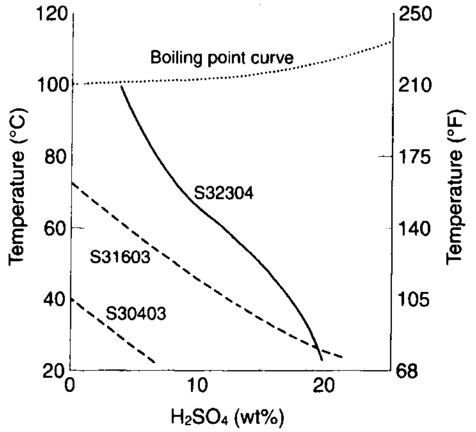
The corrosion properties of the duplex steels, and of stainless steels in general, are defined mainly by the ability to passivate and to remain in the passive state in the service environment. However, there are fundamental differences in alloy design of duplex and austenitic grades, which leads to significant variations in their corrosion behaviour, especially in environments where general corrosion is taking place. On the other hand, austenitic and duplex alloys with equivalent PRE_N (Eq. 1.1) often exhibit similar critical pitting and crevice corrosion temperatures in chloride media.

The most important alloying elements with respect to the localised corrosion properties of duplex stainless steels are Cr, Mo and N, whereas Ni mainly acts to stabilise the austenite phase. However, these elements are not evenly distributed between the two phases, with Cr and Mo enriched in ferrite and Ni and N in the austenite. In particular, nitrogen is almost entirely present in the austenite. In early grades, the austenite phase tended to be preferentially attacked, but in modern duplex steels, with higher overall nitrogen contents, it has been possible to balance the corrosion resistance of the two phases. In this respect the information presented in this chapter relates to the performance of modern duplex grades.

6.2 General corrosion

6.2.1 Sulphuric acid

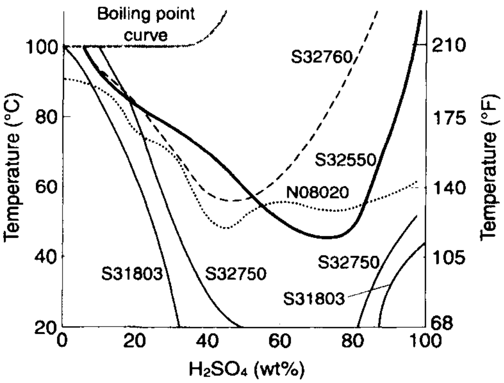
All duplex grades show lower corrosion rates than 304L and 316L in dilute sulphuric acid[1] (Fig. 6.1). Higher alloy grades are more resistant than alloy S32304, with low corrosion rates measured in both dilute (below 40%) and concentrated (greater than 85%) solutions[2–4] (Fig. 6.2) with some variation in behaviour apparent depending on the degree of aeration[5] (Fig. 6.3). These figures show that duplex grades (e.g. S32205/S31803, S32550, S32750 and



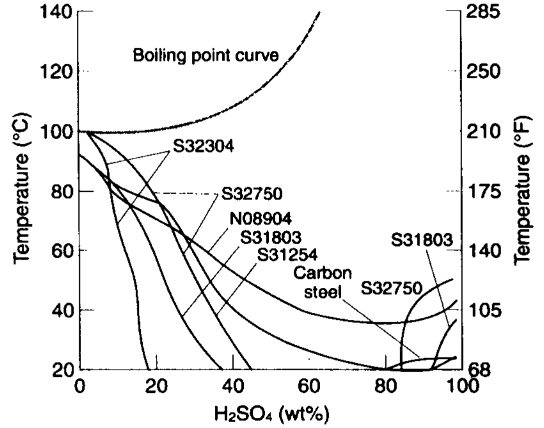
6.1 Sulphuric acid: 0.1 mm/yr isocorrosion curves: stagnant: steels S30403, S31603, S32304 (after reference 1).

S32760) compare well with high alloy austenitic and some Ni-base grades (N08020, N08028, N08904, S31254 in Appendix A) and carbon steel.

The beneficial effect of copper, as an active alloying element in reducing acids, is illustrated by the improved performance of alloys S32550 and S32760 with between 0.5% and 2%Cu compared to alloy S32750 with no copper (Fig. 6.2). In this respect, the duplex

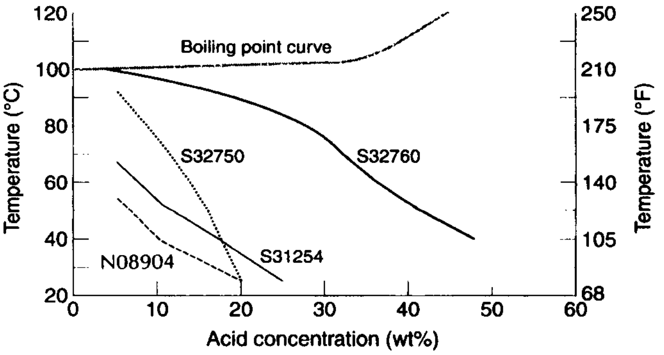


6.2 Sulphuric acid: 0.1 mm/yr isocorrosion curves: stagnant: steels S31803, S32550, S32750, S32760, N08020 (after references 2–4).

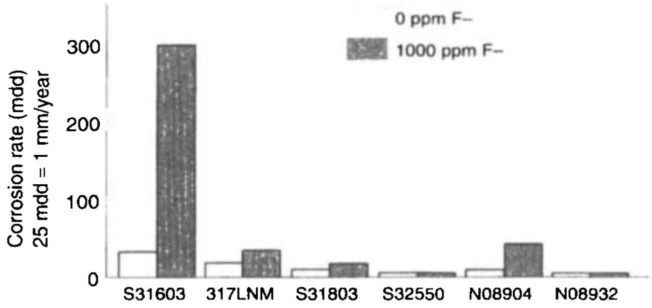


6.3 Sulphuric acid: 0.1 mm/yr isocorrosion curves: aerated: S32304, S31803, S32750, S31254, N08940 and carbon steel (after reference 5).

alloy S32550 with up to 2.5%Cu can be used between 40% and 85% H_2SO_4, with temperature limitations, say 45 °C. The superduplex grade S32760 can be used at even higher concentrations and temperatures, out-performing Ni-base alloys like N08020 (Alloy 20Cb3), and offering similar resistance as special silicon austenitic stainless steels. Further, good resistance has been obtained[6] for cast S32550 at a flow rate of 10m/s. At this flow rate it was found that the passivity was stabilised.



6.4 Sulphuric acid plus 2000 ppm chloride: 0.1 mm/yr isocorrosion curves (after references 4 and 5).

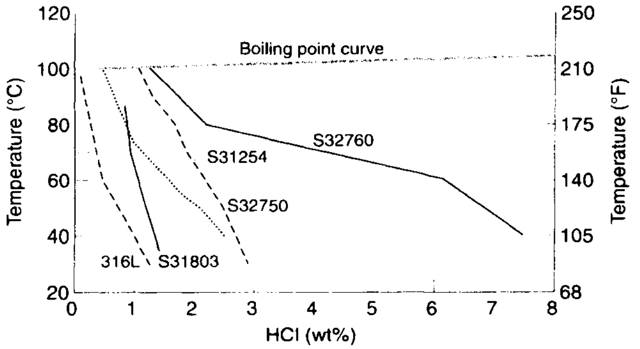


6.5 Sulphuric acid plus fluorides: simulated FGD scrubber environment (after reference 8).

In practice sulphuric acid is often contaminated, e.g. with chlorides (Fig. 6.4), which reduces the corrosion performance significantly.[4,7] Further, in Fig. 6.5 results from simulated flue gas desulphurisation (FGD) scrubber environments are presented, which are essentially sulphuric acid contaminated with halides.[8]

6.2.2 Hydrochloric acid

In strongly reducing acids, like HCl, most stainless steels have limited resistance, but can still be applied at low concentrations. Grade S32205/S31803 offers similar resistance to 316L at low temperatures, although the resistance is better at higher temperatures (Fig. 6.6). The superduplex grades show improved resistance and

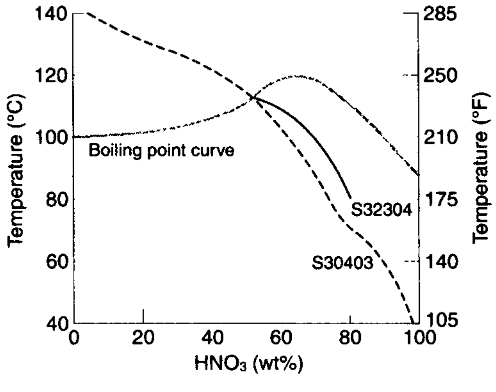


6.6 Hydrochloric acid: stagnant: 0.1 mm/yr isocorrosion curves (after references 4 and 5).

are similar to austenitic alloys N08028 and S31254.[3,4] The best performance in HCl is shown for grade S32760 with Cu and W additions, which has been shown to be acceptable in a number of applications previously thought unsuitable for stainless steels.[4]

6.2.3 Nitric acid

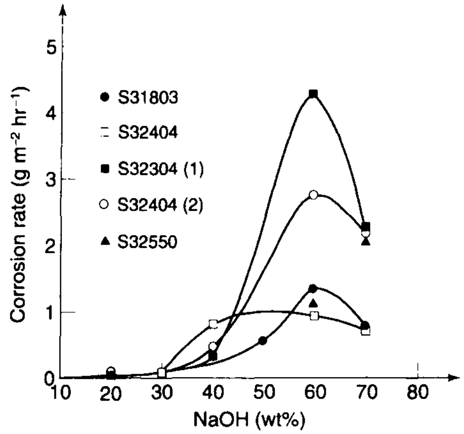
Under highly oxidising conditions, like concentrated nitric acid, the duplex steels exhibit dramatically different behaviour. In this environment, molybdenum has a strong negative effect, while chromium is beneficial. For this reason, it has been recommended that a limit of 2%Mo content should be considered,[3] like S32950 (e.g. 7Mo Plus) or the low alloyed steel S32304. The corrosion behaviour of S32304 in nitric acid is shown in Fig. 6.7.[9,10] Further, development work indicates that a 29%Cr:6%Ni:1.5%Mo:0.4%N alloy[11] has very low corrosion rates (~ 0.05 mm/yr) in the Huey test (5 × 48hr, boiling 65% HNO_3).



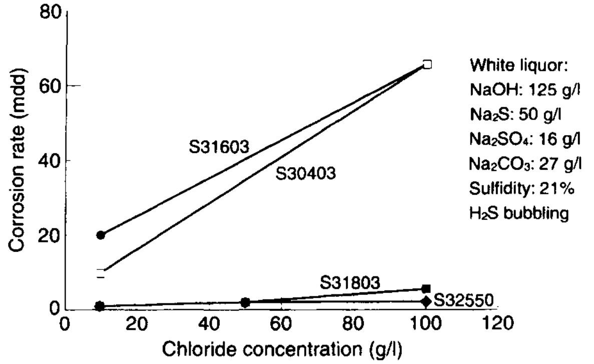
6.7 Nitric acid: 0.1 mm/yr isocorrosion curves (after reference 10).

6.2.4 Sodium hydroxide

Different duplex grades can be applied successfully in caustic environments at low concentrations,[12] e.g. <30% in Fig. 6.8. Several field studies in the pulp and paper industry have shown that duplex steels have much lower corrosion rates than standard austenitic grades in white liquors of Kraft digesters. The beneficial use of



6.8 Sodium hydroxide: boiling (after reference 12).

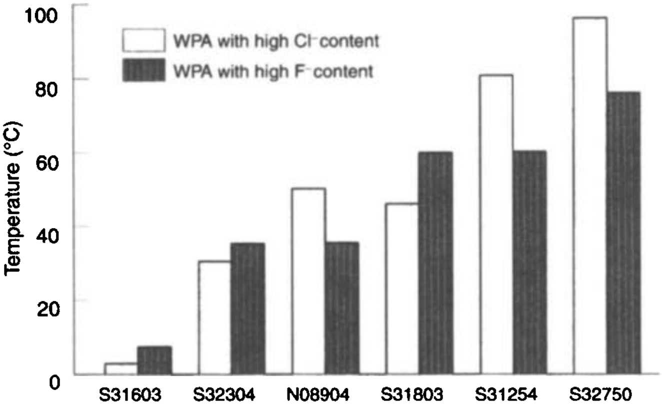


6.9 White liquors plus chlorides (after reference 13).

duplex is more marked in synthetic white liquors,[13] where chlorides are present, Fig. 6.9.

6.2.5 Phosphoric acid

In itself, concentrated phosphoric acid is not very corrosive. Contaminants in wet process phosphoric acid, such as chlorides and fluorides, can lead to high corrosion rates. Duplex stainless steels,



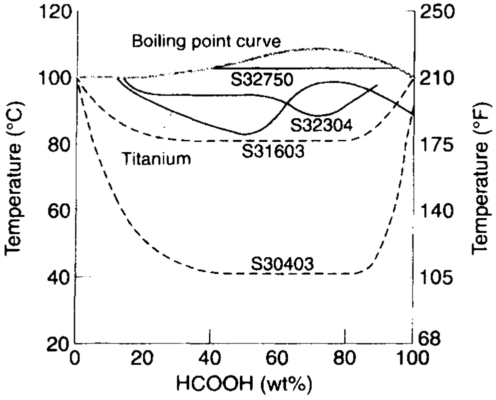
6.10 Wet phosphoric acid (WPA): minimum temperature for a corrosion rate of 0.127 mm/y (5 mpy) (after reference 7).

like S31803 and S32550, have been utilised in such media,[14] e.g. as pumps and valves, and in chemical tankers. In such media, duplex steels offer improved resistance over conventional austenitic grades[15–18] (Fig. 6.10).

6.2.6 Organic acids

Duplex steels and, in particular, superduplex grades have shown remarkably good passivation properties in pure and contaminated acids, in laboratory tests as well as in industrial in-plant exposures.[19,20] Modern duplex steels are resistant in acetic acid whereas the austenitic grade 304L corrodes at high temperatures, and may also crack at high concentrations. In formic acid, the most aggressive of the organic acids, most stainless steels and titanium corrode heavily at intermediate concentrations and high temperatures, but the superduplex steel S32750 is resistant almost to the boiling point[7] (Fig. 6.11).

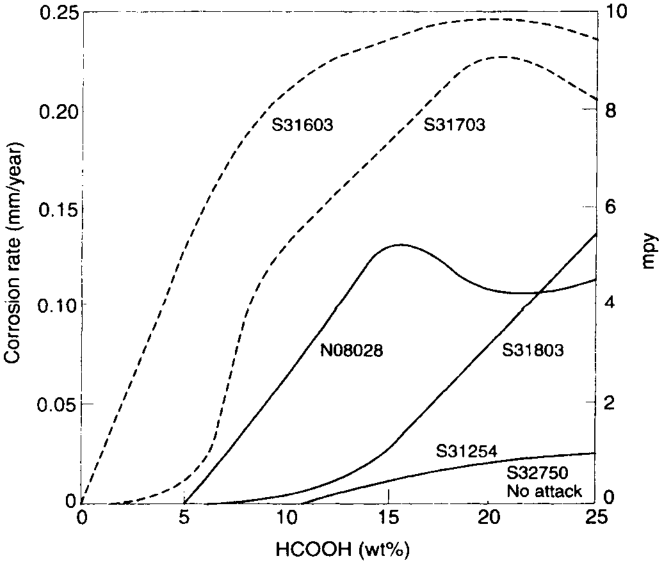
The corrosion rates of several stainless steels and nickel base alloys in mixtures of boiling acetic acid and formic acid are presented[19] in Fig. 6.12. The duplex grade S32205/S31803 has excellent properties, while only the superduplex grades, e.g. S32750 (and nickel base alloy N10276 in Appendix A), are completely resistant. In Fig. 6.13 corrosion rates for N06625, N06455 and the super duplex S32750 are shown for a mixture of 50% acetic acid



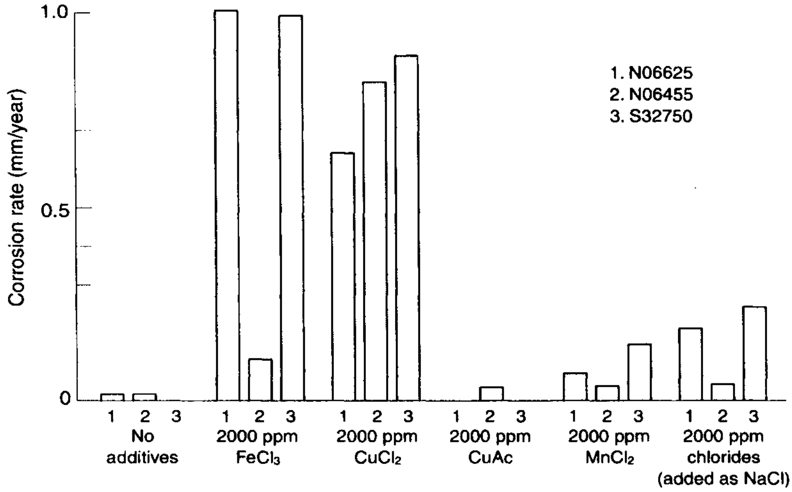
6.11 Formic acid: 0.1 mm/yr isocorrosion curves (after reference 7).

and 25% formic acid, with and without additions of various salts, common as catalysts in acetic acid processing.[19]

In Table 6.1 corrosion rates from exposures in a terepthalic acid plant are shown,[19] which comprises hot acetic acid with traces of other ions. The duplex alloys have much lower corrosion rates



6.12 Acetic (50%) plus formic acids (and water): boiling (after reference 19).



6.13 Acetic (50%) plus formic (25%) acids plus other salts (after reference 19).

compared to the austenitic grade S31703, that is often used in these applications.

Table 6.1 Corrosion rates in a terepthalic plant (after reference 13)

Alloy	75% acetic acid at 175°C with traces of Br-, Cu, Mn (mm/yr)	96% acetic acid at 150°C with traces of Br-, Cu, Mn (mm/yr)
S31703	0.44	0.67
welded	0.47	0.68
S31803	0.012	0.06
welded	0.027	0.072
S32750	0.004	0.011
welded	0.006	0.016

6.3 Localised corrosion

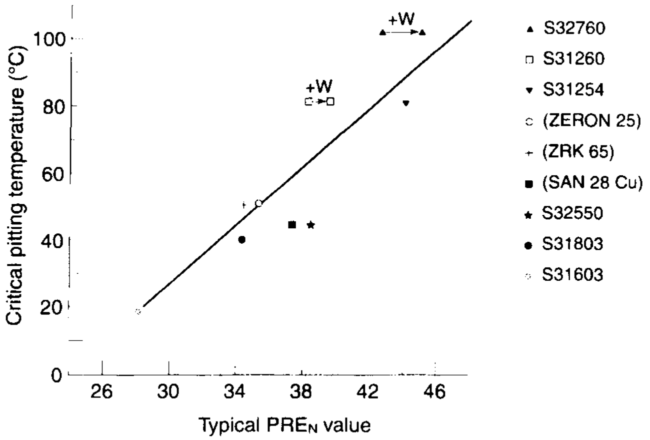
6.3.1 Pitting attack

All alloying elements, to varying degrees, affect the pitting resistance of duplex stainless steels in chloride environments[3] (Table 6.2), but the main elements are Cr, Mo and N. Several attempts have been

Table 6.2 Influence of different alloying additions and microstructure on the pitting and crevice corrosion resistance of duplex stainless steels (after reference 3)

Alloying	Effect	Reason	Practical limitation
C	Negative	Causes precipitation of chromium carbides with accompanying chromium depleted zones	About 0.03 % maximum
Si	Positive	Si stabilises the passive film	About 2 % maximum, due to its effect on structural stability and on nitrogen solubility
Mn	Negative	Mn-rich sulphides act as initiation sites for pitting. Mn may also destabilise the passive film.	About 2 %. Higher levels might also increase the risk of intermetallic precipitation
S	Negative	Sulphides, if not Cr- Ti- or Ce-rich, tend to initiate pitting attack	About 0.003 %, if maximum pitting resistance required. For reasonable machinability, up to 0.02 % allowed.
Cr	Positive	Cr stabilises the passive film	Between 25 and 28 % maximum depending on the Mo-content. Higher Cr-content increases the risk of intermetallic precipitation.
Ni	Negative	Increased Ni, other elements constant, dilutes the γ-phase with regard to N, which in turn decreases the PRE of the γ–phase. If the alloy is very sensitive to precipitation of chromium nitrides, Ni can have a positive effect.	Ni should primarily be used to give the alloy the desired austenite content.
Mo	Positive	Mo stabilises the passive film, either directly or through enrichment beneath the film.	About 4–5 % maximum depending on the Cr-content. Mo enhances the risk of intermetallic precipitation.
N	Positive	N increases the PRE-number of the γ-phase dramatically, not only by increasing the N-content of that phase, but also by increasing the Cr and Mo contents through their partitioning coefficients.	About 0.15 % in Mo-free grades. About 0.3 % in superduplex grades and some 0.4 % in 25 %Cr, high Mo, high Mn alloys.

Cu	Disputed	Marginal positive or negative effects	About 2.5% maximum. Higher levels reduces hot workability and undesirable hardenability
W	Positive	Probably the same as for Mo	Increases the tendency for intermetallic precipitation.
Ferrite	Positive	Increased ferrite content increases the N, Cr and Mo contents of the γ-phase	Too high ferrite can enhance chromium carbide/nitride precipitation in a coarse microstructure
Intermetallic phases	Negative	Precipitates with accompanying depletion of alloying elements (Cr, Mo)	If steel manufacturers' recommendations are followed, intermetallic precipitation should not occur during heat treatment or welding.
Chromium carbides and nitrides	Negative in oxidising and corrosive chloride-containing media	Precipitation of carbides/nitrides causes Cr-depleted zones which are selectively attacked in certain corrosive media	In older generations of duplex alloys, nitrides were frequently present in welded joints and in base metal with a coarse microstructure. This has rarely been the reason for a corrosion failure



6.14 CPT data for wrought stainless steels in sea water using potentiostatic polarisation techniques and plotted against PRE_N. (reference 21).

made to establish a mathematical formula describing the relationship between the amount of these elements and the corrosion properties. The most commonly used expressions are the so called pitting resistance equivalents (PRE):

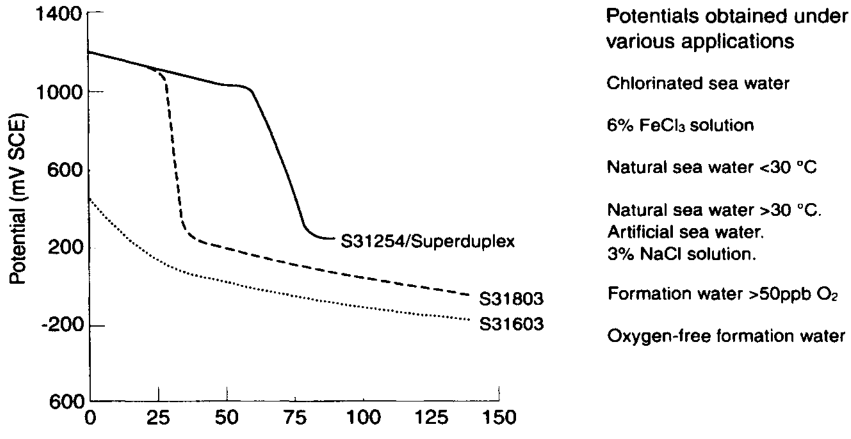
$$PRE_N = \%Cr + 3.3 \times \%Mo + 16 \times \%N \qquad [1.1]$$

or

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

The PRE expressions may be used[21] as an approximate ranking between different wrought stainless steels, Fig. 6.14 but it is necessary to consider the pitting resistance of ferrite and austenite individually due to the partitioning of the alloying elements between the phases (see Section 3.2), especially if the heat treatment is not optimised. An alloy with a high nominal PRE may produce a lower CPT than expected if one of the phases is depleted in Cr, Mo (W or N) compared to the other phase, in other words, it has a lower localised PRE_N-value. In particular, the effect of partitioning on corrosion resistance should be considered in relation to weldments, which will be addressed in detail in Section 10.5.

Initiation of pitting comprises local breakdown of the surface passive layer and, for duplex steels as well as for austenitic steels, the condition of the surface, e.g. grinding, pickling, cold work, dirt etc., has a more marked influence in chloride environments than in environments where general corrosion takes place. The pitting



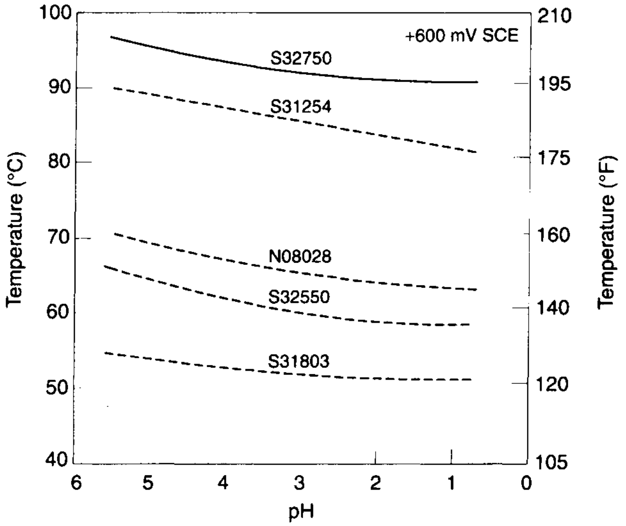
6.15 Critical pitting potentials determined for different stainless steels (and welds) in 3%NaCl and 2.5bar CO_2. Also included are potentials of various industrial and laboratory media (after references 22 and 23).

resistance is further influenced by factors such as grain size, inclusion distribution and possible precipitation of intermetallic phases. For these reasons, some degree of conservatism should be accommodated for between laboratory results and site fabrication where controlled conditions cannot be adhered to.

From Fig. 6.15 it can be inferred that the application range of a particular alloy (and welding conditions) may vary considerably depending on the conditions.[22,23] In oxygen-free water with chlorides (low potential), S32205/S31803 can be used at very high temperatures, while in chlorinated sea water (around +600 mV SCE) only superduplex or superaustenitic steels can be applied. There is only a small effect of pH on pitting resistance with lower pH conditions being more aggressive[24] (Fig. 6.16).

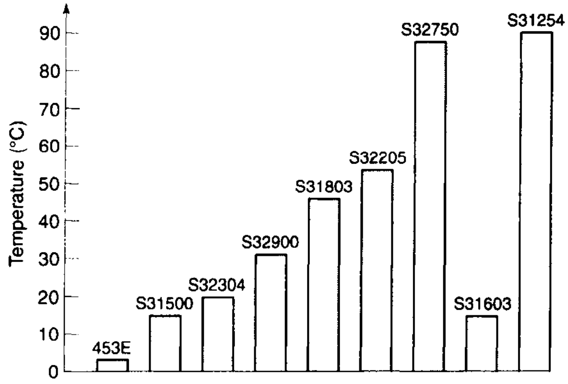
The ranking order of different duplex and austenitic grades can be obtained from standard laboratory data,[25] e.g. Fig. 6.17. As expected, improved resistance is obtained with the higher alloy grades and the modern grades with nitrogen additions perform better than the nitrogen lean grades, i.e. S31500, S32304 and S32900. In addition, grade S32304 has similar resistance to the austenitic steel S31603, while superduplex alloys, e.g. S32750, are comparable to the 6%Mo austenitic grades, e.g. S31254.

Further laboratory data generated in NaCl solutions at +300 and +600 mV SCE are provided[3,10] in Figs. 6.18 and 6.19. The same ranking order of alloys emerges, in both mild (Fig. 6.18) and aggressive (Fig. 6.19) conditions. In mild conditions, alloy

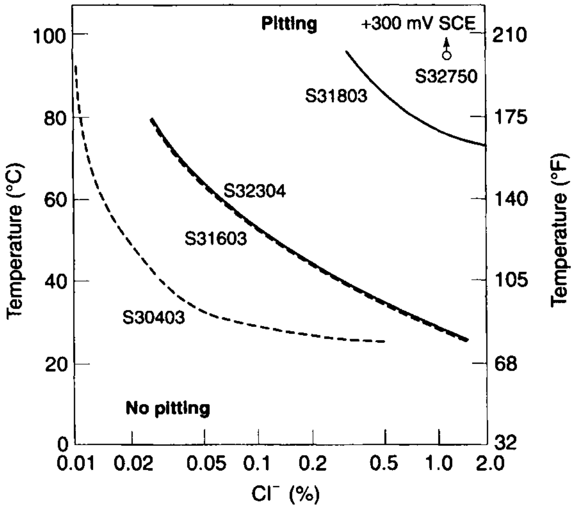


6.16 CPTs in 3%NaCl with varying pH at +600 mV SCE with 600-grit finish (after reference 23).

S32205/S31803 is resistant to pitting up to about 80°C in 1.5%NaCl (0.90%Cl^-) solution, while superduplex grades are immune up to the boiling point. On the other hand, in more aggressive media, i.e. higher potential and chloride levels, lower critical pitting temperatures (CPTs) are obtained.



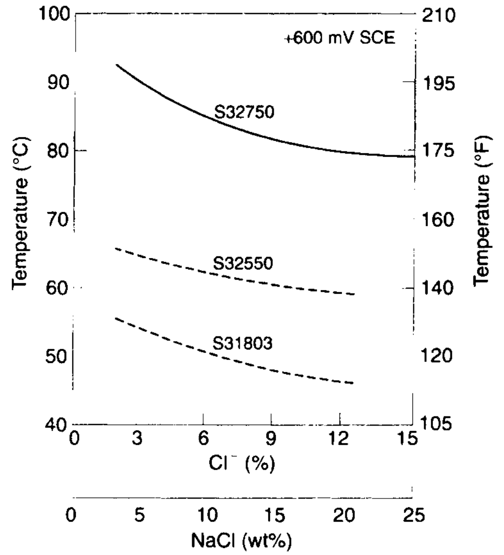
6.17 CPTs determined by a potentiodynamic technique for duplex unwelded sheets in 1M NaCl (after reference 25).



6.18 CPTs in various NaCl concentrations at +300 mV SCE, neutral pH. (after reference 3).

One further laboratory test medium which is of interest when studying the pitting resistance of stainless steels is ferric chloride solution, due to the widespread employment of ASTM G48 Practice A.[26] This test solution allows for a quick assessment of a materials performance in chloride media, as it is extremely aggressive and can give results in 24 or 72 hours. It is often used as a quality control test, especially for the WPQ of welded joints. For this purpose, a specific recommended practice for duplex weldments has been developed.[27] It has been reported that ferric chloride gives a similar potential to chlorinated sea water (Fig. 6.15), but pH is low[28] (around pH1). CPT and CCT data generated in ferric chloride solution are shown[24] for several unwelded grades in Fig. 6.20.

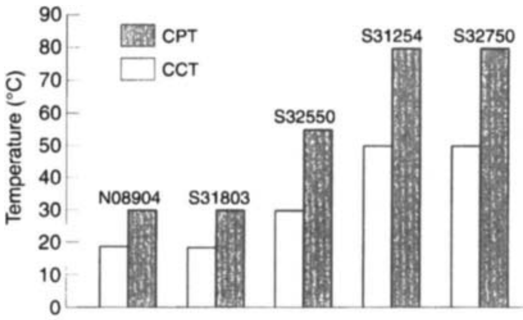
A CPT test based on a potentiostatic electrochemical method in 3%NaCl has been developed by ASTM.[29] This specification allows for even quicker CPT evaluation of material and the test medium is more realistic to service. Nevertheless, there are still concerns that short-term laboratory tests do not accurately predict long-term service behaviour.[30] Two such concerns lie with the incubation time for pit initiation, which may be outside the time frame for short-term tests, and the sensitivity of these tests to detect initiated sites. Further, as weldments are invariably the weak link in a structure, it is the corrosion properties of these regions which should be evaluated. This subject will be covered in Section 10.5.



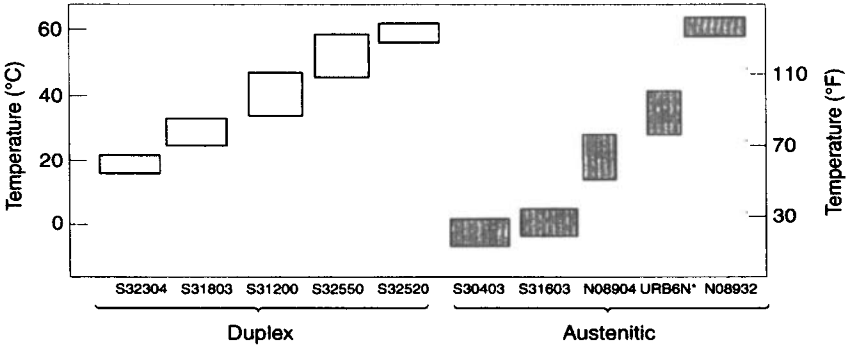
6.19 CPTs in various NaCl concentrations at +600 mV SCE, neutral pH. (after reference 10).

6.3.2 Crevice corrosion

Crevices can be formed at flanged joints, beneath weld spatter etc. and, as a rule, the tighter the gap the more likely that crevice corrosion will occur for a given bulk environment. For instance, soft non-metallic materials, which can mould to the metal surface are considered severe crevice formers. The crevice corrosion resistance



6.20 CPTs and CCTs in 6% ferric chloride solution, 24 hours (after reference 24).



6.21 Typical CCTs determined for several stainless steels in 6% ferric chloride, 72 hours (after reference 31). *Proprietary grade of Creusot–Loire Industrie.

of stainless steels can be related to the pitting corrosion resistance, as the critical crevice temperatures (CCTs) are roughly proportional to the CPTs, although considerably lower[24] (Fig. 6.20).

Figure 6.21 compares CCTs obtained in 6% $FeCl_3$ solution for various duplex and austenitic grades.[31] It should be stressed that in crevice corrosion testing the tendency for corrosion is strongly related to the experimental parameters, such as: surface condition of the steel (roughness and method of grinding); material in crevice formers (metal, glass, ceramic, plastic etc.) and crevice width (applied pressure).[32–33] In other words, the conditions of crevice corrosion testing are very difficult to control and reproduce, even when following standards such as ASTM G48 Practice B[26] and MTI2.[34]

Practical experience in chlorinated sea water has shown that grade S32205/S31803 and S32550 can suffer from crevice attack in 1 ppm chlorine at 16 °C[35] and 0.8 ppm at 10 °C,[36] while superduplex grades are resistant at 45 °C in sea water with 0.8 ppm chlorine.[37] Further, it has been stated[38] that superduplex grade S32760 has a 50% chance of suffering from crevice corrosion during upset conditions, say 24 hours at 70 °C, while repassivation will occur when the temperature is dropped to 30–40 °C. In this respect, superduplex alloys perform better than 6%Mo superaustenitic alloys. This is believed[38] to be a function of the improved resistance of duplex alloys to hydrochloric acid compared to the 6%Mo alloys (Fig. 6.6) and the model for crevice corrosion described by Sutton and Oldfield.[39,40] In this model, oxygen is consumed in the crevice and further metal dissolution leads to the formation of metal chlorides. The chlorides are hydrolysed to form hydrochloric acid, the pH falls and attack perpetuates.

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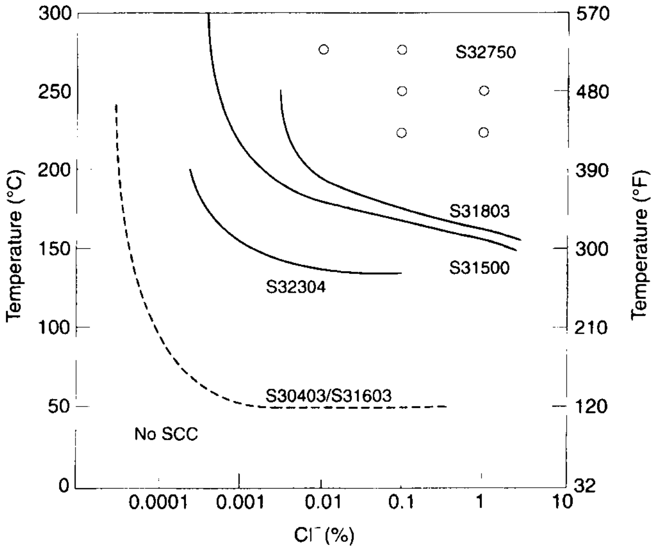
7 Stress corrosion cracking

7.1 Introduction

One of the most common failure mechanisms in stainless steels is chloride induced stress corrosion cracking (SCC). In particular, the conventional austenitic grades are susceptible to this failure mode. Duplex stainless steels offer much greater resistance to this form of cracking (Fig. 7.1) with all grades being superior to 316L and the superduplex grades apparently immune[1] in 3%NaCl up to 250°C. Nevertheless, duplex alloys do suffer from SCC given concentrated chloride solutions. And, at least for austenitic alloys, this will also



7.1 Compilation of practical experience and laboratory test data in neutral aerated (~8 ppm) aqueous NaCl environments. Testing time 1000 hours Load ≥ R_p at test temperature (reference 1).

be dependent on the cation present, i.e. Mg>Ca>Na in order of increasing aggressivity.[2] In addition, high applied stress to tensile strength ratios, with elevated temperatures and high oxygen contents enhance susceptibility, combined with the presence of a crevice/deposit.[3,4]

Another environmental cracking mechanism of concern for duplex alloys is sulphide induced stress corrosion cracking, defined here as SSCC. Again there are a number of factors which define the susceptibility of a duplex steel with a given stress level to SSCC, namely temperature, sulphide concentration, pH and chloride content. These factors will be addressed later and will be the subject of Section 7.3.

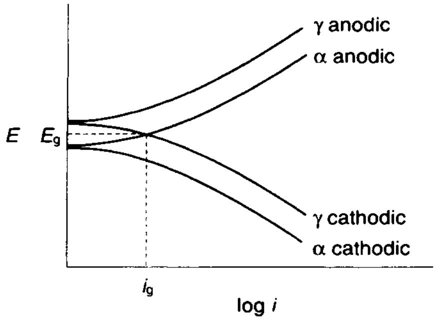
The final subject of this chapter (see Section 7.4) covers the effect of cathodic protection and the risk of hydrogen embrittlement. Although this is not strictly a form of SCC, it is a mechanism that involves hydrogen evolution (at the cathode) and high stresses.

7.2 Chloride stress corrosion cracking

7.2.1 Mechanism for SCC

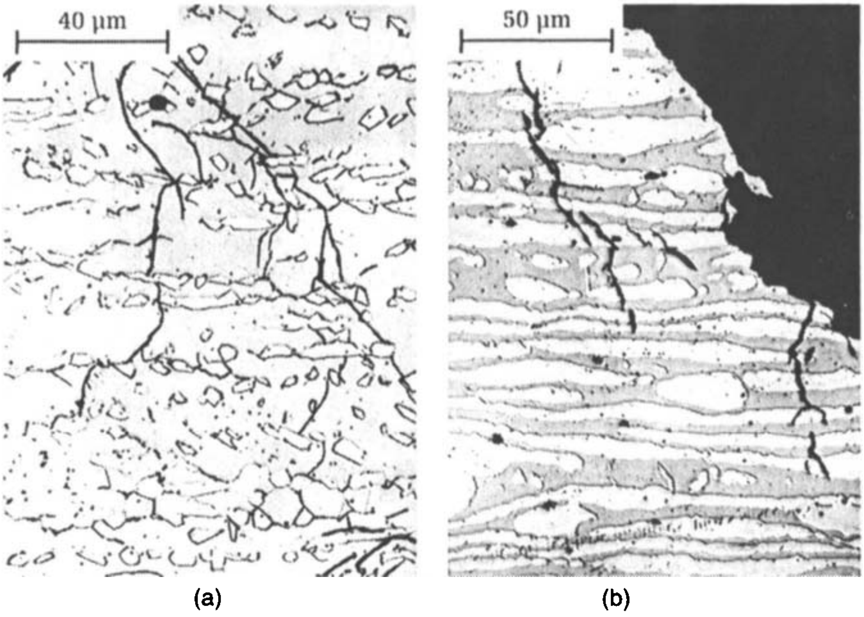
The beneficial effect of a two phase, austenite and ferrite, microstructure has been known since the early days of duplex stainless steels. Work[5,6] in the 1950s and 1960s on austenite-rich microstructures concluded that the ferrite protects the austenite against SCC, as the ferrite has a lower corrosion potential in an acidified (hydrolysed) crack solution, such that, once a crack in the austenite reaches ferrite, the mixed potential inside the crack is depressed and the austenite is protected (Fig. 7.2). This explanation[7] follows normal galvanic corrosion theory, but requires a potential drop between the crack and the external surface and so assumes that the crack can behave as a relatively isolated electrochemical system.

The extent of alloy partitioning, and so the resistance to SCC, is also linked to the phase balance. In the extreme, about 15% of a minor phase constitutes the achievement of an inter-connected network, such that a crack can pass entirely through the minor phase. As the content of the minor phase increases, the crack propagation becomes more denominated by the characteristics of this phase until another threshold is reached at the 50% level, which may relate to the maximum resistance to forcing a planar crack through the 'brittle' phase.



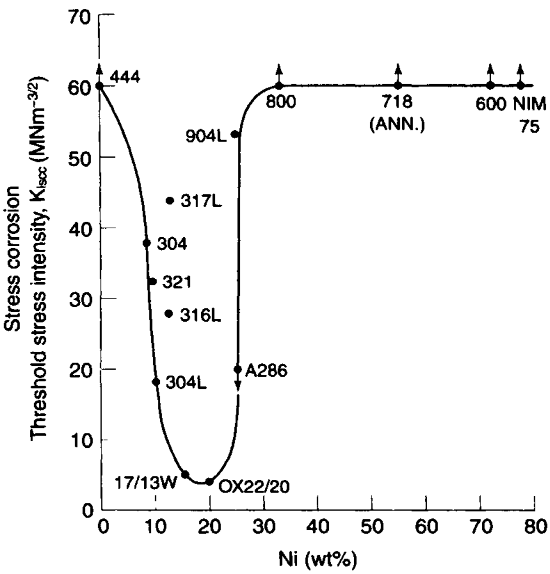
7.2 Sacrificial protection of γ-austenite by α-ferrite (reference 7).

However, in modern duplex alloys, where there are roughly equal proportions of the two phases, cracking can occur[8] preferentially in the ferrite phase, or through both phases (Fig. 7.3). This may seem surprising as the resistance of ferritic stainless steels to SCC is normally considered high, while the susceptibility of austenitic



(a) (b)

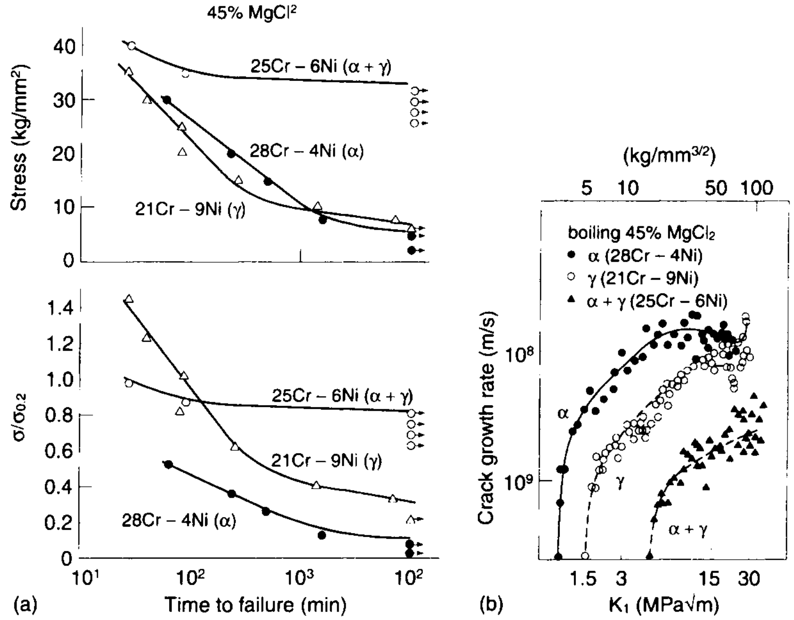
7.3 Examples of crack propagation in steel S32550, $CaCl_2$ at 130°C (reference 8). (a) Through the ferrite, × 500 and (b) Through both phases, × 400. Etch: electrolytic sulphuric acid.



7.4 SCC resistance of stainless steels and Ni-base alloys as a function of Ni-content in 22%NaCl at 105°C (after reference 9).

grades is renowned, due to the higher Ni-contents[9] (Fig. 7.4). However, the ferrite in a duplex microstructure contains at least 3%Ni, in comparison to common ferritic grades which are largely nickel-free. This makes the ferrite phase in duplex alloys susceptible[10] to SCC (Fig. 7.5).

Cottis and Newman[7] explained the cracking behaviour of duplex stainless steels using appreciation of electrochemical behaviour and mechanics of crack propagation through the two phases. With reference[11] to Fig. 7.5, the SCC resistance of a duplex alloy is compared with ferritic and austenitic alloys of similar composition and shows that, in general, the duplex alloy performs better than either of the single phase alloys. Given that a crack has formed in the ferrite and has reached an austenite island, for the crack to pass through the austenite, the prevailing potential and pH would need to be favourable to cracking in this phase. However, conditions that would favour corrosion or cracking of the ferrite will tend to leave the austenite intact, Fig. 7.2, unless the stress is sufficiently high to cause ductile tearing, which will require high stress intensities. Thus, as the potential in the crack is similar to that of the ferrite, the cracking resistance of the bulk alloy will be higher than the individual phases at their free corrosion potentials.

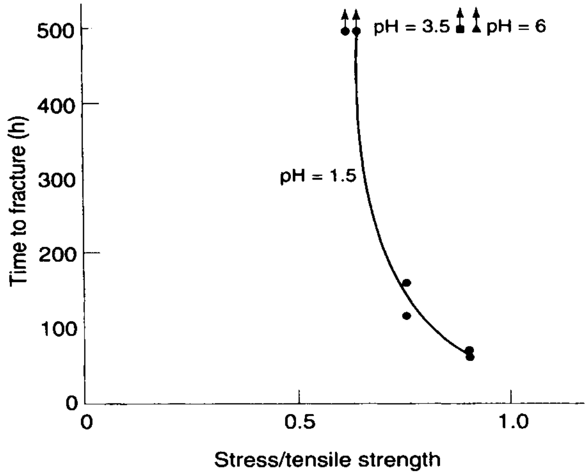


7.5 Comparison of duplex, austenitic and ferritic alloys of similar composition to chloride SCC (after reference 11). (a) Constant load; (b) crack growth rate.

This mechanism has one important outcome regarding the composition of the individual phases. If the compositions, or more importantly the free corrosion potentials, of the phases are similar, then the mechanism of enhanced SCC resistance of duplex alloys cannot operate. As discussed in Section 3.2, the compositions of the ferrite and austenite are different in solution annealed and quenched microstructures, explaining their resistance. Nevertheless, higher solution annealing temperatures reduce element partitioning and may increase susceptibility to SCC.[7]

7.2.2 Solution chemistry and temperature

In Fig. 7.1, the resistance of duplex alloys to SCC in sodium chloride solutions is presented.[1] It indicates that superduplex grades (e.g. S32750) are resistant to cracking in aerated 10%Cl^- (i.e. 16.5% NaCl) with temperatures approaching 300°C. These data sets have been compiled using both practical experience and laboratory tests, although they do not tell the whole story. For instance, the data are



7.6 Constant load (smooth sample) SCC tests on S31803 in aerated 40%$CaCl_2$ (256 g/l Cl^-) 100°C, with 0.008M PO_4^{-3} added as $H_3PO_4 + NaH_2PO_4$. (after reference 1).

pertinent to aerated neutral solutions and so, if the oxygen content is lowered, higher chloride concentrations can be tolerated, while more acidic conditions may reduce resistance[1,12] (Fig. 7.6). On the other hand, limits for chloride concentration generated with NaCl should be used with caution if Mg or Ca cations are present, due to their more aggressive nature.[2]

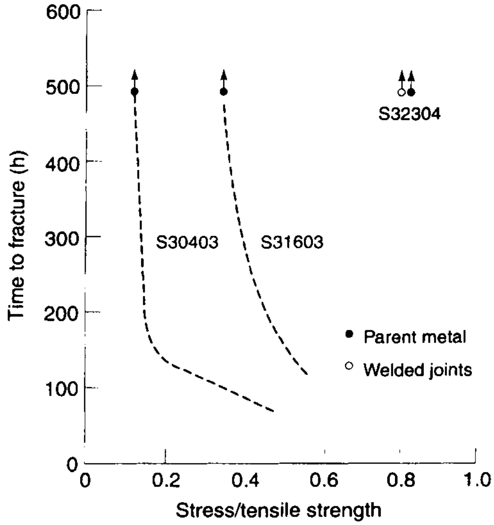
It has been demonstrated[13] in slow strain rate tests in laboratory conditions (e.g. deaerated 50%$LiCl_2$ at 100°C) that low alloy duplex grades can be slightly more resistant than their more highly alloyed cousins. This result can be obtained in such hot dilute acids with some chlorides, where the low alloy grades suffer from general corrosion, such that any cracks that initiate are immediately corroded and blunted. On the other hand, high alloy stainless steels are more resistant to general corrosion, but could still crack due to the temperature, stress and presence of chlorides. For this reason it is feasible that, under certain conditions, the more pitting resistant grades can be more prone to cracking.

Care must be taken when using diagrams such as Fig. 7.1 to select material for a known (or presumed) set of service conditions. For instance, in marine environments, the chloride content is always in doubt due to evaporation, condensation and wetting. Further, evaporation of sea water produces a concentration of Mg ions, which, in the extreme, can be equivalent to boiling $MgCl_2$ solution, with the added problem of a crevice formed by the salt deposit and a supply of oxygen.[7] To simulate these conditions the continuous drop evaporation test using sea water has been proposed.[10,14,15] This test maybe too aggressive as wetting is not continuous in practice, which allows for the steel to repassivate. Alternatively, an interrupted drip test has been proposed[16] as more representative of service.

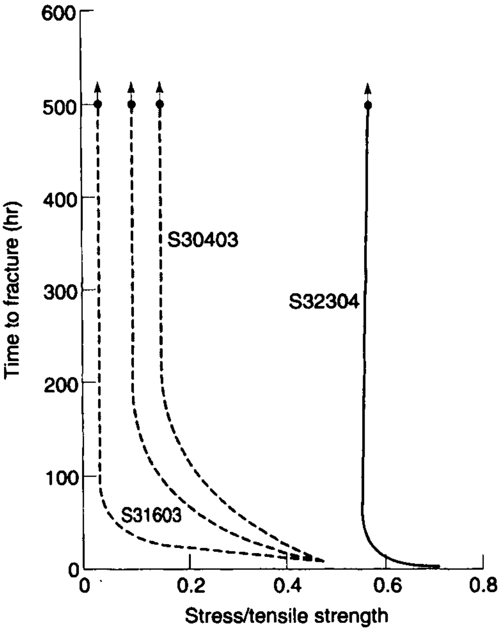
7.2.3 Stress level

The data reproduced in Fig. 7.1 are reported to be generated with stress levels equal to or above the proof stress of the material at the given temperature. Results[17] of constant load tests at lower applied stress to tensile strength ratios are shown in Figs. 7.7 and 7.8. The improved resistance of the alloy lean duplex grade S32304 over 300-series austenitic grades is again demonstrated in $CaCl_2$ and $MgCl_2$ solutions.

More severe evaporation test data have been produced[18,19] on a range of alloys (Table 7.1). As a proportion of the $R_{p0.2}$ at 200°C, the duplex grades compare well with the 300-series and 4%Mo (e.g. N08904) austenitic grades, but if the higher tensile strength of duplex alloys is taken into consideration, then the superduplex grades show



7.7 Constant load tests in aerated 40%$CaCl_2$ (256 mg/l Cl^-), pH 6.5, 100°C (after reference 17).



7.8 Constant load tests in aerated 45% $MgCl_2$ (336 g/l Cl^-), 150°C (after reference 17).

some benefit also over the 6%Mo superaustenitic grades (e.g. S31254).

Table 7.1 Relative threshold stresses for the drop evaporation test (DET) (after reference 18)

UNS code (Refer to Table 1.1 and Appendix A)	% of $Rp_{0.2}$ at 200°C below which no failure due to SCC is expected	Corresponding threshold stress, MPa
S32654	>100	>333
S31254	90	230
N08904	70	155
S32750	70	300
S31803	40	180
S32304	40	140
S30403/S31603	<10	–

7.3 Sulphide stress corrosion cracking

7.3.1 The effect of H_2S

Hydrogen sulphide may be evolved in oil wells or polluted waters due to bacterial activity. The resistance of duplex stainless steel to stress corrosion cracking in the presence of H_2S and chloride is reduced, if compared to similar environments where only chloride is present. Reduced sulphur species are known[20] to catalyse the anodic dissolution of iron and nickel, and therefore can be assumed to control the kinetics of localised corrosion in stainless steels. In fact, corrosion products within pits show increased nickel contents,[21] suggesting formation of NiS by:

$$Ni^{2-} + H_nS_{n\;\;2} \rightarrow NiS + nH^{+} \qquad [7.1]$$

The reduction in H_2S activity by NiS formation may lead[22] to attack at the edge of the pit, rather than at the base. Nonetheless, Eq. 7.1 does predict a reduction in pH within the occluded region, which will enhance[7] active dissolution and restrict repassivation. Pitting may occur in either ferrite or austenite for the same steel condition dependent on the test conditions, i.e. H_2S partial pressure (pH_2S), and so prediction of preferential attack using the bulk PRE relationship is not appropriate. The situation is further complicated because, at least in the early stages, penetration can take place preferentially along the austenite/ferrite interface. However, once cracking starts this always occurs in the ferrite (Fig. 7.9).

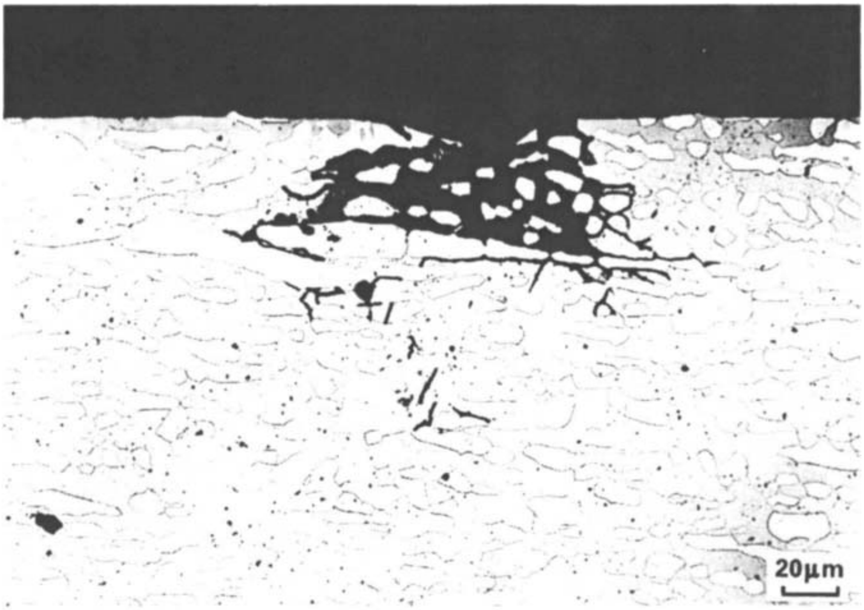
The presence of H_2S in a solution will remove oxygen to form elemental sulphur and water, i.e. Eq. 7.2.

$$H_2S \text{ soln} + O_2 \text{ soln} \rightarrow S \text{ ppt} + H_2O \qquad [7.2]$$

The removal of oxygen restricts the cathodic reaction to hydrogen evolution, or, to a lesser extent, reduction of sulphur to a sulphide. (This source of hydrogen is in addition to any that might form from an electrochemical reaction, i.e. localised corrosion.) Further, as H_2S has been established to restrict the recombination reaction, Eq. 7.3:

$$2H \text{ ad} \rightarrow H_2 \text{ g} \qquad [7.3]$$

the surface of the steel becomes enriched in atomic hydrogen, which enhances hydrogen diffusion into the steel. The concentration of hydrogen that can build up in the substrate just below the passive film is dependent on several factors, including the electrochemical



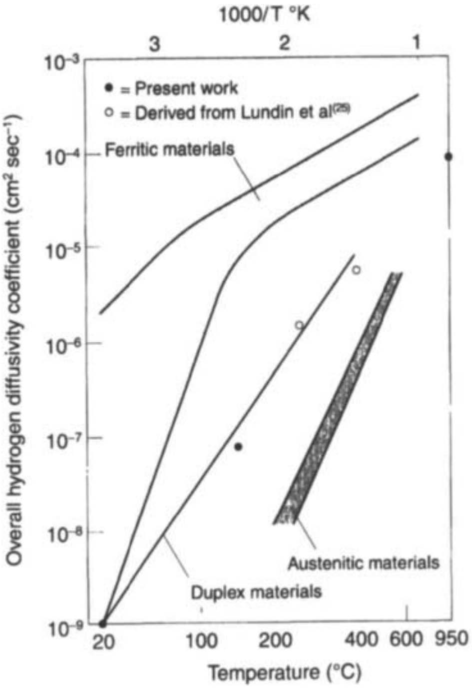
7.9 Preferential attack of ferrite and phase boundaries, followed by hydrogen cracks in the ferrite, × 500. Etch: electrolytic sulphuric acid.

potential, the solution pH, the temperature and the condition of the metal surface.

7.3.2 Hydrogen entry

In general, the rate of hydrogen entry into the steel increases as the potential becomes more negative, which is the case for cathodically protected components (Section 7.4). In addition, lower pH solutions necessarily have higher hydrogen ion concentrations and so accelerate adsorption, which is further enhanced as acid conditions tend to destabilise the passive film. In turn, the passive film will differ depending on the condition of the metal surface, for instance mechanical removal of the film encourages hydrogen ingress.[23]

Once the hydrogen is in the steel, diffusion through the structure is activation controlled and is thus a function of temperature.[7] Nevertheless, the diffusion of hydrogen through austenite is slower than through ferrite by a factor of 10^4, and so the overall diffusion rate in a duplex structure lies somewhere in between[24,25] (Fig. 7.10). On the other hand, as austenite has a much higher hydrogen



7.10 Effect of temperature on diffusion rate for ferritic, austenitic and duplex steels (after references 24 and 25).

solubility limit than ferrite (about 30 times) the solubility limit in austenite may never be achieved in practice. Further, it has been shown that hydrogen tends to diffuse to the ferrite:austenite phase boundaries.[26] These sites act as hydrogen sinks and so can give low apparent diffusion coefficients. This effect may not be evident given the properties of ferrite and austenite mentioned above.

7.3.3 Hydrogen embrittlement

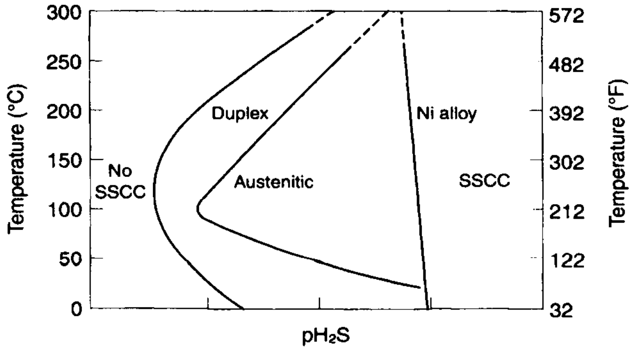
Section 7.3 has explained how the presence of H_2S in an environment can lead to hydrogen ingress into duplex stainless steels. In turn, once the hydrogen is in the steel, the mechanism of cracking is similar to hydrogen embrittlement of ferritic steels.

However, as indicated above, diffusion of hydrogen through the duplex microstructure is relatively slow, such that the hydrogen is only expected to travel a short distance beneath the surface (say 1 mm), unless exposed to elevated temperatures (>100°C) for extended periods (months). Nevertheless, this hydrogen profile is sufficient to initiate cracking, at which time hydrogen rapidly diffuses to the plastic zone beneath the crack tip and aids propagation. In practice, this mechanism is associated with cleavage of the ferrite, sometimes associated with mechanical twinning,[27] and ductile failure of the austenite.

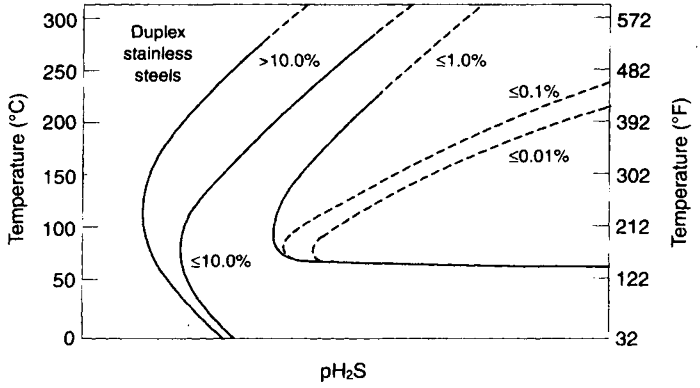
Ferrite-rich microstructures have an increased risk of cracking, especially if they are coarse grained:[28] consistent with hydrogen cracking in duplex weld metals (see Section 8.4.3). In such structures, the crack can propagate through the ferrite avoiding the austenite. It should be noted that austenite is not immune to hydrogen embrittlement,[29,30] but it is only under extreme circumstances that this phase will contain sufficient hydrogen to induce cracking.

7.3.4 Effect of environmental variables

The effect of H_2S content, normally expressed as the partial pressure in the gas phase, and other environmental variables on the cracking behaviour of duplex stainless steels is presented in Figs 7.11, 7.12 and 7.13. These figures are produced from a compilation[31] of published laboratory test data, covering some 274 references. One effect is clear, in that the risk of cracking increases with H_2S partial pressure. The influence of temperature on the SSCC susceptibility of duplex alloys requires explanation, as it peaks at around 80 to

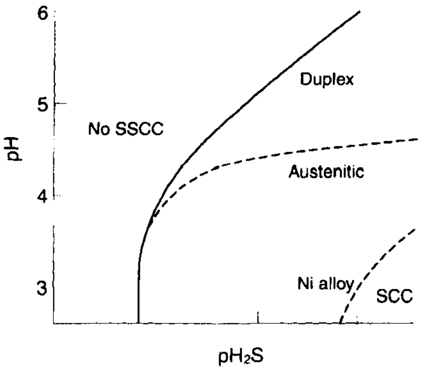


7.11 Effect of temperature and pH_2S on the SSCC of duplex, austenitic and Ni-base alloys. The bounding curves will be set by cold worked 22%Cr material, stressed above R_p, with low pH and high chloride concentrations (after reference 31).

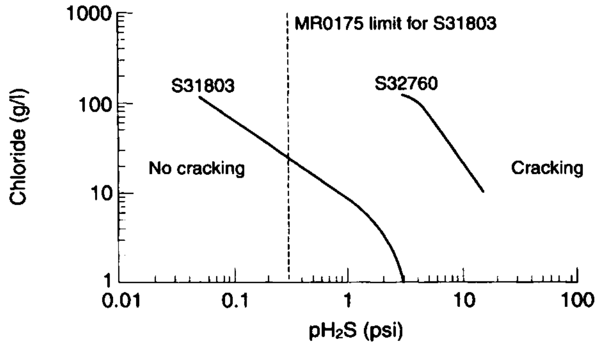


7.12 Effect of chloride content (%NaCl) and pH_2S on the SSCC of duplex stainless steels. The bounding curves will be set by cold worked 22%Cr material, stressed above R_p, in low pH environments (after reference 31).

100°C,[32] with both higher and lower temperatures reducing susceptibility (Fig. 7.11). An increase in cracking susceptibility up to 100°C is considered[21] to be due to an enhanced passive film breakdown, corrosion and acidification and thus hydrogen ingress. At temperatures above 100°C it is thought that the sensitivity of the ferrite to hydrogen embrittlement is reduced, as the hydrogen diffusion rate increases, even though localised corrosion and chloride SCC of the austenite may still occur.



7.13 Effect of pH and pH_2S on the SSCC of duplex, austenitic and Ni-base alloys. The bounding curves will be set by cold worked 22%Cr material, stressed above R_p, with high chloride concentrations at about 100°C (after reference 31).

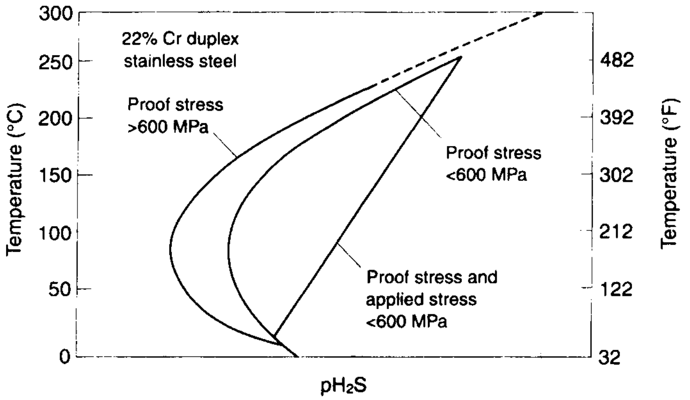


7.14 Suggested chloride and pH_2S limits for cold worked (34–35 HRC) 22%Cr (S31803) and a superduplex (S32760) stainless steel (pH < 4) (after reference 16).

Increasing chloride concentration reduces the critical pH_2S which can be tolerated at a given temperature[31] (Fig. 7.12). Higher pH_2S can be withstood at low and high temperatures, as long as chloride contents are low, i.e. below 0.1% NaCl. The effect of pH, which is governed by pCO_2 and pH_2S, is shown[31] in Fig. 7.13. As for ferritic steels, the risk of SSCC is enhanced in more acidic conditions, although solutions above pH 5 can provide some tolerance to higher pH_2S for duplex grades. Further, at lower pH values (i.e. from 3.5 to 2.5 pH) the decrease in resistance has been claimed[33] to fall by a factor of ten at 90°C.

Given that the risk of SSCC is a function of chloride content and pH, the superduplex grades offer greater resistance to SSCC than the 22%Cr grades,[16] everything else being equal (Fig. 7.14). Moreover, the condition of duplex materials in terms of cold work is also highly influential, combined with the applied stress[31] (Fig. 7.15). Higher pH_2S can be tolerated if the material is not heavily cold worked, defined here as when $R_{p0.2}$ is below 600 MPa and the applied stress is below $R_{p0.2}$.

Clearly, the resistance of duplex alloys to chloride/H_2S/CO_2 media is complex with many interactive factors. For this reason, safe operating limits cannot easily be judged from simple two-dimensional diagrams, such as Figs. 7.11 to 7.15. Some degree of confidence can be gained from computer run software which can provide an operating envelope for given process conditions. Such software includes CRASOUR™ and SOCRATES™, which may allow for material selection to be undertaken if similar environments are



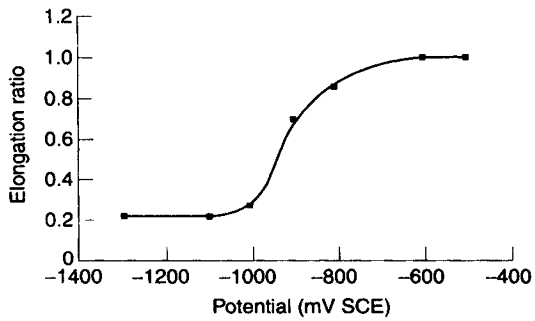
7.15 Effect of applied stress and R_p on the SSCC of 22%Cr duplex alloys. The bounding curves will be set by solutions with high chloride concentrations and low pH (after reference 31).

expected in service, as contained in these databases. Notwithstanding this, the need for simulated service tests, as recommended by EFC[34] should be considered for extra confidence, especially if welded components are envisaged (see Section 10.6.2). Further, guidance on how to carry out such tests is covered in the EFC publication.

7.4 Cathodic protection

There is an increasing use of duplex alloys subsea, particularly by the oil and gas industry. In many of these applications, the duplex stainless steels are cathodically protected, either by design, or because they are connected to protected steel work. The cathodic protection (CP) is usually by aluminium alloy anodes with a potential of about −1000 mV SCE. At this potential, hydrogen is generated by the cathodic reaction, and, if it diffuses into the metal, hydrogen embrittlement can result.[35]

The severity of embrittlement depends on the amount of hydrogen evolved, the ability of hydrogen to be absorbed into the surface and the diffusion rate into the bulk steel. Slow strain rate (SSR) tests under cathodic charging over a range of potentials show that the elongation ratio (i.e. elongation in media/elongation in air) drops at negative potentials[36] (Fig. 7.16). Given that an elongation ratio of 75% does not necessarily indicate a detrimental loss of properties, a critical potential for the onset of appreciable embrittlement is



7.16 Effect of applied potential on the elongation ratio in SSR tensile tests on a cold worked (34–35 HRC) superduplex stainless steel (S32760) (after reference 16).

about −900 mV SCE in cold worked material. A typical potential for aluminium alloy anodes is −1000 mV SCE (although this can be as low as −1150 mV SCE for some Al-alloy anodes), and the potential drop between the anodes and the protected stainless steel maybe about 100 mV. This difference should significantly reduce the hydrogen charging of duplex stainless steel,[16,37] although this will depend on the separation distance between the anode and the structure.

Several workers[36,37] have indicated that very small cracks originate in the ferrite and are blunted when they reach austenite; hence, the finer the grain size, the greater the resistance of duplex stainless steels to hydrogen embrittlement. It has been found that cracks will only propagate under very high loads,[38] i.e. above R_p, when the austenite can be plastically deformed. In these circumstances, the crack can propagate through the austenite or along the ferrite/austenite phase boundary.

A number of projects have utilised S31803 and superduplex grades, such as S32760, for subsea applications such as manifolds and flowlines. Many of these have been subject to cathodic protection. In the case of the 22%Cr duplex, this may be because of its lower resistance to crevice corrosion in sea water. With the superduplex grades, CP has been considered necessary typically where the process temperature is very high and crevice corrosion of the surface in contact with sea water was considered possible. Duplex and superduplex steels have been used in several offshore projects with CP and no failures due to hydrogen embrittlement have been reported in these applications.[15] Cracking, however, has been experienced in heavily cold worked material, as indicated in Section 13.2.

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8 Welding metallurgy

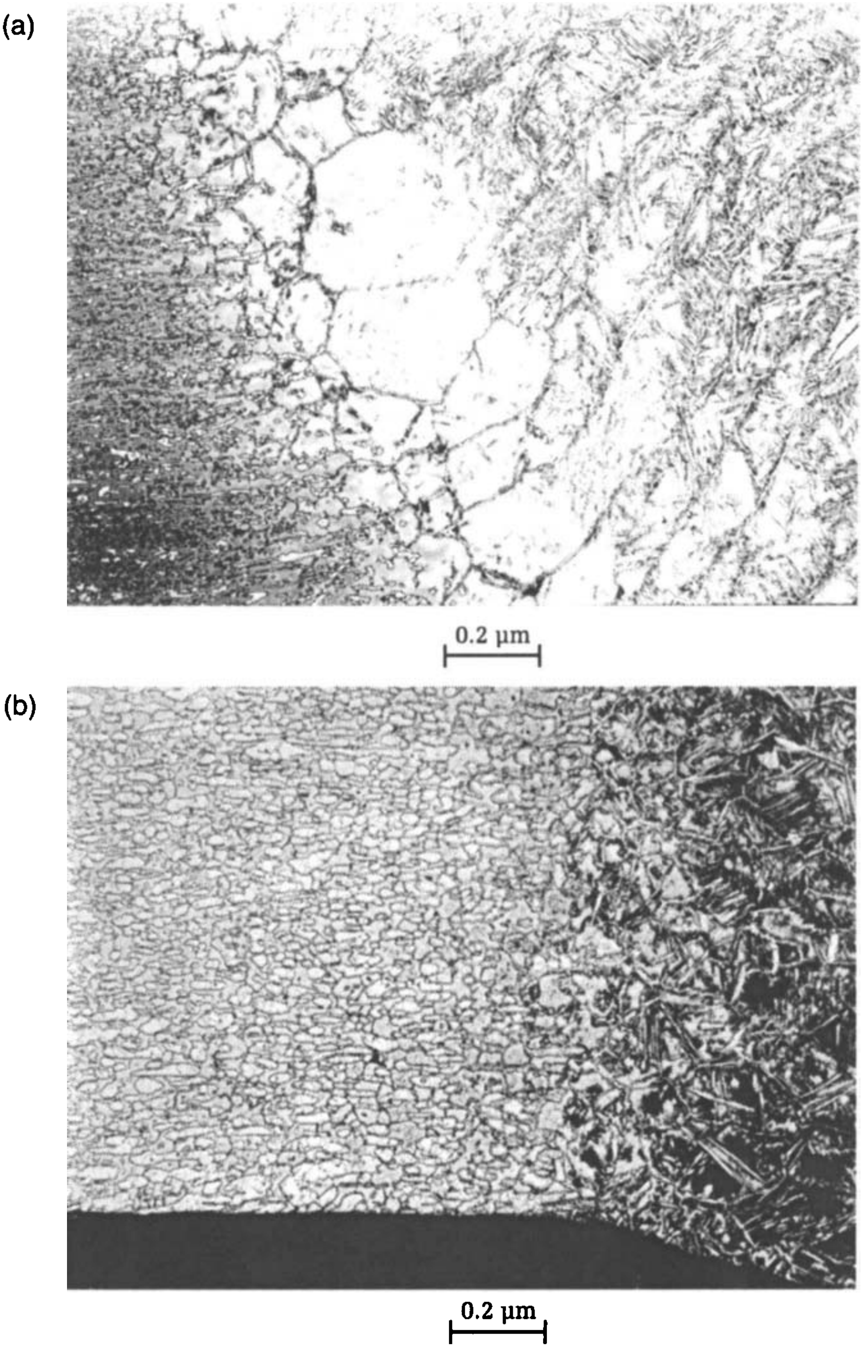
8.1 Introduction

Welding metallurgy has played a key role in the alloy development of duplex stainless steels. The earliest grades had high carbon contents and tended to form a ferrite-rich heat affected zone (HAZ). Although some austenite reformation occurred due to these high carbon levels, this also led to carbide precipitation and a loss in intergranular corrosion (IGC) resistance. Later grades had lower carbon levels, but the high Cr/Ni ratio enhanced ferrite-rich microstructures in the HAZ and promoted grain growth.

In the early 1970s, a 22%Cr duplex stainless steel was developed. The patent[1] claimed that this new steel was not sensitive to IGC upon welding due to a balanced chemistry including the addition of nitrogen. However, the composition ranges permitted were very wide, which allowed for melts to be produced which could still produce almost fully ferritic HAZs with an associated reduction in corrosion resistance.[2] Although the national specifications for the 22%Cr duplex stainless steel, e.g. UNS S31803, still have quite wide ranges, most producers and end users specify closer limits to control the weldability. In particular, nitrogen contents within the upper range of the specification are common, as typified by the sub-set grade S32205, and so the modern duplex stainless steels have a much better weldability than the earlier grades (Fig. 8.1).

8.2 HAZ transformations

The high temperature HAZ (HTHAZ) can be defined as the zone next to the fusion boundary which approaches the melting point and will become almost completely ferritic on heating. On the other hand, the low temperature HAZ (LTHAZ) is where the phase balance has remained substantially unchanged. There are transitions between the LT and HT HAZ and the complexity is increased further if repeated exposures from multipass welds are superimposed.



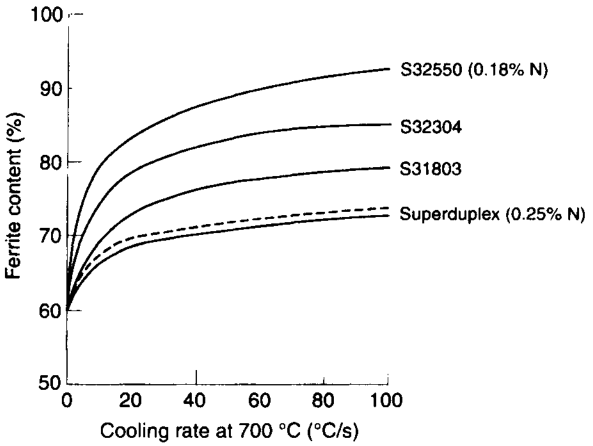
8.1 Comparison of duplex stainless steel HAZ microstructures. Etch: Electrolytic sulphuric acid: (a) old (low nitrogen), × 63; (b) modern (higher nitrogen), × 100.

8.2.1 High temperature HAZ

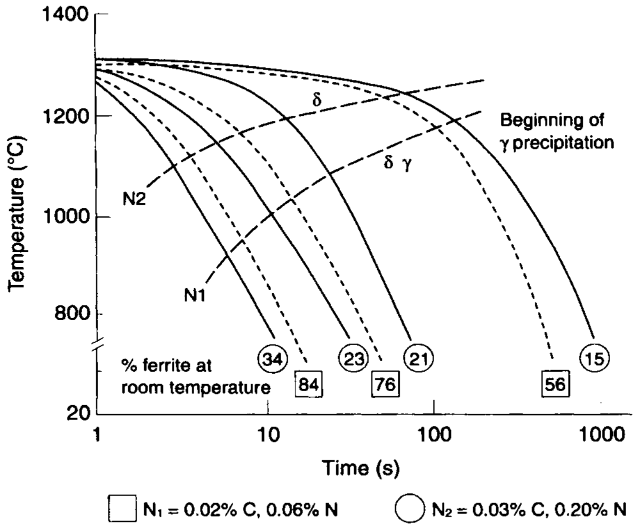
The transformed microstructure in the HTHAZ is controlled only by the welding procedure and steel composition.[3,4] With the arc energies normally used in practice, the problems associated with almost fully ferritic zones (see Section 8.1) have largely been solved by means of optimising the chemical composition of the base material. In particular, this has been done by increasing the nitrogen levels of the steels, Fig. 8.1. As a result, the modern duplex steels normally show ferrite levels in the HTHAZ in the range 50–70%, provided that appropriate welding practices are used (Fig. 8.2).[5]

For a given steel composition, the microstructure in the HTHAZ is controlled by the imposed thermal history and so heat input, material thickness, preheat and interpass temperatures are all influential. More specifically, it is the peak temperature and exposure time to the single phase ferritic region,[3,6] which controls austenite dissolution and ferrite grain size. Diffusion controlled austenite reformation, which largely involves nitrogen redistribution, occurs at the ferrite grain boundaries and by Widmanstätten or intragranular side plate growth and can be described[7] by CCT diagrams, as illustrated in Fig. 8.3. A large ferrite grain size has a retarding effect on austenite formation.[8]

An experimental prediction model for the HTHAZ microstructure



8.2 Variation in the maximum HAZ ferrite content as a function of steel nitrogen content and cooling rate (after reference 5).

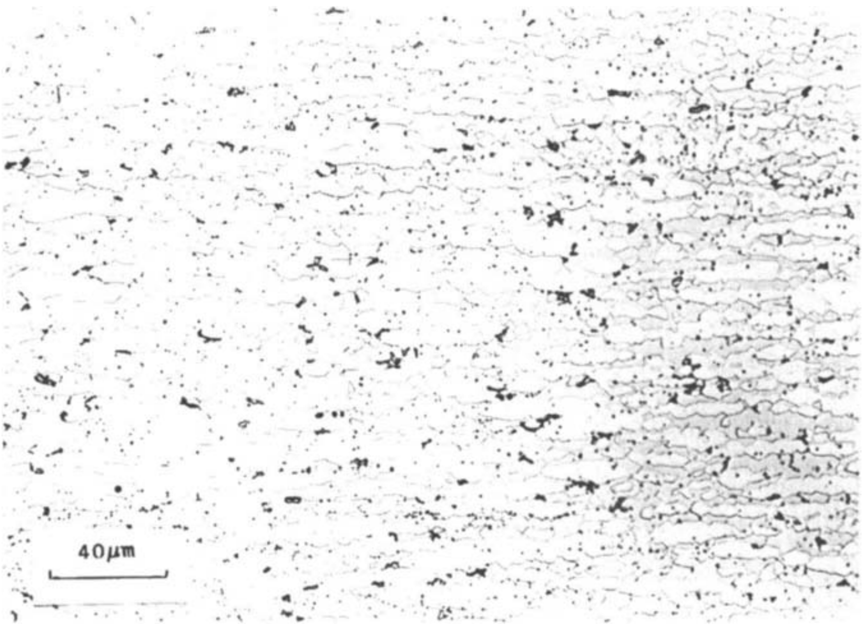


8.3 CCT diagrams for 24.5 Cr/7Ni duplex steels with different nitrogen contents (after reference 7).

has been derived[9] for various grades. Further, a theoretical kinetic model[10] for austenite reformation, assuming a nitrogen controlled diffusion reaction has been developed. The latter model shows the beneficial effect of a small ferrite grain size and gives a good correlation to experimental data. It also confirms the faster austenite reformation in superduplex grades compared to 22%Cr and low alloy duplex grades.

Certain effects on HTHAZ may occur if welding is performed with fillers giving weld metals with different nitrogen activities. During a weld thermal cycle the diffusion distance of nitrogen is 50–100 μm.[11] Use of a nickel-base filler, such as type 625, will result in nitrogen migration into the fused region and may increase the ferrite level in the HTHAZ.[12]

In the HTHAZ, lower temperature reactions may occur in rapidly cooled welds, such as nitride formation if insufficient austenite reformation takes place (see Section 3.4.6). However, adjacent to the austenite phase a precipitate free zone is sometimes observed[13] in the ferrite, as the nitrogen required for nitride precipitation has diffused to the austenite. Similarly, in interpass regions, secondary austenite may precipitate (see Section 3.4.2).



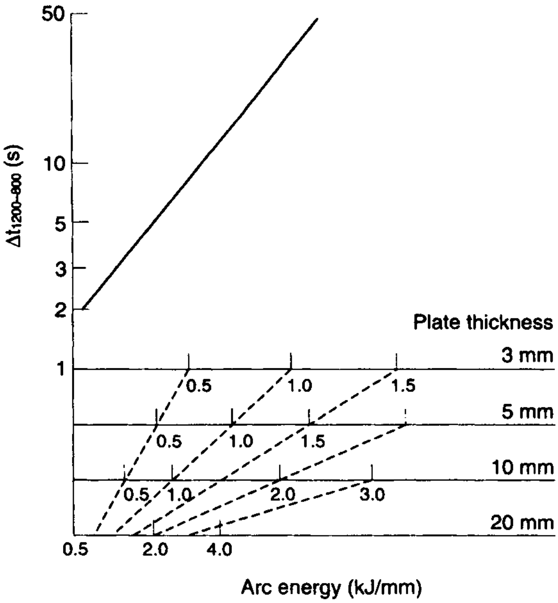
8.4 Sigma phase in the LTHAZ of a superduplex weld. Etch: electrolytic sulphuric acid, × 500.

8.2.2 Low temperature HAZ

The LTHAZ is located further away from the fusion boundary and has a thermal history that may cause the formation of intermetallic phases (Fig. 8.4). This is primarily a problem[14] encountered in the higher alloyed superduplex stainless steels, but with extremely slow cooling rates lower alloy grades can also be affected.[15] As for heat treatment of parent material (see Section 3.3), the key factors are the composition of the steel, its condition, i.e. prior heat treatment, and the total time exposed to elevated temperatures, i.e. the total thermal cycle.

8.2.3 Control of HAZ transformations

Welding parameters should be controlled to ensure that the overall cooling conditions are slow enough for adequate austenite formation in the HTHAZ and fast enough to avoid deleterious precipitation in the LTHAZ. Traditionally these guidelines have provided rec-



8.5 Nomogram for prediction of Δ_{12-8} for duplex stainless steels (after reference 18). Note: for guidance only.

ommended heat input (arc energy) ranges and maximum interpass temperatures. However, this approach does not fully define the appropriate thermal cycles for optimum properties, since the effect of the joint geometry and heat sink (material thickness) requires consideration. Better practical limits can be provided by the cooling times between 800 and 500°C, $\Delta t_{8/5}$, or between 1200 and 800°C, $\Delta t_{12/8}$. The latter of these is more appropriate for duplex alloys, as it covers the temperature range over which austenite formation occurs.[16] Preferred[17] cooling times lie in the range 8 to 30 seconds for $\Delta t_{8/5}$ which correspond to approximately 4 to 15 seconds for $\Delta t_{12/8}$ or, alternatively,[3] a cooling rate of 20–50°C/s. Furthermore, these cooling times can be equated[18] to an arc energy for a given material thickness from nomograms, as shown in Fig. 8.5.

8.3 Weld metal

8.3.1 General

The weld metal microstructure differs from the parent material, as a result of variations in chemical composition and its total thermal history. It is thermodynamically impossible to get an austenite fraction higher than the annealed equilibrium level, although, in deposits with high nitrogen and nickel contents, equilibrium austenite contents have been reported.[19] In practice, autogenous weld metal can be almost fully ferritic from an as-annealed level of about 50%, while the composition and cooling rate of most deposits ensure that the equilibrium fraction of austenite is not attained. Consequently, the chemical composition of the weld metal is crucial. Welding consumables generally have a 'more austenitic' composition than the parent steel for improved mechanical and corrosion properties. The fillers are today normally made with 2–4% more nickel than the base metal. ANSI/AWS A5.4 (SMAW) and A5.9 (bare electrodes and rods) classify such consumables as E/ER 2209 for welding the 22%Cr grade (S32205/S31803), while the code E/ER 2553 covers 25%Cr grades like S32550. Alternatively, the CEN code for 22%Cr consumables is X22.9.3L and for more highly alloyed grades two codes exist, namely: X25.9.3CuL and X25.9.4L which cover the superduplex consumables (see Appendix B).

8.3.2 Solidification and austenite formation

In the weld metal, ferrite solidification involves epitaxial growth from the parent material at the fusion boundary,[20] i.e. the HTHAZ. The initial dendrite growth is oriented in relation to the thermal gradient,[21] and produces a columnar ferritic structure (Fig. 8.6). This provides the starting conditions for further solid state transformations upon cooling and will dominate the final weld metal structure. The ferrite grain size and orientation, together with ferrite content and morphology, influence weld metal properties (see Chapter 10). For example, the morphology affects the weld metal Charpy impact toughness.[13] As mentioned above, the microsegregation due to solidification is normally negligible in the fully ferritic mode. However, solid state partitioning of elements between the phases can have a significant effect on properties.

8.6 Multipass duplex weld (GTAW root and SMAW fill) showing columnar structure. Etch: magnetic colloid, × 5.

Austenite precipitation starts below the A4 or ferrite solvus temperature (see Fig. 3.2), which is dependent on the weld metal composition. Initial formation occurs intergranularly, followed by Widmanstätten side plates or intragranular plates depending on the ferrite grain size and cooling rate.[22] Austenite precipitation is a diffusion controlled nucleation and growth process[7,8,16,23] and, at least, in low arc energy welds, the austenite reformation is controlled by a para-equilibrium transformation mechanism whereby the diffusion of interstitial elements (carbon and nitrogen) is the controlling process.[8,10,24] Thus, the cooling rate is of major importance in determining the extent of transformation. Slow cooling rates result in more austenite formation, while fast cooling rates give less austenite. However, as the nucleation of austenite is facilitated at grain boundaries, a small ferrite grain size, in principle, favours high austenite contents.[8] In general, duplex weld metals have ferrite contents in the range 30–70% depending on composition and cooling rates.

8.3.3 Ferrite measurement

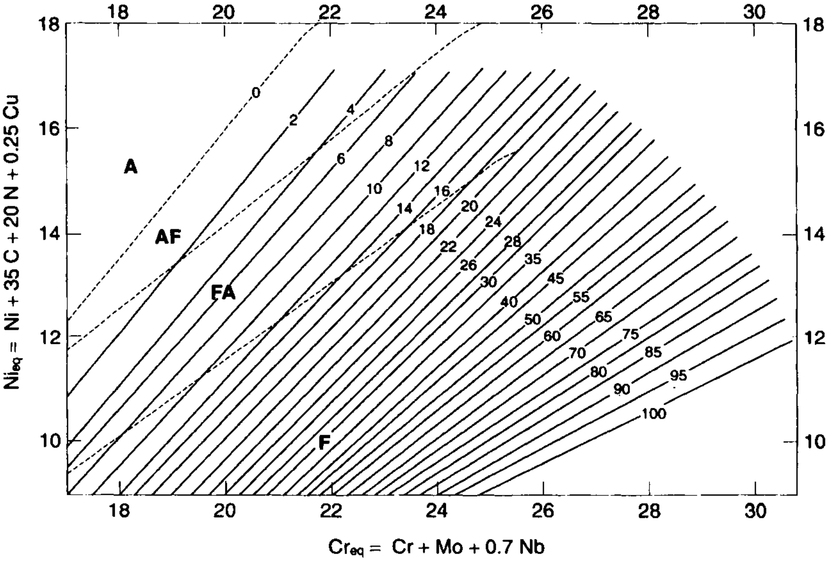
Essentially there are two methods for measuring the ferrite content of weld metals and parent materials, both of which have advantages and disadvantages. The first requires careful metallographic preparation to a 1 μm finish, followed by an etch in 40% KOH solution at 7–8 V.[25] The ferrite phase becomes a brown/orange colour in contrast to the white austenite and so the volume content of ferrite can be measured using a point count procedure, following the essence of ASTM E562.[26] Image analysis systems can be employed for parent material assessment, but it is not advised for weld metal due to the more variable etching response. The advantage of point counting is that it can be applied to all microstructures, including the narrow HAZ, but is difficult to undertake *in situ* (i.e. generally considered a destructive technique) and is relatively slow/expensive. The accuracy of this method, in terms of the 95% confidence interval, is at best ±5% ferrite at the 50% ferrite level.[27]

The second technique takes advantage of the different magnetic properties of the two phases: ferrite is ferro-magnetic while austenite is not. In this case an arbitrary 'Ferrite Number' (FN) is assigned to a given level of magnetic attraction, defined from primary standards[28] (coating thickness standards) and a magnetic beam balance known commercially as a MagneGage instrument. At low ferrite levels, typical of those found in nominally austenitic weld metals, FN values were once considered to be approximately the same as ferrite per cent[29] (say up to 6% or 6 FN), while higher FN values overstated the ferrite per cent. It now seems that FN overstates ferrite per cent at all levels.[30] As the FN of a particular weld metal depends not only upon the amount of ferrite, but also upon the composition of the ferrite (in particular iron content), no simple correlation between the two scales can be drawn.[30] A correlation made for one alloy is not likely to carry over to another alloy. There is a wealth of experience which allows specification of FNs appropriate to particular applications.[31] Inter-laboratory reproducibility of FN measurements has been found to be ±10% of the mean value (i.e. ±3 FN at a mean value of 30 FN, or ±7 FN at a mean value of

70 FN).[30] The two advantages of the FN system are that it lends itself to portable non-destructive instruments,[28] although there are some cases where the accuracy and working practice of such instruments has been questioned.[31] For this reason, it is important, for meaningful and reproducible FN results, that the calibration and working practice of such instruments be undertaken strictly according to the standard method.[28–31]

8.3.4 Phase balance prediction

The Fe-Cr-Ni system has been described in several ways since Bain and Griffiths[32] first published data on ferritic-austenitic structures in 1927. The Schaeffler diagram[33] is an empirical description of the microstructures of the weld metal that result from welding different compositions. This type of diagram has been used for many years to predict the cast or weld metal microstructures in conventional austenitic and other stainless steels and to some extent to optimise base metal and filler compositions.

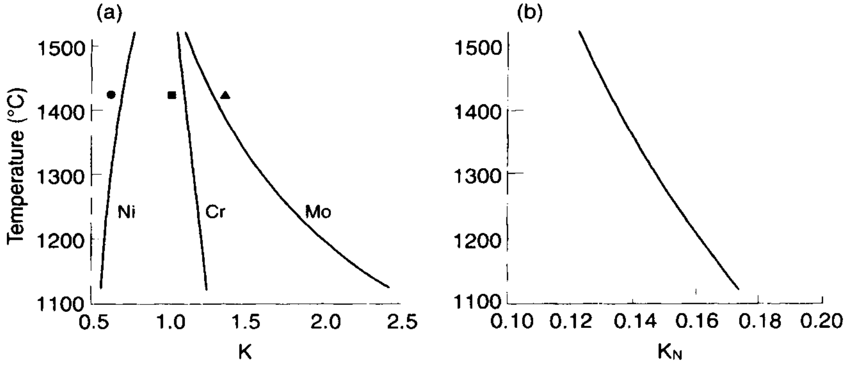


8.7 WRC-1992 diagram (after reference 36). The FN prediction is only accurate for weld compositions that fall within the bounds of the iso-FN lines (0 to 100 FN) that are drawn on the diagram. The limits of the diagram were determined by the extent of the database and extension of the lines could result in erroneous predictions.

It became apparent that the Schaeffler diagram did not predict duplex microstructures very well[34] and so other diagrams and relationships were proposed,[18,35] culminating in the WRC-1992 diagram[36] (Fig. 8.7). The WRC diagram provides reasonable agreement in many practical applications,[17] although for relatively low and high nitrogen contents (<0.19%N and >0.26%N), FN values are over- and under-estimated respectively.[37] This may imply that a variable factor for nitrogen is required, as proposed by DeLong in 1956[38] or that cooling rate should be considered.[39] Nevertheless, the WRC-1992 diagram is still recommended for first approximation of weld metal content.

8.3.5 Element partitioning

In essence, the partitioning of elements in weld metal[20] (Fig. 8.8) follows the same behaviour as for parent material (see Section 3.2). For low heat input welding, where the cooling rates are relatively fast, substitutional elements (Cr, Ni, Mo, etc.) are almost equal in both phases whereas the interstitial elements controlling the reaction are heavily concentrated in the austenite. On the other hand, if higher heat inputs are employed, slower cooling rates result, and austenite transformation is mainly diffusion controlled with subsequent partitioning of the substitutional elements.[3,20] Multipass welding has a similar effect on partitioning as slow cooling.[40]

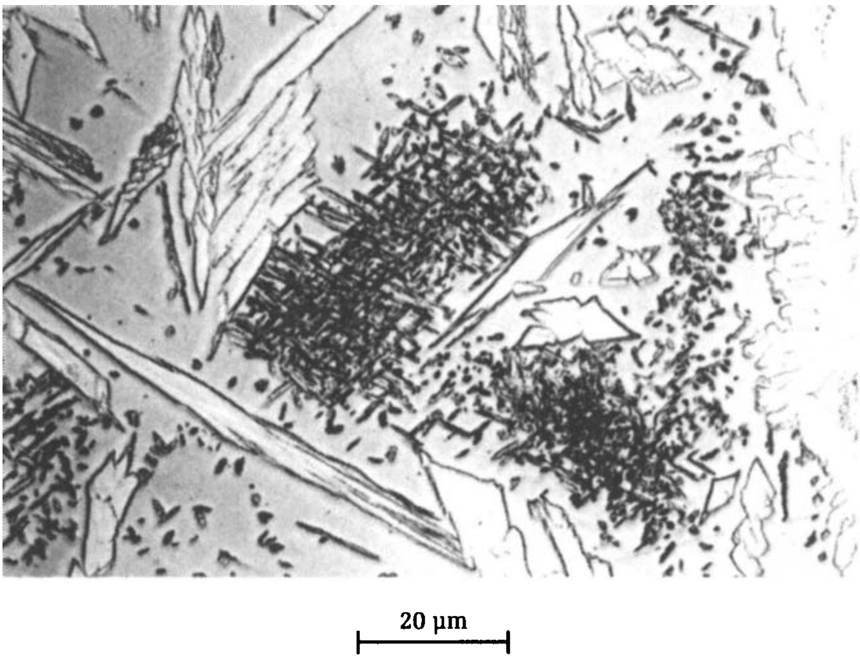


8.8 Partitioning ratios for (K) S31803 weld metal as a function of temperature (after reference 20). (a) Cr, Ni and Mo (b) N.

8.3.6 Other transformations

The as-deposited, non-equilibrium, weld metal structure can be affected by additional thermal treatment, such as multipass welding and postweld heat treatment. In both cases, secondary austenite (γ_2) can precipitate from the ferrite, which is supersaturated in nitrogen at lower temperatures (Fig. 8.9). The formation of γ_2 is reported[41] to occur particularly in low heat input weld runs followed by subsequent runs deposited with relatively high arc energy. It has been shown[42] that the secondary austenite precipitated in an interpass region contains lower Cr, Mo and N, than the primary austenite formed at higher temperatures.

Precipitation of intermetallic phases can occur in weld metal as well as in the LTHAZ, particularly for the high alloy superduplex stainless steels.[14,43] The precipitation is mainly at δ/γ and δ/δ boundaries. Exposure in the temperature range 700–900°C results[44] in a more rapid precipitation in the weld metal than in the base metal due to the higher alloy content of the ferrite. The phases



8.9 Secondary austenite (γ_2) in a superduplex weld metal. Etch: electrolytic sulphuric acid, × 1000.

observed are σ-, χ- and R-phase, although σ-phase dominates. At lower temperatures, 500–600°C, the dominating phases are molybdenum rich R- and π-phases.[45]

8.3.7 Welding consumables

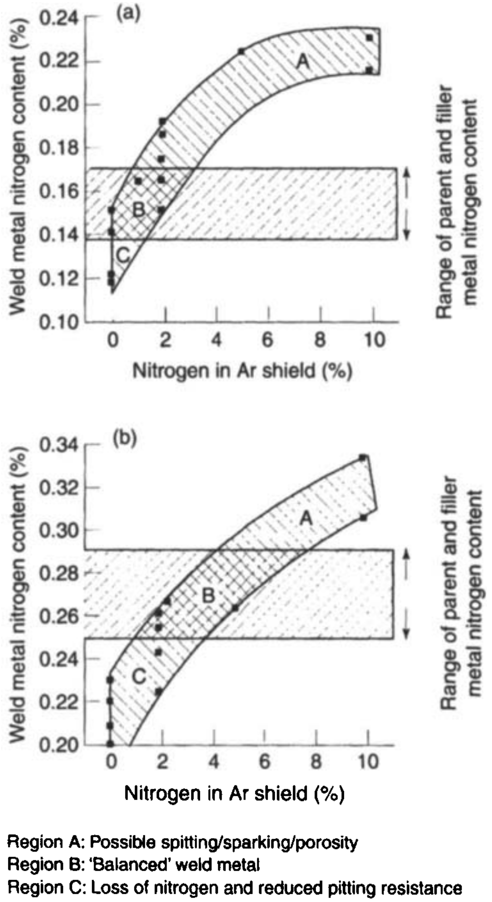
Welding consumables are normally overalloyed with 2–4%Ni to encourage the formation of austenite in the weld metal and to maintain the phase balance. In turn this helps to avoid the precipitation of nitrides and secondary austenite and improves impact strength and corrosion resistance. However, if the filler composition has a high austenite potential, there is a risk of promoting a ferrite/austenite solidification mode rather than fully ferritic solidification. This has been observed[46,47] for both 22%Cr and 25%Cr superduplex materials and results in increased segregation and reduced ductility. Nickel also seems[48] to have a minor adverse effect on corrosion resistance by changing the partitioning of certain elements. Another consequence of increased nickel contents, compared to parent steel, is that a postweld heat treatment may result in low ferrite contents.

If the dilution from parent steel is small, as in large welded sections, ferrite levels as low as around 20–25% may be measured,[13,49] which might affect the weld metal properties.[50] It has been shown[51] that this ferrite has higher Cr and Mo contents than solution annealed parent steel which makes it more prone to formation of intermetallic phase. Thus, to avoid such precipitation, a higher solution heat treatment temperature is necessary, or, if welded components are to be subjected to a postweld heat treatment, consumables with the same composition as the parent steel have been recommended;[41] the latter situation may arise with repairs of castings, for example.

For certain applications, nickel-base fillers may be chosen. The alloy 625-type, with approximately 21%Cr, 9%Mo and 3%Nb, has been used to achieve high pitting corrosion resistance in the root run weld metal. However, it has proven difficult to provide the same strength level, while maintaining corrosion resistance, toughness and ductility. Consequently, the use of nickel-base fillers, so regularly used for superaustenitic stainless steels, must be approached with caution for duplex stainless steels, and, in this regard, niobium-free variants may be preferred,[52] such as types C-276 and alloy 59.

8.3.8 Nitrogen bearing gases

As nitrogen influences weld metal microstructure and properties (see Sections 2.2.4, 3.2.2 and 10.5.3), it is important to control nitrogen during welding. When using nitrogen-free gases for gas shielded processes, the result is normally a nitrogen loss (Fig. 8.10), due to the low nitrogen solubility in the molten pool. The extent of this loss is dependent on the nitrogen content of the steel in question,[11] the arc length (voltage) and arc energy.[53] To solve this problem, commercial binary and tertiary (with He) mixtures are available for use as shielding or plasma gases (0.5–2.5%N). Their



8.10 Effect of nitrogen level in Ar shielding gas on GTAW weld metal nitrogen content (after reference 56). (a) S31803/S32205 steels and (b) superduplex steels.

use can prevent nitrogen loss and even result in an increase in weld metal nitrogen content.[54–57] The nitrogen transfer to the weld metal increases with the nitrogen content in the shielding gas according to Sievert's Law,[58] i.e. 'The solubility of molecules that dissociate during solution, varies as the square root of the pressure.'

Nitrogen additions to the shielding gas can be used in gas tungsten arc welding (GTAW), gas metal arc welding (GMAW) and plasma arc welding (PAW) and have been employed in the oil and gas industry with varying success. Normally the nitrogen loss is negligible when using slag-shielded processes, particularly SMAW.[59] The slag layer can be very effective in protecting the molten pool from emitting nitrogen.

GTAW welding with a shielding gas of different nitrogen partial pressures results in substantially higher nitrogen level than the equilibrium values at 2000°C and 1600°C in 22%Cr and 25%Cr grades respectively.[55,60] This probably explains why there is no noticeable enhancement of nitrogen in the weld metal by having nitrogen in the backing gas.[59] Further, it would appear that different levels of nitrogen in the shielding gas are appropriate for different duplex grades. For instance, the presence of some 0.5% to 1.5%N is required[53] to prevent loss in 22%Cr manual GTAW deposits, while between 2% and 4%N seems necessary for similar superduplex weld metals (Fig. 8.10). The use of nitrogen-containing shielding gas to control nitrogen in the weld metal is very attractive in automatic GTA and GMA welding,[61,62] particularly in cases where filler addition is limited.

Porosity

Too much nitrogen can lead to weld metal porosity. The nitrogen solubility in the liquid phase increases as the temperature drops, which ensures that there is no risk of pore formation during the liquid state. In contrast to austenitic stainless steels, nitrogen solubility is lower in the solid state thus providing a risk of pore formation during solidification. The probability of formation is dependent on welding parameters and alloy composition/solidification mode. For instance, it seems that longer arc lengths (high arc voltages) are detrimental. This is presumably a function of the increased probability of air ingress into the shield, which can effectively enhance the nitrogen content of the shroud. This also explains why some workers[61] have been able to use high nitrogen contents in the shield (up to 10%) where the arc length is kept short as in mechanised GTA welding. Further, it seems that the weld metal nitrogen content increases along the weld length, possibly increasing the chance of porosity.

Superduplex stainless steels having high chromium and molybdenum contents can be welded with up to about 0.30–0.35%N without porosity (Fig. 8.10). The maximum nitrogen level for alloy S32205/S31803 is approximately 0.20–0.25%N, while the low alloyed grade S32304 can only tolerate about 0.15%N. It has been stated that weld metals produced with fillers overalloyed with nickel exhibit[63] a lower nitrogen solubility than the parent material.

In some instances of multipass GTAW joints using gas mixes with relatively high proportions of nitrogen, there is an increase in weld metal nitrogen content in successive passes. In the extreme, this can lead to porosity in the subsequent passes. This may be explained as hot and fill passes have low dilution from the parent steel and thus the weld metal nitrogen content depends on the nitrogen content of the gas and of the previous pass. And so, if the previous pass is close to the nitrogen solubility limit, the following pass may become super saturated and produce pores. For this reason, it has been recommended that certain Ar-N_2 mixtures be only used for root and hot passes with a switch to pure Ar during joint completion.

Other problems with nitrogen gases

Contamination and wear of the tungsten electrode when using nitrogen-bearing gases[56] can be explained by the emission of very fine weld metal droplets from the weld pool,[64] known as sparking. This effect is thought to be due to out-gassing of nitrogen from the weld pool and is more likely with higher nitrogen contents in the shielding gas As the superduplex steels have the higher solubility limit, sparking and electrode wear is less likely for these steels. Nevertheless, at such high nitrogen levels, weld metal 'spitting' can take place, which can lead to a crevice on the parent steel and subsequent localised corrosion in service.

8.4 Fabrication cracking

8.4.1 General

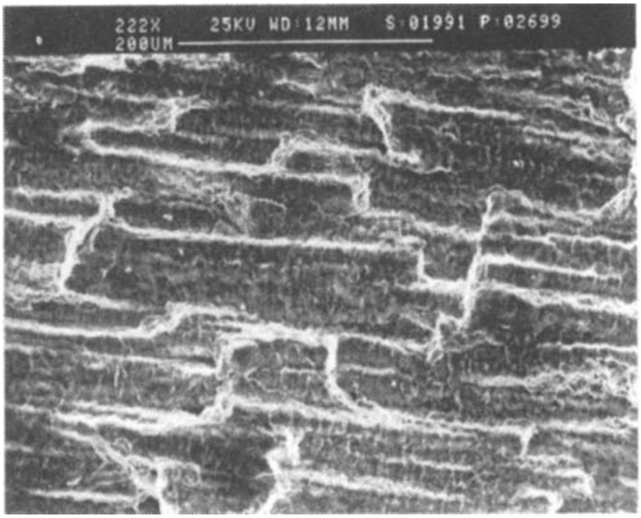
Duplex stainless steels are more resistant to solidification cracking than austenitic grades. Further, as the risk of hydrogen cracking is low for duplex alloys, the ferritic steel requirement for preheating and PWHT is not normally necessary. One exception for duplex

8.11 (a) Example of a solidification crack: transverse view. Etch: magnetic colloid, × 100.

alloys occurs in thick section products including castings. Nevertheless, both forms of cracking can occur, if simple precautions are not adhered to.

8.4.2 Solidification and liquation cracking

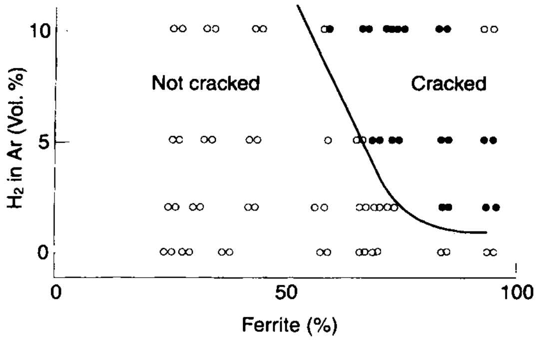
Varestraint tests show that commercial duplex stainless steels are less susceptible to weld metal solidification cracking than austenitic alloys with primary austenitic solidification. However, austenitic stainless steels that solidify as primary ferrite have higher resistance to solidification cracking than the duplex stainless steels.[3,65] The general practical experience is that solidification cracking is not a significant problem for the duplex stainless steels, albeit that, in



8.11 (b) Example of a solidification crack: fracture face. SEM image, × 220.

highly restrained constructions, hot cracking may occur, e.g. heavy section submerged arc welds.

It is well established[66,67] that austenitic stainless steels having a primary ferritic solidification are less susceptible to solidification cracking than those which solidify primarily as austenite. The beneficial effect of the ferritic mode is often ascribed to the greater solubility of impurities like sulphur and phosphorus in the ferrite. In addition, solidification shrinkage and thermal expansion are less marked. A solid state transformation to austenite just below the solidus gives an increased grain boundary area and reduces the risk of low melting point elements wetting the δ/δ grain boundaries. This phase transformation might also have a crack arresting effect by making the propagation path more irregular. As duplex stainless steels solidify to ferrite, the austenite formation occurs solely in the solid state. This may reduce the beneficial effects of austenite formation on solidification cracking hindrance, and it has been shown that compositions solidifying in a ferritic mode (5–20% ferrite) can be susceptible to solidification cracking.[67] Some workers have even stated that alloys with higher ferrite content, e.g. the current duplex steels, have a coarser columnar structure and are more likely to exhibit solidification cracks,[65,68] as shown in Fig. 8.11.



8.12 Effect of weld metal ferrite content on the susceptibility to hydrogen cracking with Ar + H_2 shielding gas (after reference 75).

The occurrence of HAZ liquation cracking in duplex stainless steels has been evaluated.[69] It was shown that the susceptibility is roughly comparable to that of austenitic steels with low ferrite levels. This indicates that duplex steels have good overall resistance to HAZ liquation cracking under low to moderate restraint conditions. In fact the editor has had no reported practical instances of this cracking mechanism in duplex alloys.

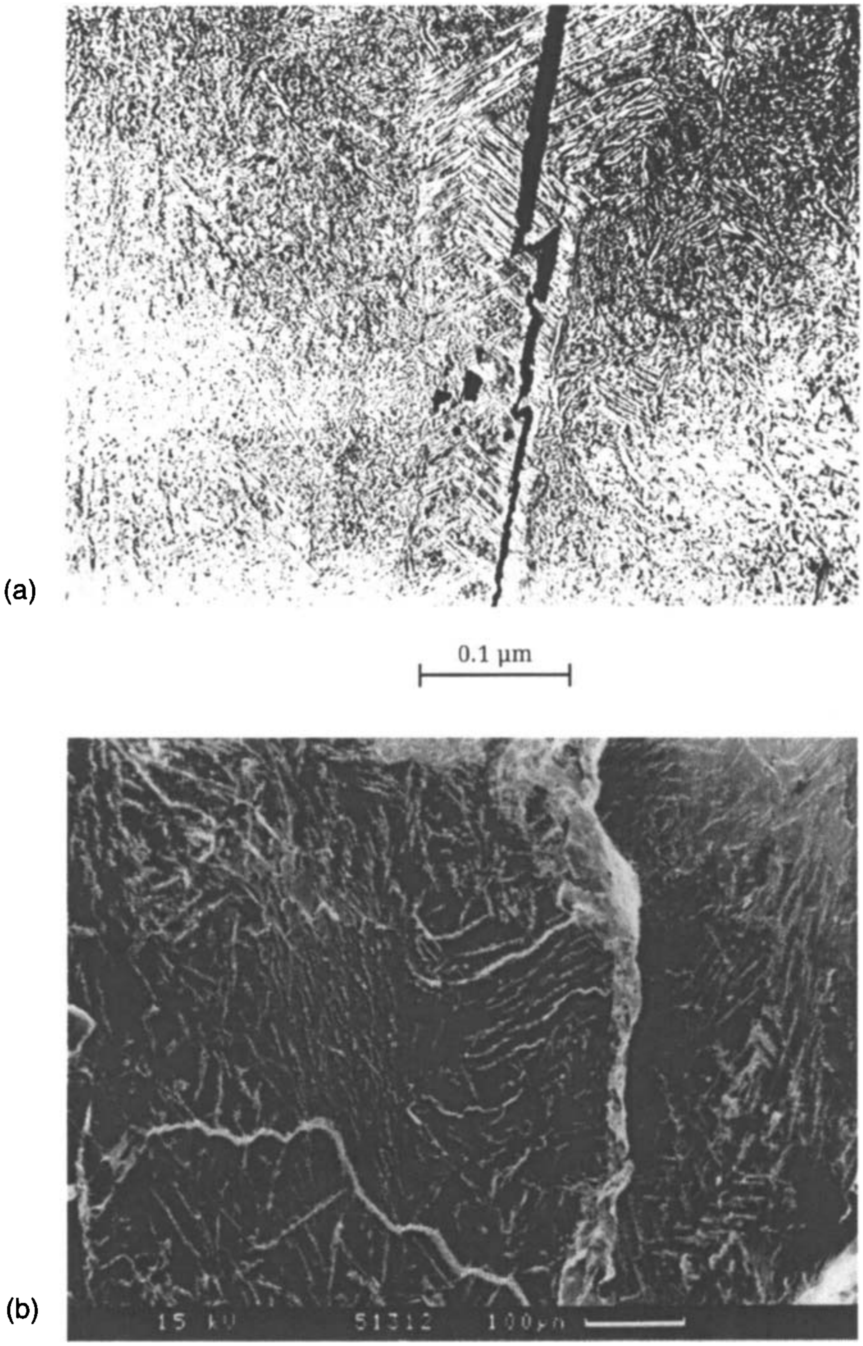
8.4.3 Hydrogen cracking

Hydrogen can be absorbed in the weld pool due to:

1. Contamination of the weld joint.
2. The presence of hydrogenous material in electrode coatings or submerged arc flux.
3. The use of hydrogen addition to the shielding gas.

High weld metal hydrogen contents can be avoided by baking SMAW electrodes at appropriate temperatures, but inadequate drying can result[70] in sufficient diffusible hydrogen to cause weld metal cracking in high ferrite welds.

In automated welding of austenitic stainless steels, such as on tube mills, hydrogen-bearing shielding gases are used to increase penetration or travel speed. They are used also, with good results,[56] in the longitudinal welding of duplex tubes. At the same time, seam welded tubes are normally given a rapid heat treatment, which will promote hydrogen diffusion out of the solidified material, since 2–10% hydrogen in the shielding gas during GTAW welding can



8.13 Example of a hydrogen crack. (a) Transverse view. Etch: electrolytic sulphuric acid, × 200. (b) Fracture face. SEM image.

result[71,72] in hydrogen cracking in as-deposited weld metal. This delayed cold cracking occurs after a certain incubation time in highly restrained welds and if the ferrite content is above 50–60%, as shown in Fig. 8.12. As with nitrogen, hydrogen in the root gas does not seem to give any absorption in the weld metal.

The diffusivity of hydrogen in the ferrite is much higher than in the austenite and the solubility of hydrogen in the austenite is 30 times higher than in the ferrite.[73] The ferritic matrix provides a rapid transport of hydrogen to the austenite islands which act as a barrier to hydrogen escape. However, trap occupancy is the factor in relation to cracking, with the ferrite–austenite boundaries acting as the dominant trap sites.[74] And yet the influence of the austenite phase dominates and so cracking tends to occur in the ferrite. (Fig. 8.13). If hydrogen pick-up during welding cannot be precluded, it may be possible to avoid cracking by preheating to 200°C, by soaking for about 100 hours at 200°C after welding, or by PWHT immediately after welding.[70–73]

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9 Welding processes

9.1 Introduction

All the common welding processes have been applied to duplex stainless steels with varying degrees of success. The more established processes include shielded metal arc welding (SMAW), gas tungsten arc welding (GTAW), gas metal arc welding (GMAW), submerged arc (SAW), flux cored arc welding (FCAW), and plasma arc welding (PAW). For these processes suitable procedure ranges are well defined, and filler metals, generally enriched in nickel as compared to the base metal composition, are widely available (see Appendix B). Other welding processes, generally characterised by very low or very high welding heat input, are used only for duplex alloys in specialised applications. These processes include resistance welding (RW), laser welding (LW), electron beam welding (EBW), friction welding (FW), and electroslag welding (ESW).

Modern duplex stainless steels can be welded to meet very high design and service requirements, but it is also shown that incorrect weld procedures can lead to failure of the component.[1] The choice of welding process and procedure depends on the material thickness, type of joint, other design factors and fabrication economics.

9.2 General considerations

9.2.1 Material handling and pre-weld procedures

Care should be taken to ensure that stainless steels do not come into contact with ferritic steels during handling. Cleaning brushes should be made from stainless steel wire and grinding wheels should not be used for any other materials, e.g. ferritic steels. Only approved marking pens shall be employed which have been shown not to support corrosion.

Pre-welding procedures should follow normal practice for austenitic stainless steels.[1] This includes joint design, joint preparation and cleaning of the joint area. Plasma cutting can be used in joint preparation, but it is recommended to remove heat affected areas

(1 or 2 mm) and oxides on the joint surface using machining and grinding. The heat conductivity for duplex steels is similar to austenitic grades (see Section 5.1), e.g. about 40% lower than ferritic steels. On the other hand, the thermal expansion coefficients for duplex alloys are slightly higher than ferritic steels and some 30% less than austenitic grades. This means that distortion of duplex weldments is greater than ferritic steels, but substantially less than for austenitic joints. This should be taken into account when drawing-up fabrication sequences.

9.2.2 Autogenous welding

Welding without filler addition (autogenous welding) is not normally recommended, especially for high quality, demanding applications where a solution anneal is not envisaged after welding. Notwithstanding this, thin section autogenous joints in the lower alloy grades (e.g. S31803 and S32304) have been used for less corrosive environments,[1] although specialised welding procedures must be used.

9.2.3 Consumable types

For demanding service, the need to obtain a satisfactory phase balance in the weld metal is paramount (see Chapter 8). One common approach, is to use a filler material (consumable) overalloyed with nickel, with joint design allowing for sufficient filler addition to minimise dilution from the base steel. Even then the weld metal may be prone to attack due to nitrogen loss and element partitioning. Thus, for aggressive environments, a superduplex wire is commonly employed for welding 22%Cr grades (S31803/S32205). Even higher alloyed wires are not available to weld the superduplex grades, due to the increased risk of intermetallic formation. Further, most welding wire frequently contains less nitrogen than the base material, due to manufacturing problems. Another approach is to weld without filler addition (thin walled products) or with a matching filler, but restore the phase balance and properties by a solution anneal.

9.2.4 Cooling time and arc energy

As discussed in Section 8.2.2, the key parameter for describing the effect of welding (austenite and intermetallic formation) is the cooling time between 1200 and 800°C ($\Delta t_{12/8}$). The cooling time is affected by several parameters, such as joint configuration, component thickness, arc energy and preheat and interpass temperature. Due to the complexity of calculating the cooling time, weld procedures are written in terms of more manageable parameters such as arc energy, interpass temperature and, in the case of SMAW, run out length. The first of these parameters is defined hereafter as:

$$\text{Arc energy (kJ/mm)} = \frac{\text{Voltage (V)} \times \text{Current (A)}}{\text{Travel speed (mm/sec)} \times 1000} \qquad [9.1]$$

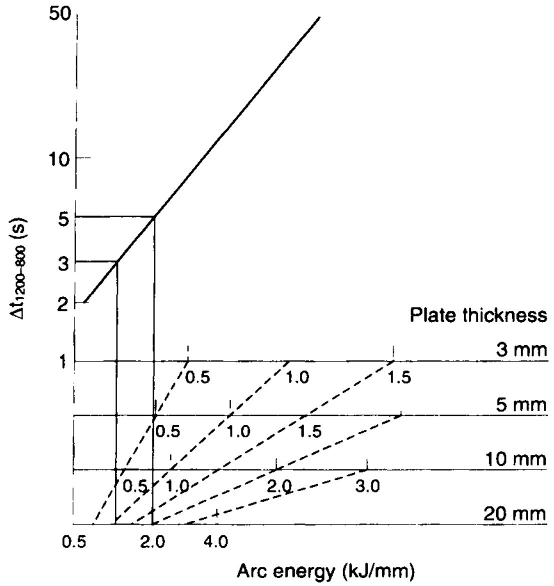
(NB. The term 'Heat Input' is defined as 'Arc Energy times Arc Efficiency'.)

The recommended arc energy 'window' depends primarily on the material type, e.g. 22%Cr (S31803) or superduplex grades, and thickness. For the 22%Cr grades, 0.5–2.5 kJ/mm has been recommended for 10–15 mm thick material,[2] which can be increased if the interpass temperature is restricted. An estimation of similar arc energy limits for other thicknesses can be made from nomograms, as in Fig. 9.1. Lower arc energies should be employed for the superduplex grades to prevent intermetallic formation. For these materials, common recommended limits are about 1.5 to 1.7 kJ/mm (15–20 mm thick).[3]

The arc energy throughout the joint should be balanced. It has been recommended that the arc energy of the hot pass should be about 80% of the root pass, while the arc energy of subsequent passes may be relaxed, say up to 130% of the root pass.[4]

9.2.5 Preheat and interpass temperatures

Preheat is not normally necessary, but slight warming of field welds may be recommended to above 5°C, in order to dry the joint area and avoid condensation. The maximum interpass temperature will depend on the grade concerned and arc energy employed. For the 22%Cr grades, such as S31803 and S32205, 150°C has been recommended for an arc energy of 1.5 kJ/mm and thickness of 10–12 mm, although this may be increased to 225°C if lower arc energies are guaranteed.[2] For the superduplex alloys, a maximum interpass



9.1 Nomogram for prediction of Δ_{12-8} for duplex stainless steels (after reference 18). Note: 3–5 seconds represents the maximum Δ_{12-8} for superduplex alloys (after reference 12). For guidance only.

temperature of 100 or 150°C has been stated,[3] which should be further restricted to 75°C for GTA welding thin walled pipes (less than or equal to 5 mm).[5]

9.2.6 Backing gas

For optimum corrosion resistance of the root run, a good back shield is essential to minimise oxidation (see Section 10.5.3). Although this practice is appropriate to all welding processes, it is of particular concern in gas shielded welding. To this end, the oxygen content in the back shield should be controlled prior to the start of welding[6] (<25 ppm). Further, most specifications require that the back purge be maintained until the root and hot pass, and sometimes the first fill pass, are completed. This is equivalent to the deposition of a weld height of some 4 to 6 mm before the back purge requirements can be relaxed or until the root region is kept below 250°C.[1] However, it is beneficial to reduce the gas flow rate slightly after the root pass of pipe welds, as otherwise an over-pressure may build up.[7] This is particularly important where the root bead is thin and is nearly remelted by the second bead, as this can result in a negative root bead or gas cavities. Needless to say, this situation will also be detrimental to phase balance and corrosion properties.

Backing gases with nitrogen have been examined and have produced good results in pitting tests[8] (see Figs. 10.9. 10.10, 10.11 and 10.12). Such gases can contain up to 100%N_2, such as formier gas (e.g. 90%N_2/10%H_2). However, the control of purge rate in the root is essential as, if these gases pass into the shield through the root gap, they can lead to excessive nitrogen and hydrogen contents. This can produce porosity, spitting, sparking and even hydrogen cracking.

9.2.7 Post weld treatment

After welding, the weld area should be properly cleaned. Chemical or mechanical cleaning methods can be used according to normal practice for other types of stainless steels,[1] especially austenitic grades. Different cleaning processes are assessed in Section 10.5.3.

There is normally no need for a postweld solution anneal, provided the correct consumable and procedure has been adopted. However, for areas which have been subjected to a high degree of cold deformation, more than 15%, it has been recommended that solution anneal and quench be performed (see Section 3.3). This recommendation is valid also when there are special demands on the microstructure of the joint, for instance in PAW or SAW longitudinal welding of tubes made with little or no filler addition.

9.2.8 Repair

Repairs in duplex welds should be undertaken with caution, as the weld repair operation essentially adds another heating and cooling cycle. It is recommended that a low heat input process be employed, e.g. GTAW, and that excessive weld removal be avoided. In other words, repairs in the root and hot pass should only be undertaken after qualification. Especial care should be paid to repairs in superduplex grades and for thin walled products it is probably necessary to cut-out and replace. All repair procedures should be qualified to the same requirements as the original joint. Further, the same root configuration should be employed for repairs, as were appropriate for the primary fabrication.

9.3 Gas shielded processes

9.3.1 Gas tungsten arc welding

Gas tungsten arc welding (GTAW) is employed for welding thin section tube and sheet (up to about 7 mm wall thickness) and for root runs (and second pass) in thicker products. Such joints may be completed using processes with higher deposition rates, like GMAW, SMAW, SAW, FCAW, etc. GTAW offers a high degree of control and usually gives a good quality root profile with mechanical and corrosion properties approaching the base materials (see Chapter 10), provided that dilution is controlled (around 30%). One approach to minimise dilution is to have a larger root gap than the wire diameter, which ensures that the welder adds sufficient filler.[9] The GTAW process ensures little slag formation during welding, which eliminates slag crevices and sites for corrosion attack. On the other hand, it is impossible to eliminate stop/starts and those areas where the welder has rested the arc while repositioning himself. These areas can be the most prone to corrosion attack, due to the extended thermal cycle.

When using pure argon to shield GTAW joints, the result is normally a nitrogen loss (Fig. 8.10), particularly with the superduplex grades.[10] However, additions of a few per cent of nitrogen to the shielding gas can result in an increase in weld metal nitrogen content.[11-13] For the 22%Cr grades (S31803/S32205) this equates to some 0.5 to 1.5%N in the Ar shield, while 2 to 4%N (bal. Ar) seems necessary for superduplex weld metal. It should be noted that too much nitrogen can lead to weld metal porosity, and spitting and sparking of the weld pool (see Section 8.3.8) and even a change in the solidification mode.[14]

There is a potential to increase joint completion rate by the replacement of Ar in the shielding gas by some He.[8,15] Helium produces a hotter arc through an increase in the arc voltage. For an arc energy identified as producing a suitable cooling rate, He in the shield can lead to an increase in the travel speed (if feasible) in proportion to the increase in voltage. However, too much He can make the pool difficult to control. In a similar manner to He, hydrogen additions to the shielding gas enhance the arc voltage and can be used to increase travel speed for the same arc energy as pure Ar. Nevertheless, the use of Ar-3%H_2 should be treated with extreme caution due to the possibility of hydrogen cracking.[4]

9.3.2 Gas metal arc welding

Mechanised pulsed gas metal arc welding (GMAW) has been used successfully in field welding of large diameter pipelines,[16] such as oil and gas transmission lines. Notwithstanding this, GMAW still has a reputation for lack of fusion and its use is precluded for critical applications by most engineering companies and operators. GMAW uses the same wire as GTAW, but does not seem to be as prone to nitrogen loss and frequently gives better corrosion properties.

There is some indication that pulsed GMAW is not as easily applied to positional welding of duplex stainless steels, as it is to austenitic stainless steels.[17] Good weld profiles have been obtained with a proprietary gas mix of 11%He, 0.4%CO_2, balance Ar. In addition, He-containing gases have been developed which have also shown good results.[19]

9.3.3 Plasma arc welding

Plasma arc welding (PAW) is not much used in fabrication, but has found use in longitudinal welding of tubes and fittings,[1] followed by a quench anneal. Economically this is a very tempting proposition also for butt joints, but many questions need to be answered with respect to the closing of the seam and the need for a quench anneal. This part has many of the same metallurgical properties as stop/start areas of GTAW joints and many of the same problems are expected. Although plasma welding of the standard 22%Cr steels seems to work well in some fabrication yards, considerable problems have occurred when welding superduplex grades. Sigma phase formation has been encountered with a loss of impact properties.

9.4 Flux shielded processes

For all flux shielded processes it is important to avoid moisture pick-up in the flux/coating which can lead to hydrogen cracking after welding. To this end, flux and electrode drying procedures and storage conditions should be carried out after consultation with the flux/consumable supplier.

9.4.1 Shielded metal arc welding

Shielded metal arc welding (SMAW) is the most common process employed in the UK to fill thick section joints, say 7 to 15 mm. This is mainly due the flexibility of the process and welder appeal. However, the selection of coating (or flux) type will be a balance between the joint property requirements (see Section 10.3.1) and ease of use. For instance, acid-rutile coatings are described as all-positional electrodes, but do not offer the best low temperature impact toughness. On the other hand, basic-type electrodes produce higher impact toughness but have lower welder appeal, partly due to the increased frequency of inter-run deslagging by light grinding or chipping. It is helpful to provide the welder with guidance on the electrode run out length in accordance with the arc energy requirements.

9.4.2 Submerged arc welding

Submerged arc welding (SAW) is an attractive process for larger pipes, vessels and heavier wall thickness components in general. Practical experience is generally good, although nitrogen-induced porosity and transverse and longitudinal cracks have been observed.[7] These cracks are not always easy to observe on X-ray films and can be the source of problems at a later stage. The longitudinal cracks are usually solidification (hot) cracks and can frequently be alleviated by small changes in welding conditions, such as reducing wire feed speed and travel speed together.

An additional consideration for SAW of duplex stainless steels relates to the recovery of alloy elements, especially chromium, depending upon the flux chosen. SAW fluxes for stainless steels are, in general, not well classified. Loose grouping of fluxes according to chromium and ferrite recovery in the deposit have been proposed,[18] as compared to measured chromium and calculated ferrite for the wire. Thus, fluxes high in silica (acid fluxes) consume chromium, so that the deposit chromium content is much less than in the wire and the deposit ferrite is correspondingly reduced. Typical reductions are 2–4%Cr.

A second group of fluxes is very low in silica (basic fluxes) and these recover nearly all of the chromium, so that typical reduction is 0.5–1.0% Cr, and the deposit ferrite content is nearly the same as would be predicted from the wire composition. The third group of fluxes is those containing metallic chromium additions (chromium compensating fluxes), so that the deposit chromium is increased slightly (or more than slightly) as compared to the wire composition. For these fluxes, the deposit ferrite content is greater than that calculated from the wire composition.

For duplex and superduplex stainless steels, the second group of fluxes (low silica, high basicity) would normally be preferred.[19]

9.4.3 Flux cored arc welding

Flux cored arc welding (FCAW) is an attractive alternative to pulsed GMAW and SMAW for positional welding. Such FCAW duplex stainless steel wires offer higher deposition rates, and permit the use of lower cost conventional welding power supplies and lower cost shielding gases.[20] In this regard, they have often been used with Ar-CO_2 gas mixtures which can produce a smooth stable arc.[1]

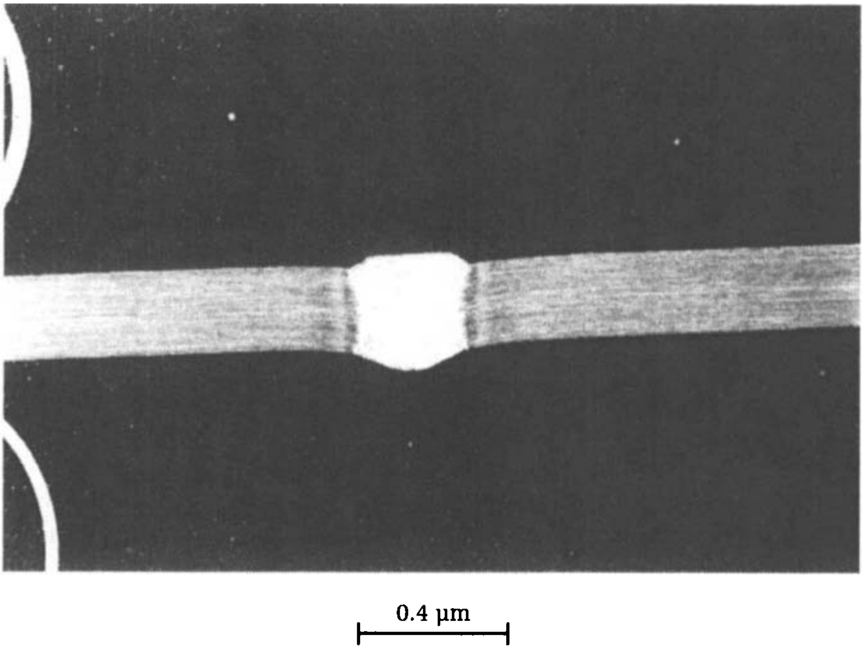
9.4.4 Electroslag welding

Toughness studies of simulated HAZ microstructures show that, in very slow cooling (2 °C/sec), as might accompany electroslag welding (ESW), both S31803 and S32550 experienced loss of toughness.[21] This has been attributed to a coarse ferrite grain size. But others have used both conventional SAW and ESW strip cladding of S31803 strip on mild steel at heat input of 9 kJ/mm.[22] As the strip employed was 60 mm wide, the heat input mentioned is not comparable to the 0.5 to 2.5 kJ/mm heat input range recommended,[23] because the heat is spread over a large area. Satisfactory results were reported in one, two, and three layers of overlay. Joints of 50 mm and thicker have been produced by ESW in grades S31500 and S31803.[24,25]

9.5 Solid state processes

9.5.1 Resistance welding

Very little is reported in the literature concerning application of RW to duplex stainless steels. However, in one study covering the fabrication of S32550 heat exchangers for the chemical industry, an unsatisfactory level of 99% ferrite was reported in the fusion zone,[26]



9.2 Cross-section of a resistance weld in 1 mm thick S32304 sheet. Etch: electrolytic sulphuric acid, × 10.

primarily a result of the low heat input and absence of filler metal. Similarly, when conventional RW schedules are applied to S32304 base metal (1 mm thick, 6.9 kA, 7 cycles of 50 Hz power, 4 kN force), the weld fusion zone was virtually austenite free, and the ferrite grains are very large[27] (Fig. 9.2).

With the introduction of an austenitic filler (25Ni-20Cr-4Mo-1.5Cu) between the sheets of S32550, and, by manipulating the welding schedule of the resistance welder, successful RW joints have been produced.[25] Alternatively postweld annealing can obtain suitable toughness and corrosion resistance.[24] To this end, annealing can be included in the RW schedule to obtain satisfactory properties. Other workers[28] reported successfully producing bimetal strips of S32304 duplex stainless steel and ordinary carbon steel by RW.

9.5.2 Radial friction welding

Joining duplex stainless steels by the one-shot radial friction welding (RFW) process can significantly increase production rates and reduce installation costs when applied to submarine pipelines.[29] Trials have shown that RFW joints produce high integrity welds in the as-welded condition, with pitting corrosion resistance almost equal to the base steel and with only a slight reduction in toughness and tensile properties.[30] Prototype RFW machines and procedures have been developed, which can weld pipe of 273 mm OD and 12.7 mm wall thickness. This technology has been applied to full rigid pipe-lay systems.[31]

9.6 Power beam processes

9.6.1 Electron beam welding

Electron beam welding (EBW) is especially suited to producing joints of heavy section materials (around 50 mm) in one or two passes. It tends to produce rapid cooling rates and therefore highly ferrite in the melt zone (91% ferrite in S31803),[32] particularly in thin sections. Nevertheless, the toughness remains high which can be attributed to the very low oxygen content in the weld. About 20% of the base metal nitrogen content is lost[33] and so with highly alloyed grades, it may be possible to design base metals for autogenous EBW, although this does not appear to have been done to date.

Other work has examined the use of filler additions using 0.15 mm thick 309-type or pure nickel SAW strips.[34] By varying the amount of strip added, satisfactory phase balances have been achieved in 50 mm thick S31803 and S32760 plates. The corrosion and mechanical properties recorded for the S31803 joint were found to be comparable to fusion joints.

9.6.3 Laser welding

Laser welding is an attractive process for the joining of thin sheet, as it can attain fast travel speeds. Similar to EBW, the low energy input of lasers tends to give fast cooling rates. Thus, autogenous laser welds in duplex grades will produce virtually 100% ferrite[35] and an anneal is recommended to obtain acceptable properties.[24] Alternatively, the use of filler additions and nitrogen-bearing gases should prove successful, although no published data on this subject have been reported.

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10 Weldment properties

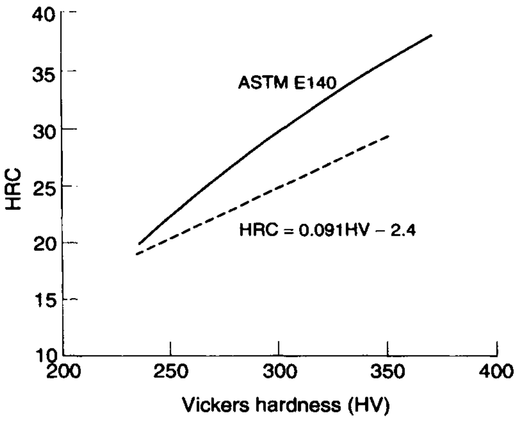
10.1 Tensile behaviour

Provided that suitable duplex fillers are employed, there is no real difficulty in meeting the tensile strength values specified for the parent steel over the temperature range normally used for duplex stainless steels.[1–4] Further, there is little change in the tensile properties over a wide range of ferrite levels in the weld metal.[5] If nickel-base fillers are used, the weld metal may be fully austenitic resulting in reduced tensile strength. Further, with high dilution from the parent steel there is a risk of intermetallic precipitation, which can jeopardise the ductility[6] etc. The elongation of the weld metal is normally lower than that of base metal, but values around 25% can be reached.[2,7] And yet, some examples of quite low ductility have also been reported.[8,9]

10.2 Hardness

The hardness of duplex weldments is often higher than base material (see Section 5.3.), due to the strain induced by the heating and cooling cycle. Further, there would appear to be an effect of alloy addition, as superduplex grades are invariably harder than lower alloy grades. The increase in hardness is manifest in both weld metal and HAZ, particularly in the root region. This strain induced hardening is caused by compression of the region during cooling and is a function of the number of weld passes, i.e. multipass welds in thicker material produce higher hardness values.[10]

As mentioned in Section 5.3, the hardness of parent material is of concern for cold worked material intended for service in sour conditions, where NACE standard MR0175[11] is invoked. In this standard, it is stated that the hardness of weldments should meet the same hardness limits as the base material, quoted in the Rockwell C scale (HRC). However, the Rockwell hardness measurement system (C scale) uses a relatively large conical indentor, which is somewhat coarse and not ideal for accurate measurement of discrete



10.1 Compilation of hardness data for a range of duplex parent materials and weldments showing the best fit line and ASTM E140[12] conversion for ferritic steel.

regions, such as small weld passes or narrow HAZs. For such purposes, a smaller Vickers indent is preferred. And yet, there is no standardised conversion between these two scales and so the ASTM E140[12] conversion for carbon steels is invoked. Figure 10.1 shows HRC and HV10 data for duplex materials, including different weldment regions. The figure demonstrate that the ASTM conversion is not appropriate for duplex materials. A line of best fit has been calculated[13] to cover duplex weldments, namely:

$$\text{HRC} = 0.091\ \text{HV} - 2.4 \qquad [10.1]$$

In NACE MR0175, several HRC limits are quoted depending on the duplex grade, its condition and environmental limits. These limits are presented in Table 10.1, together with estimated Vickers hardness equivalents determined from Eq. 10.1. It is recommended that, when duplex weldments are to be subject to sour conditions and SSCC of the base material is of concern, Vickers (or comparable technique) hardness survey of the weldment be undertaken and compared with the NACE standard using Table 10.1. If this does not induce confidence in the acceptability of the joint for service, then it is suggested that simulated environment tests should be considered, covered in EFC Publication 17.[14]

Table 10.1 Rockwell hardness limits from MR0175 and approximate Vickers hardness equivalents

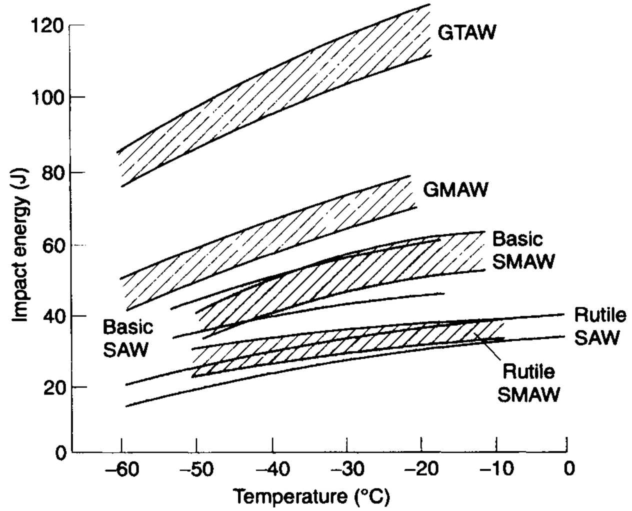
Rockwell hardness, HRC	Vickers hardness, HV10
17	213
20	246
24	290
28	334
32	378
34	400
36	422

10.3 Fracture toughness

10.3.1 Impact resistance

Normally, the absorbed energy is lower and ductile/brittle transition temperature (DBTT) is higher for the weld area compared to wrought base material[15] (see Section 5.4), particularly in the as-welded condition. For this reason, it is the achievable weld metal toughness that often settles whether duplex steels can be used for a particular low temperature application. As shown in Fig. 10.2, flux-shielded processes (e.g. SMAW, SAW) invariably have lower toughness compared to the gas-shielded methods.[16] These differences are mainly a function of the oxygen level in the weld metal and thus inclusion content.[5,7,17,18] This explains why deposits made with basic flux systems often result in higher toughness than rutile-types.

The influence of ferrite content on the absorbed energy has been reported to be negligible up to about 50–60% ferrite,[2,19] whereas there is clear negative influence at higher ferrite levels.[1] Further, there may be a negative effect of ferrite contents below 35%, apparently due to a change in solidification mode causing segregation and precipitation of intermetallic phase.[20,21] However, other investigations[17,22] show a progressive decrease in impact energy over a wider ferrite range. The general trend is that a slower cooling rate promotes austenite formation and increases toughness. Multipass deposits can also show a higher toughness as a result of further austenite formation in the reheated regions. On the other hand, excessive heat input or reheat, particularly in the superduplex grades, may cause precipitation of intermetallic phases which have an adverse effect on the toughness.[23] A PWHT can give a further

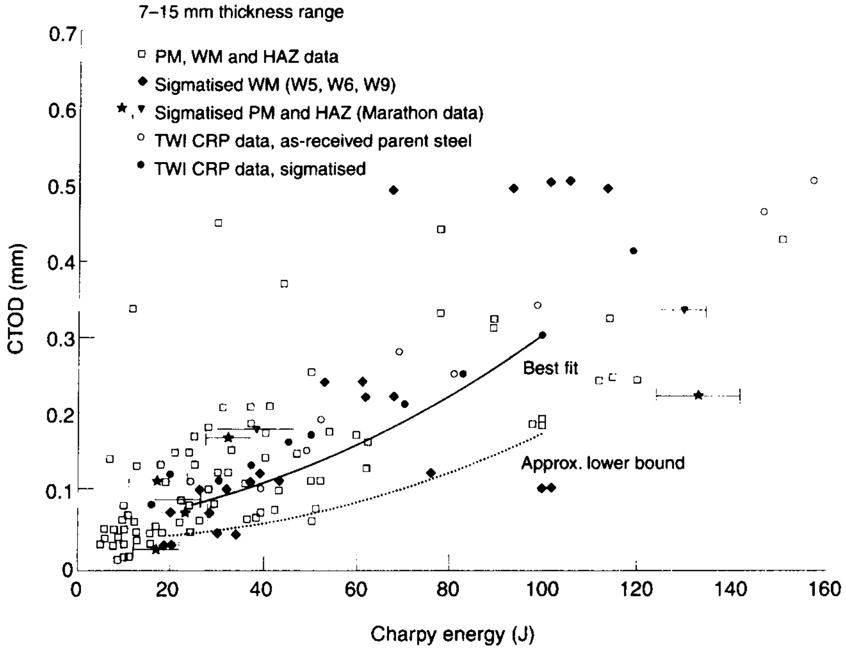


10.2 Variation of weld metal toughness with welding process and flux system (after reference 16).

improvement of toughness, if the phase balance is restored and precipitates are dissolved.[2]

Exposure of weld metals in the temperature range 600–900 °C will cause more rapid precipitation of intermetallic phases than for the base metal (see Section 8.3.6). This can result in a substantial reduction of toughness and must be controlled. It has been reported[24] that up to about 4% intermetallic phase can be present in wrought material without significant loss in impact energy (see Fig. 5.6). Comparable levels have been found also for weld metals.[25] However, as the initial toughness is normally lower in weld metals and the precipitation behaviour can vary considerably with time, temperature and morphology, it is difficult to set any acceptable level of precipitates for a given application.

The risk of 475 °C-embrittlement in weld metals appears to be higher than in the base material. The process is a spinodal decomposition of the ferrite and is mainly dependent on the alloy composition of the ferrite[26] (see Section 3.4.1). Due to a more austenitic microstructure the ferrite is richer in chromium and molybdenum than in the base metal. A practical implication of the accelerated embrittlement in the weld metal is that welded structures have to be limited to a lower maximum service temperature than the base material, 250 °C instead of 280 °C for 22%Cr steels.[27,28]



10.3 Correlation between Charpy and CTOD data for different duplex weldments, intermetallic contents and test temperatures (after reference 33).

The HTHAZ has a potential for high ferrite contents and low toughness, but, due to its narrow nature, it is difficult to assess the significance in practical welds. HTHAZ thermal simulations have demonstrated a reduction in toughness compared to the base metal and that the cooling rate has a definite effect on austenite reformation which in turn affects the toughness.[29,30] Subsequent thermal cycles with sufficiently high peak temperatures (> 800°C) have a tendency to recover toughness. Nevertheless, it is generally observed that the HAZ exhibits higher absorbed energy than the weld metal.[2,7]

10.3.2 Fracture toughness

Up until 1996, toughness criteria employed for duplex stainless steels were frequently based on properties and validation tests for lower strength ferritic steels, which show quite different transition behaviour. For this reason, the toughness requirements for duplex welds were considered to be too conservative. More recently, fracture toughness data for duplex weld metals and HAZs, measured via CTOD, have been shown to correlate fairly well with Charpy toughness data,[1,27,31–33] e.g. Fig. 10.3, although dependent on thickness. Also for quite low impact strengths, reasonable CTOD-values are obtained.

Given the correlation presented in Fig. 10.3, it is now possible to state more appropriate Charpy toughness limits for weld procedure qualification (WPQ), based on the fracture toughness requirements of a particular component at the service temperature. For instance, some workers[32] have proposed that Charpy energy requirements should comprise 35 J average, 27 J minimum, for thicknesses less than 35 mm, to be determined at the minimum design temperature not lower than −40°C. Other workers[33] have recommended a requirement of 40 J at the minimum operating temperature irrespective of thickness (up to a thickness of 50 mm). This last database includes specimens containing up to 8% intermetallic phases,[34] and shows that the correlation between CTOD and Charpy values still holds. These results indicate that the requirement to quantify the level of intermetallic precipitation from a toughness point of view becomes unnecessary, provided that appropriate toughness requirements are met.

10.3.3 Code requirements

Toughness requirements are laid down for duplex alloys in the pressure vessel codes: ASME VIII,[35] DIN AD Merkblatt HP5/2[36] and BS 5500.[37] As mentioned in Section 5.4, ASME is based on base material tests with the impact requirements dependent on material thickness (see Table 5.4). On the other hand, DIN considers service temperature with different absorbed energy requirements for weld metal and HAZ (see Table 10.2). The British Standard limits the low temperature use of duplex and superduplex steels, at present, to −30°C, with no requirements above 0°C, and 40 J average in weld

Table 10.2 DIN AD Merkblatt HP5/2 toughness requirements for S31803

Service temperature	Charpy requirement (J) WM	 HAZ
−10°C and above	40	27
−10°C and below	32	16

Table 10.3 BS 5500 toughness requirements for S31803 and S32760

Service temperature	Weldment* Charpy requirement (J)
Above 0°C	No requirements
0°C to −30°C	40 J average, 28 J min

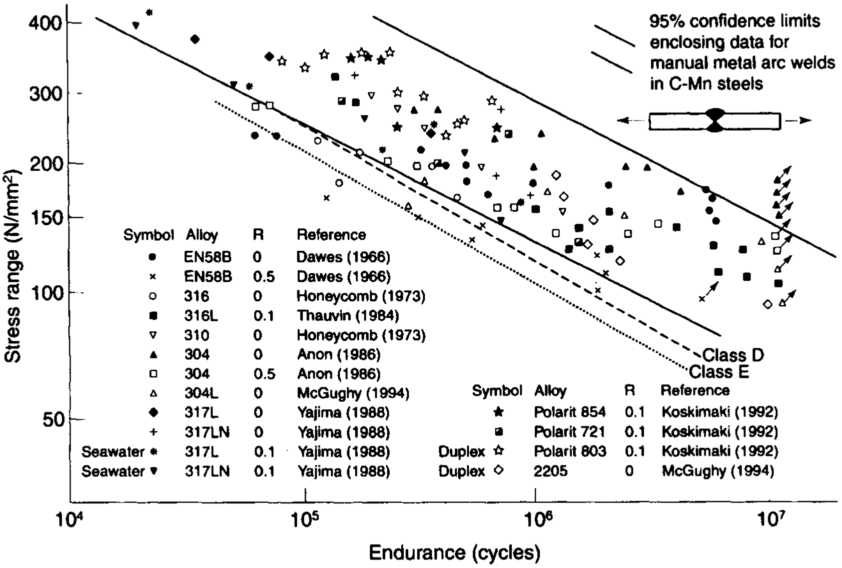
* Weld metal, fusion line and HAZ

metal, fusion line and HAZ for service temperatures between 0°C and −30°C (see Table 10.3).

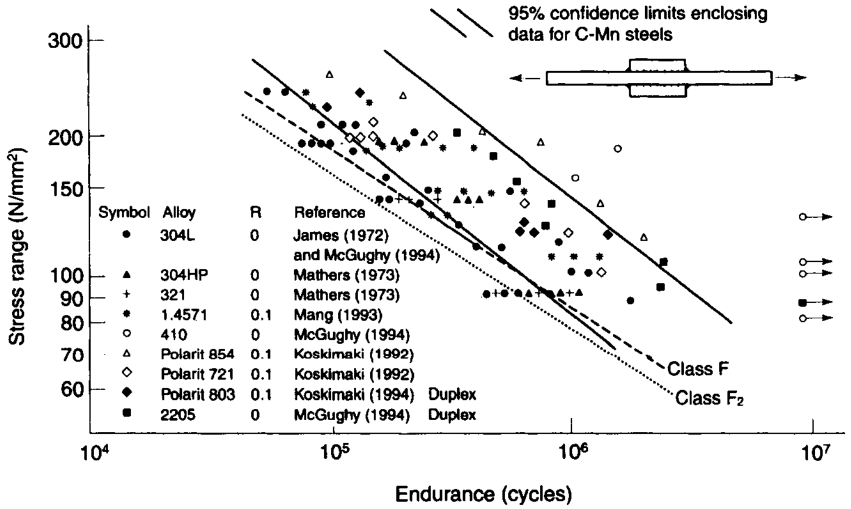
10.4 Fatigue

Owing to a high tensile strength, unwelded duplex stainless steels exhibit high fatigue strength (see Section 5.5). And yet there is limited information in the literature as regards fatigue of duplex welds. Some data for heavy sections joints made using the ESW, SAW and SMAW processes, and subjected to a postweld heat treatment, have shown no adverse effect of the welding on fatigue strength.[38–40] However, these data were generated using machined flat specimens in order to simulate particular applications for the pulp and paper industry. Nevertheless, many other applications will necessitate that the weld profile is left intact, which, while dependent on the joint geometry, is expected to significantly reduce fatigue life. Experience with austenitic weldments has shown that the poor fatigue strength can be attributed to three factors. First, even in good welds, flaws are present which act as fatigue initiation sites. This effectively removes any significant crack initiation period from the total fatigue life, which is spent almost entirely in the propagation of cracks. Second, in T-butt and fillet welds, there are sharp discontinuities at the weld toes which act as stress concentrators. The situation is often exacerbated by weld flaws at the toes, such as under-cut, intrusions etc. Third, large residual tensile stresses can be present in the weldment region and act perpendicular to the weld length. This has the effect of increasing the mean stress acting on the weld.

A recent review of the fatigue crack growth properties of stainless steel weldments,[41] included duplex data[42,43] from load-carrying butt welds (Fig. 10.4) and longitudinal stiffeners (Fig. 10.5). The results show no significant difference in behaviour between each detail and



10.4 Compilation of fatigue test results for transverse butt welds in stainless steels (after reference 41).



10.5 Compilation of fatigue test results for longitudinal non-load-carrying fillet welds in stainless steels (after reference 41).

the corresponding detail in austenitic stainless steels. Consequently, it was tentatively suggested that transverse butt welds in austenitic and duplex steels be assigned to Class E in the UK fatigue design code, BS 7608.[44] Similarly, it was proposed that the longitudinal stiffener detail be assigned to Class F_2 in BS 7608. It is interesting to note that the above recommendations amount to a down-grading of duplex alloys by one class, compared to similar details in C-Mn steels. However, further data and documentation is needed, in order that a better assessment on the performance of duplex weldments can be made. In particular, the influence of other joint geometries and the effect of corrosion-fatigue conditions both require attention.

10.5 Corrosion properties

Large quantities of welded duplex stainless steels have been produced over the years for a wide range of applications and, in general, have given satisfactory corrosion performance. However, there is potential for corrosion attack in the weldment region, because of the substantial metallurgical changes that occur during welding. The local composition and microstructure in weld metal and HAZ are crucial for resistance to corrosion in service. Most concern has been devoted to localised corrosion, e.g. intergranular corrosion, chloride pitting and crevice corrosion, and stress corrosion cracking.

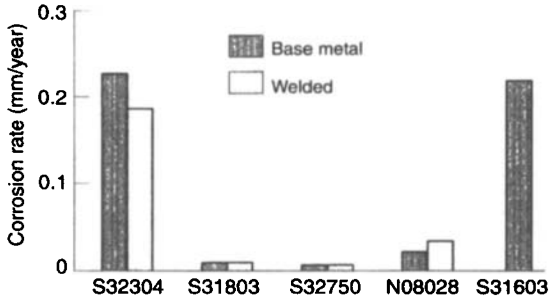
10.5.1 Intergranular corrosion

Intergranular corrosion (IGC) is associated with a fully ferritic HTHAZ in the older types of duplex stainless steels with very limited austenite reformation or possibly in modern steels subjected to thermal cycles with extremely fast cooling rates. Such a ferritic microstructure may contain chromium carbides or nitrides at the grain boundaries, resulting in susceptibility to localised attack of the chromium depleted matrix adjacent to the precipitates. The improved phase balance and, in particular, enhanced nitrogen levels mean that there is virtually no problem with IGC in the modern duplex stainless steels. However, caution must still be observed in terms of aspects giving rapid cooling like weld stop/starts, spatter etc.

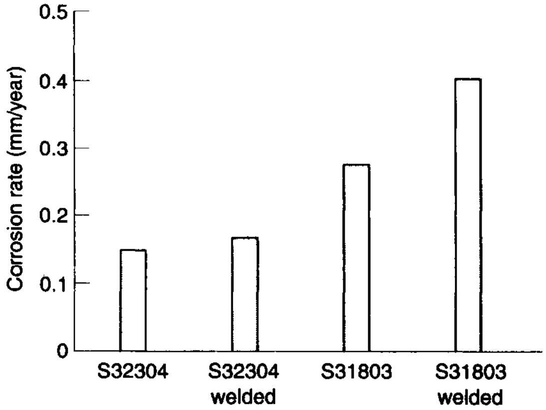
Sensitisation of the LTHAZ is less severe in duplex stainless steels than in austenitic steels for two reasons. First, the risk of carbide precipitation is greatly reduced in modern duplex steels by virtue of their low carbon contents. Second, any carbide precipitation will occur along the phase boundaries which are not linked in a continuous network, as the microstructure normally consists of a ferritic matrix with islands of austenite. The chromium carbides are formed mainly via chromium diffusion in the ferrite which can result in higher chromium level in the depleted zone compared to austenitic steel.[45]

10.5.2 General corrosion

Far less data is available on the performance of welds in general corrosion media, although it is inferred that their behaviour is similar to that of the base materials (see Section 6.2). The corrosion



10.6 Corrosion rates of base metals and GTA welded samples in a boiling mixture of 50% acetic acid and 10% formic acid (after reference 46).

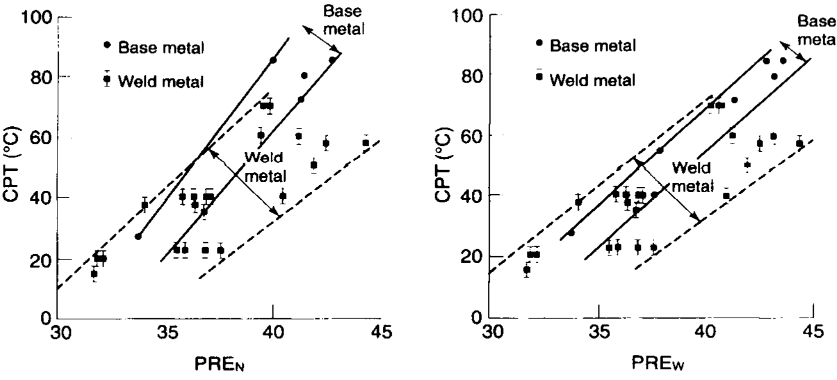


10.7 Comparison of base metal and welded sample corrosion resistance to boiling 65% nitric acid. Huey test, 5 × 48 hour periods (after reference 47).

resistance of welds in organic acids has been investigated (Fig. 10.6). The corrosion rates of welded materials exposed to a boiling mixture of 50% acetic acid and 10% formic acid are, in all cases, approximately equal to those of the base metals[46] (see Section 6.2.6). Similar data are available for boiling 65% nitric acid,[47] (Fig. 10.7). In this medium, the general corrosion resistance of the weldment is slightly reduced compared to the base metal.

10.5.3 Localised corrosion

The chloride pitting resistance of both phases can be optimised for the annealed parent steel by using thermodynamic databases and by adopting suitable factors for elements influencing the corrosion resistance[48,49] (see Section 6.3). To this end, the empirical PRE_N relationship appears to predict the ranking order for base steels. However, in a duplex weldment, a number of metallurgical reactions occur that can affect the local PRE_N value or make the conditions so complex that it is impossible to predict the pitting resistance by a single expression[50] (Fig. 10.8). The partial austenite formation creates substantial partitioning of important elements between the phases compared to the solution annealed material. Furthermore, precipitation of nitrides, intermetallic phases and secondary austenite may all contribute to a loss in pitting resistance.



10.8 Ferric chloride critical pitting temperature (CPT) data for a range of duplex and superduplex base metals and weldments against: (a) PRE_N and (b) PRE_W. (after reference 50).

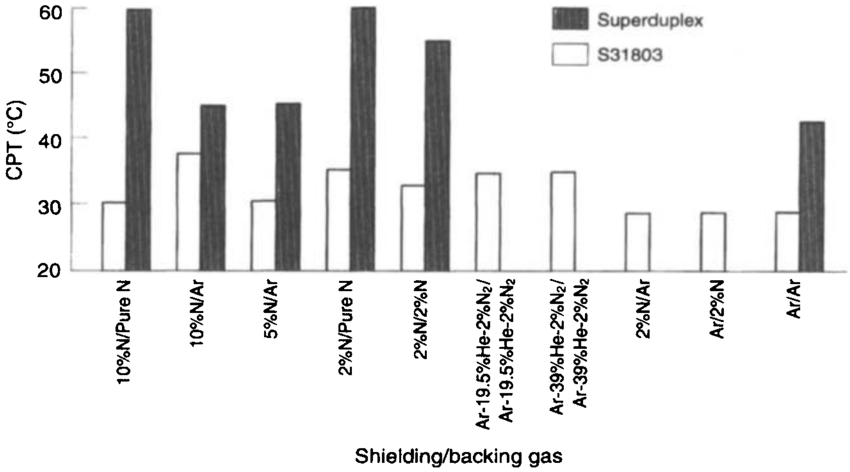
Many investigations show that the pitting corrosion rate increases[29,51–53] and the critical pitting temperature decreases with lowered heat input,[53,54] i.e. fast cooling rates. Attack can occur in the HTHAZ, due to a high ferrite content which encourages nitride precipitation, causing chromium depleted zones. Alternatively, as there is little time for element partitioning between the phases in the weld metal, the austenite contains similar Cr and Mo contents as the ferrite, but virtually all of the nitrogen. This situation renders the ferrite prone to attack.[55–57]

At sufficiently high arc energies (i.e. slow cooling rates), Cr_2N precipitation takes place in the remote LTHAZ and, for the superduplex grades, intermetallic phase precipitation can occur. Further, multipass welding can result in formation of secondary austenite with low contents of Cr, Mo and N and thus a lower pitting resistance,[19,58] if these precipitates are exposed to the environment. A PWHT can restore the pitting resistance,[2,3] although this should take account of the comments made in Section 3.3.

At intermediate cooling rates, element partitioning between the austenite and ferrite occurs within the weld metal. This provides the two phases with similar composition to solution annealed base material (see Section 3.2), although nitrogen remains concentrated in the austenite.[2,56] Further, austenite formation in the HTHAZ occurs, reducing the likelihood of nitride precipitation in the ferrite. Both factors lead to a more balanced weldment and can be described as the optimum condition for localised corrosion resistance.[51,59] In order to encourage this optimum condition, which, to some extent, can be translated into an optimum ferrite range, a more austenitic consumable is used, i.e. higher Ni-content. Nitrogen addition to the shielding gas can also have a positive effect[60] (Fig. 10.9).

The above findings illustrate that the parent steel pitting resistance is disturbed by fusion welding. This results in a reduction of the pitting resistance even if nickel-enhanced fillers and nitrogen-containing shielding gas are used. The greatest risk of poor performance exists in the root run where relatively high dilution from the parent steel and insufficient gas protection may prevail. To overcome this problem, welding consumables with higher PRE_N could be used. It has been shown that a duplex filler with a PRE_N value 2–3 units above that of the parent material is sufficient to obtain equal pitting resistance.[61] To this end, the practice of using superduplex consumables to weld 22%Cr grades (S31803/S32205) has become commonplace.

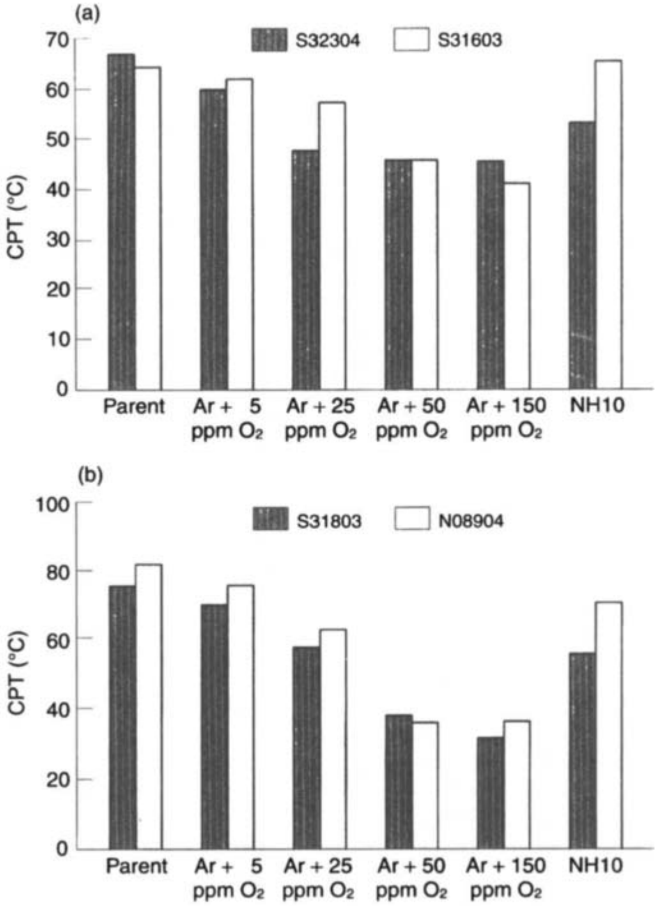
For superduplex steels, higher alloyed fillers will have a less stable microstructure and are more likely to precipitate intermetallic



10.9 Effect of shielding and backing gas on critical pitting temperature (CPT) of duplex weldments in ferric chloride solution (after reference 60).

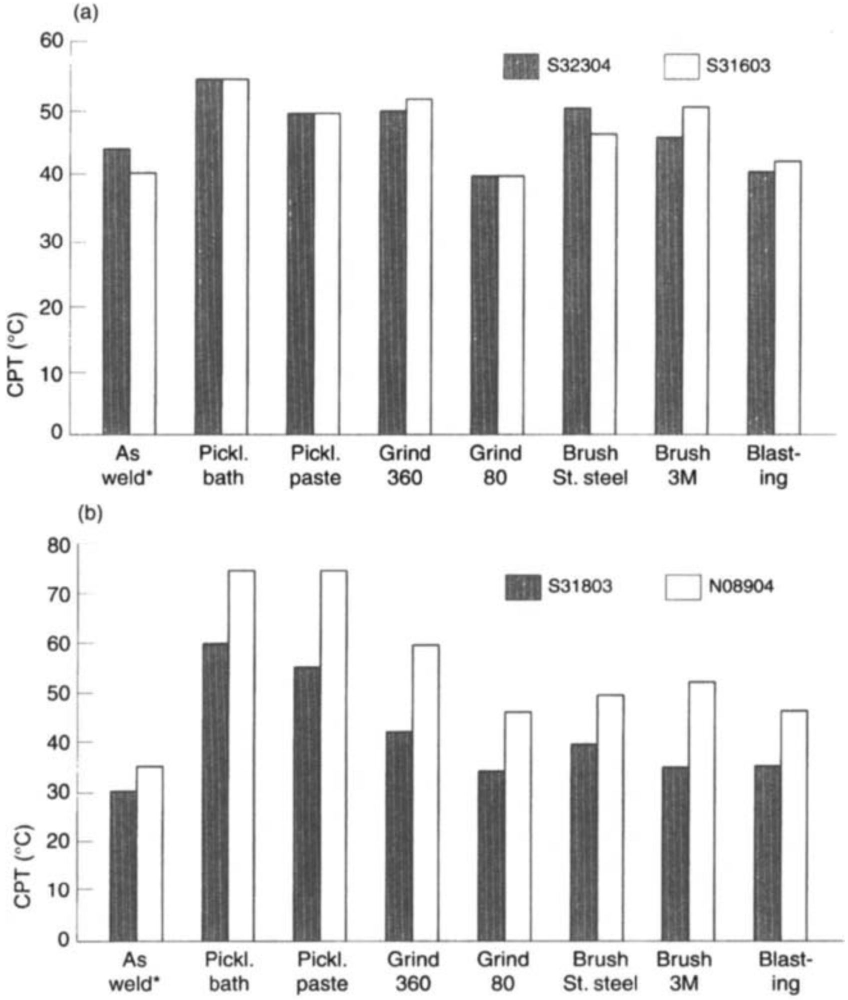
phases with an adverse effect on corrosion resistance. Also, austenitic nickel-base fillers with high chromium and molybdenum and high PRE_N can be used if the problems with toughness and fusion line precipitation are observed (see Section 8.3.7). The low nitrogen austenitic weld metal might act as a sink and drain nitrogen from the HAZ with reduced corrosion resistance as a consequence.

Surface effects, such as slag particles which act as crevices, and weld oxidation have decisive influence on the pitting corrosion. It is almost impossible to avoid oxidation even if proper gas protection is used. Weld oxidation is determined by the oxygen content in the backing gas, and the efficiency of the purge. The presence of only 25 ppm O_2 in argon backing gas is apparently sufficient to cause a significant reduction in pitting resistance of duplex steel[62] (Fig. 10.10). Pitting resistance can be restored by postweld treatment, i.e. brushing or pickling[62–64] (Figs. 10.11 and 10.12) although it should be noted that powered brushes can lead to the formation of microcrevices on the root run and produce erratic corrosion behaviour.[65] Further, postweld treatment of the root run may be impractical in many cases, e.g. root runs in pipe girth welds. In this respect, purging with pure nitrogen or $90\%N_2 + 10\%H_2$ have been used to

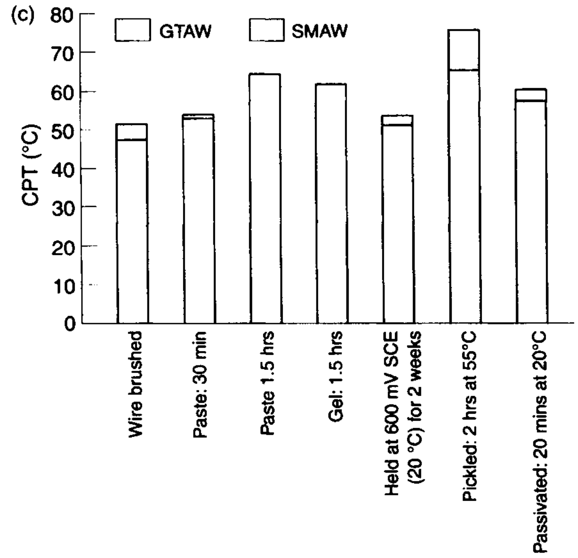


10.10 Critical pitting temperature (CPT) determined at +300 mV SCE for weldments with different backing gas oxygen contents (after reference 62). (a) Steels S32304 and S31603 in 0.1% NaCl solution and, (b) Steels S31803 and N08904 in 3% NaCl solution.

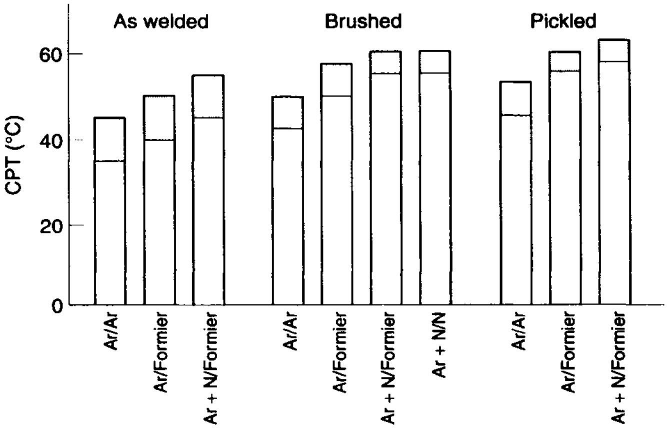
good effect[64,66] (Fig. 10.12). These gases produce a root region with reduced oxidation, a moderate increase in weld metal nitrogen content and a skin of austenite on the root run surface,[60] which is about 10 μm thick and presumably N-rich. But the potential problems associated with these gases should be noted (see Section 8.4.3).



10.11 Critical pitting temperature (CPT) determined for weldments with different postweld cleaning methods (after references 62 and 63). (a) Steels S32304 and S31603 in 0.1% NaCl solution at +300 mV SCE and, (b) Steels S31803 and N08904 in 3% NaCl solution at +300 mV SCE. (*Ar + 150 ppm O_2 in the backing gas.)



10.11 Critical pitting temperature (CPT) determined for weldments with different postweld cleaning methods (after references 62 and 63). (c) Superduplex steel S32760 in sea water at +600 mV SCE.

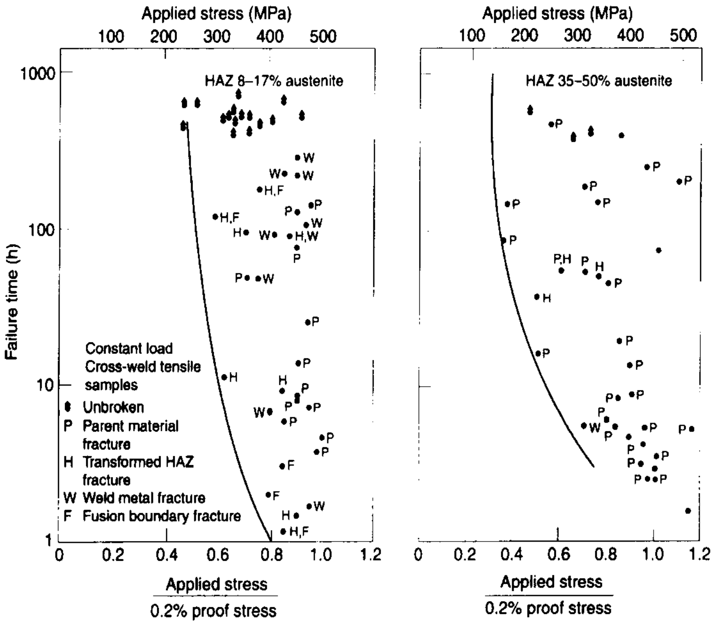


10.12 Compilation of critical pitting temperature (CPT) data determined in ferric chloride solution for weldments in superduplex steel S32750 with different shielding/backing gas combinations and postweld cleaning methods (after reference 64).

10.6 Stress corrosion cracking

10.6.1 Chloride SCC

As discussed in Section 7.2, the duplex stainless steels are frequently selected because of their high resistance to chloride SCC. In practice, welding results in both metallurgical changes and residual tensile stresses that may affect the SCC behaviour. Laboratory data have shown that duplex weldments with normal ferrite levels have similar resistance to base materials[1] (Fig. 10.13). Whereas service experience has indicated that welded S32205/S31803 duplex steel may crack at about 100°C under evaporative conditions,[67] with the cracking apparently being associated with the welds. The susceptibility of duplex steels to evaporative conditions has also been observed in laboratory drop evaporation tests.[68] In this test, standard austenitic steels also failed while higher alloyed austenitic steels showed significantly better resistance. Weld metals having very high austenite contents seem to be more susceptible to chloride SCC than welds with normal levels.[69] Cracking that initiated in high austenite



10.13 Compilation of chloride SCC resistance data for cross-weld tensile samples exposed to $CaCl_2$ solution at 130°C (after reference 1). Base steels: (a) 26%Cr:5%Ni:1.5%Mo and (b) 26%Cr:5%Ni:Mo:Cu:N.

weld metal has even been found to arrest at the HTHAZ which was high in ferrite.[70]

10.6.2 Sulphide SCC

The effect of ferrite content on hydrogen cracking is well known and has been evaluated for welds with varying results.[71-74] It would seem that SSCC is not controlled by a single mechanism, although it would appear that an optimum ferrite level is about 40–45%. Therefore, welding with good practice is not believed to deteriorate the resistance to cracking.[73] However, a high ferrite HAZ is reported to reduce the cracking resistance.[74] Tests with superduplex steels showed that the crack path is primarily in the ferrite phase by a hydrogen embrittlement mechanism and no clear difference in corrosion attack between weld area and base material was observed.[75] This supports the predominant observation that high ferrite levels are detrimental to the SSCC resistance. No doubt, the metallurgical changes taking place during welding will have some reducing effect on the cracking resistance (for instance the presence of intermetallic phases), although work to date implies that welded duplex steel components can be used in sour environments provided correct practice is followed.

The NACE standard for sour service places hardness limits on parent materials and requires that weldments meet the same limits. To this end, the reader should refer to the problems with hardness measurements and results covered in Section 10.2.

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11 Non-destructive testing of welds

11.1 Introduction

It is a common requirement to undertake non-destructive testing (NDT) of duplex welded joints. In most applications, it would be beneficial to enhance visual examination for surface breaking flaws with penetrant testing (PT) techniques, such as magnetic particle inspection (MPI), or eddy current testing (ECT). In other more integrity-critical applications, a volumetric NDT technique to detect buried flaws is necessary. Radiographic testing (RT) can be applied using techniques specified in national standards covering all steels. However, it is often advantageous to use ultrasonic testing (UT), as it is less disruptive to production and can be applied where the welds are too thick for RT to be practical. Further, UT is better for the detection of certain flaw types, e.g. cracks. Unfortunately, there are problems in the use of MPI, ECT and UT on welds in duplex stainless steel due to the metallurgy of such joints.

11.2 Penetrant testing (PT)

For surface examination, liquid penetrant testing (PT) is the traditional method and, in practice, the main method employed. Improved detection sensitivity is normally achieved with magnetic particle inspection (MPI), but this method can only be applied on magnetic materials. Duplex steels contain about 50% of magnetic ferrite, although this can vary significantly in welds. This means that duplex steels are less magnetic than ferritic steels, but more magnetic than austenitic steel on which MPI is ineffective. Although MPI is theoretically feasible for duplex steels, in practice, it has a much reduced capability.

Maximum relative magnetic permeabilities (Hr) for duplex welds of between 25 and 94 have been recorded. The British Standard for

MPI (BS6072:1981), assumes a relative permeability of 240, in specifying a field strength of 2.4 kA/m to achieve a flux density of 0.72 T. The implication is that with duplex, a significantly higher field strength is necessary to achieve a comparable sensitivity to flaws to that achieved with ferritic welds. However, the difference in relative permeability between parent and weld metal, and between the austenite and ferrite phase boundaries, is likely to give rise to spurious indications, especially if the field strength is greater than 2.4 kA/m. It is recommended that these limitations be taken into consideration if MPI is specified.

11.3 Eddy current testing

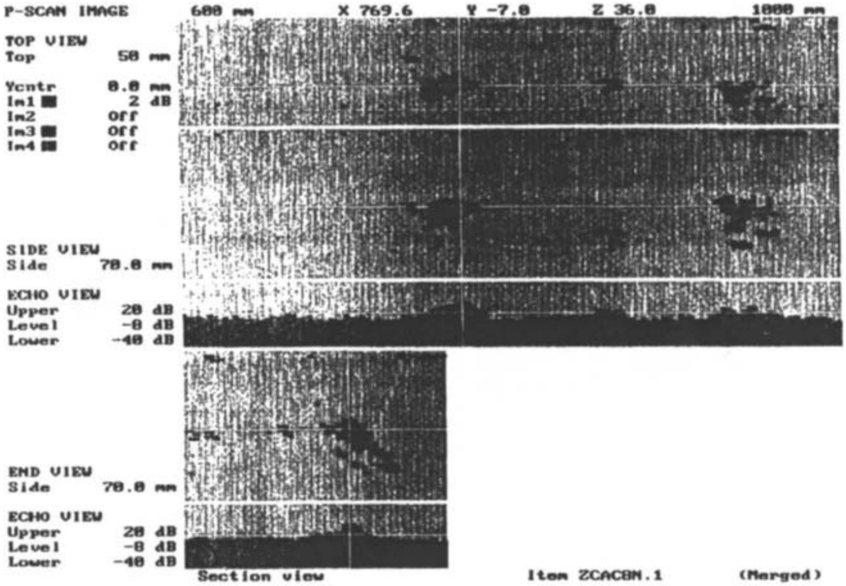
Eddy current testing (ECT) is affected by the characteristic changes in magnetic permeability across a duplex weld. This can give rise to much larger indications than the changes in conductivity due to a flaw: i.e. the signal-to-noise ratio may be too poor. The relatively high magnetic permeability of duplex compared to austenitic steels, produces high noise levels which make 'flaw' detection difficult. Techniques based on novel probe designs may have some potential, but conventional techniques are not recommended. Computerised field measurement and electromagnetic array systems have a demonstrated capability for flaw detection in ferritic steel welds. These may prove more effective than conventional ECT for applications in duplex.

11.4 Radiographic testing

Traditional X-ray examination (radiographic testing (RT)) is relatively straightforward for duplex alloys and so techniques employed for ferritic and austenitic steels can be employed.

11.5 Ultrasonic testing

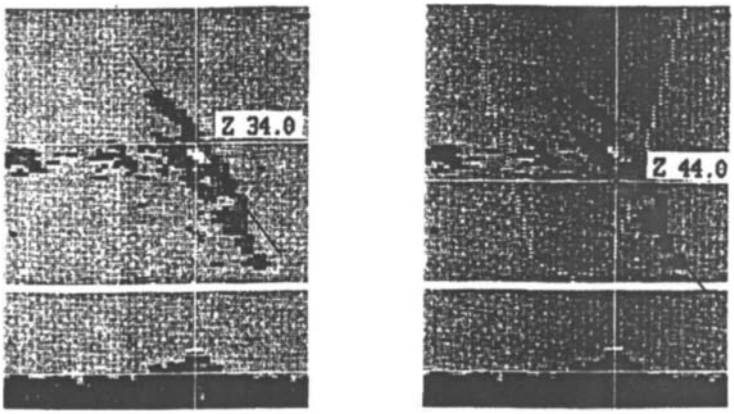
Stainless steel welds are anisotropic, i.e. they have different ultrasonic testing (UT) properties in different directions. The UT properties of a duplex weld are therefore strongly influenced by the grain structure which in turn depends on welding process, weld procedure and composition. The net result is that:



11.1 P-scan image of a simulated centreline crack in a 70 mm thick super-duplex weld (S32760). (4 MHz, single crystal, 60° compression probe from one side (cap side) of weld only) (after reference 3).

1. Weld metal anisotropy means that the velocity and attenuation of ultrasonic pulses propagating through the weld are a function of the orientation of the beam to the predominant axis of the grains. Hence, the beam (particularly if shear wave) will tend to be skewed through the weld volume and indications can be plotted-out in the wrong position.[1]
2. The boundaries between the large grains give rise to scattering and mode conversion of the ultrasonic energy which manifests itself as high levels of noise or grass and a high degree of attenuation through the material.[2] This makes flaws more difficult to detect.

Nevertheless, UT can be an effective detection (Fig. 11.1) and sizing (Fig. 11.2) method provided that special techniques,[3] based possibly on angled compression probes, are developed. Clearly, it should be possible to group certain duplex weld designs together as having generic properties with respect to NDT procedures. However, this will not be possible until much more data are available. Presently, welds for which UT procedures are required should be considered

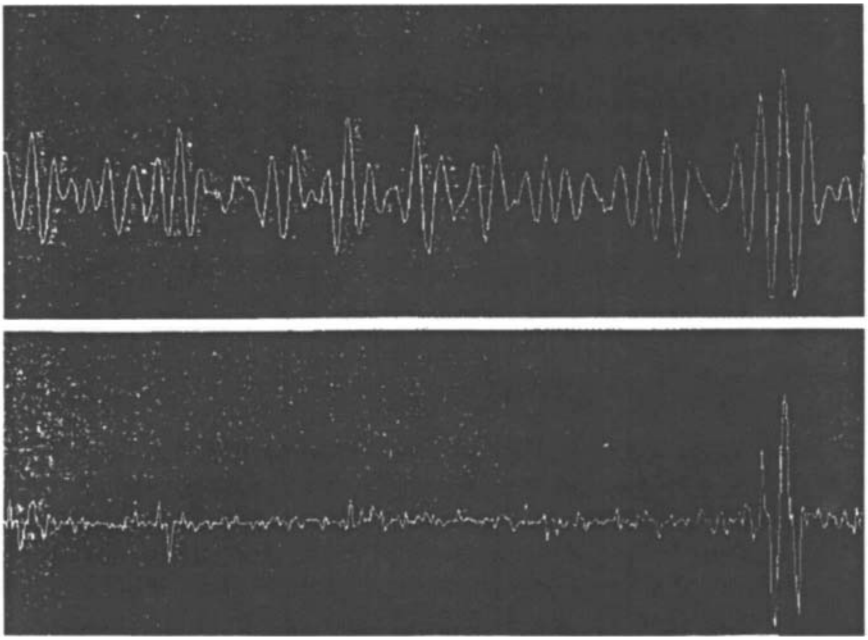


11.2 Through wall height sizing of simulated 10 mm high centreline crack from P-scan end views (after reference 3).

on a case-by-case basis. The same approach should be adopted as for UT of austenitic stainless steel welds, i.e. wherever possible the UT procedure should be developed and qualified on a representative welded test piece. Automated techniques can offer significant advantages over manual techniques for the ultrasonic testing of stainless steel welds.[4,5]

For automated UT, signal and image processing techniques exist, such as split spectrum processing, to enhance the S–N ratio of ultrasonic indications (Fig. 11.3). The precise algorithms required to achieve this may depend on the nature of the indication, the position of the indication in the weld and the design of the welded joint. Further, mathematical models exist to predict the path of ultrasonic beams through anisotropic grain structures, provided that the characteristics of the structure are known.[6] It is theoretically possible therefore to compensate for both grain noise and beam skewing.

The most important recommendation for effective manual ultrasonic testing (given an effective procedure) is that the operator be suitably qualified and experienced as special probes and techniques are generally required to achieve an effective inspection. Angled compression probes, for instance, may give rise to useful mode-converted signals such as self-tandem response or to spurious shear wave 'noise'. In other respects they can be used in a similar fashion to the way in which shear wave probes are used to inspect ferritic welds, for example characterisation of indications by analysis of



11.3 A-scan signal from a simulated lack of root penetration flaw in 70 mm thick superduplex weld (S32760). [4 MHz, single crystal, 45° compression probe] (after reference 3).

their echodynamic behaviour and sizing using 6 dB drop and maximum amplitude techniques.

11.5.1 Acceptance criteria

Acceptance criteria based on the characterisation and sizing of indications can be applied, although these should recognise that the errors in sizing and positioning of flaws are generally larger than for ferritic welds. A criterion based on amplitude is more difficult to achieve. Clearly, the maximum amplitude of indications that do not require evaluation/reporting must be significantly greater than the local grain noise to avoid 'false calls'. Further, it is normal to specify the evaluation/reporting level with reference to a repeatable standard such as a DAC level. The grain noise amplitude for a given probe relative to such a DAC is dependent upon the design of both the probe and the weld itself and is one of the factors taken into consideration when choosing a probe.

11.5.2 Scanning sensitivity

The amount of gain required during scanning will depend to some extent on the acceptance criteria. However, in the absence of prior knowledge regarding the amplitude with which deleterious discontinuities will reflect, it is recommended that the operator use a sensitivity at which grain noise is clearly visible (5–10% full screen height (FSH) for instance) on the timebase over the examination range.

11.5.3 Examination range

In most cases, it is recommended that the examination range be 0 to full skip for shear wave probes and from 0 to the range at which self-tandem signals occur (between half and full skip) for angled compression wave probes. However, scans performed at a fixed stand-off, such as root scans, may have an examination range starting just before and extending to just beyond the half skip range.

11.5.4 Probe choice

The weld grain structure, which is determined by weld process geometry etc., influences the UT characteristics. Favourable ultrasonic characteristics have been observed when the ultrasonic beam makes an angle of about 45° to the predominant major axis of the columnar grains in an austenitic stainless steel weld.[7]

Beam angles of 0°, 45°, 60° and 70° are recommended as standard. Whether shear or compression wave angled probes are optimum will depend on the weld design, as will the other probe variables (size, frequency etc.). Wherever possible, 'creeping' wave probes to augment the angle beam probes should be used to cover the following possibilities:

1. The thickness of the weld is such that 45° beams from one surface are too attenuated to detect flaws near to or breaking the far surface by use of the corner effect. A 'creep' wave probe should be scanned on the far surface.
2. In the root of an undressed single 'V' weld, it may not be possible to discriminate between root profile anomalies, such as excessive penetration, and planar root flaws, such as lack of root fusion or indeed cracking. A 'creeping' wave probe should be scanned on the root side of the weld.

3. It may not be possible to use shear wave probes and compression waves are not generally used beyond half skip, so a creeping wave probe may be required to achieve adequate near-surface coverage.

11.5.5 Coverage

Coverage is maximised if access is gained to, and the weld can be dressed flush on, both sides. If access to only one side of the weld is available, it is recommended that: (i) the cap (or indeed root) be dressed flush to allow for scanning of all angled beam probes right across the weld (as compression waves cannot simply be 'skipped' off the backwall) (ii) 0° probes are used to inspect the weld volume and (iii) angled beam probes are directed along the weld for detection of transverse flaws.

If access to only the cap side of a single 'V' weld is available for subsequent ultrasonic scanning, wherever possible, the root should be dressed flush. Otherwise it may not be possible to discriminate between root profile and planar root flaws. Further, if the weld is of thick section, access should be made from both sides of the weld, as the attenuation may be too great to cover the far wall adequately. In particular, this occurs with higher angle beams.

11.5.6 Time-of-flight diffraction

Without further image enhancement, the time-of-flight diffraction (TOFD) technique (in the so-called forward scattering configuration) is not recommended, as the tip-diffracted signals may be lost in grain noise when using 'standard' (divergent) TOFD probes.

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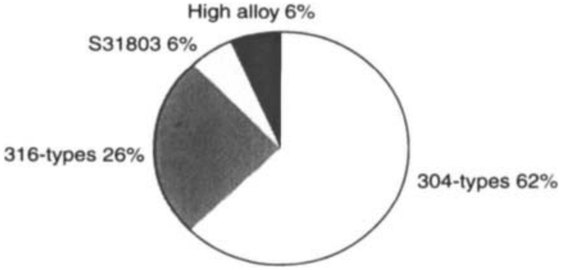
12 Applications

12.1 Chemical and petrochemical

Duplex stainless steel grades have found widespread use in the chemical and petrochemical industries, some of which are listed in Table 12.1. For instance, if pressure vessel materials are considered, then carbon and low alloy steels still maintain 65% of the market, leaving 35% for stainless steels and Ni-base alloys. Figure 12.1 illustrates[1] how the remaining 35% of the market can be subdivided, which presents the S31803 grade with 6%. This grade is chosen over the 300-series austenitic stainless steels, due to its higher corrosion and stress corrosion resistance in many environments, together with markedly higher tensile properties (Fig. 12.2) and only a moderate increase in price.[2] To this end, approval `has been obtained by major national and international vessel codes. (Refer to the listings at the end of this chapter.)

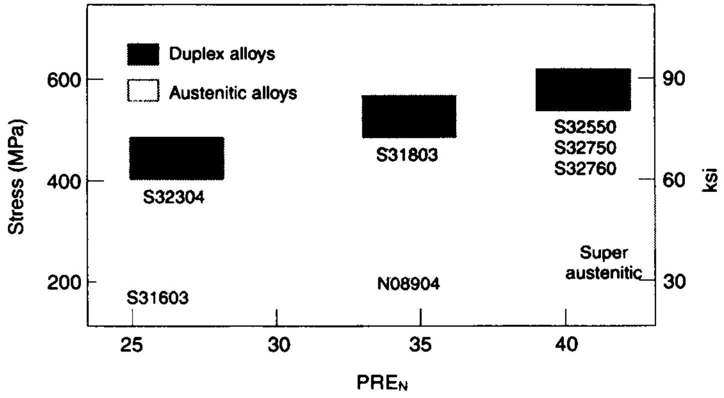
Historically, grades S31500 and S32304 have been used for clean duties replacing austenitic grades in hot aqueous chloride media.[3] Today, grade S32304 is selected for exchanger tubing in natural gas preheaters where low grade steam is used for heating purposes; while in nylon production, S32304 tubes are employed with S31803 tubesheets. For applications where higher chloride contents are present, e.g. brackish water, hot coastal conditions, both tubing and tubesheets are made from grade S31803/S32205.



12.1 Proportion of high alloyed pressure vessel materials used in the petrochemical industry (after reference 1).

Table 12.1 Applications of different duplex stainless steels by industry sector

Industry	Alloy lean 23%Cr	Standard 22%Cr	Alloy lean 25%Cr	Superduplex
Chemical	Piping; instrumentation tubing	Pumps; fans; centrifuges; sulphur melting coils; chemical tankers	Urea strippers; reactor agitators; heat exchangers	Salt evaporation tubing; pumps; amine equipment; sea water cooling systems
Petrochemical	Tubular reactors with a carbon steel shell	Desalination; desulphurisation; distillation	Pump casings; desulphurisation equipment	Tubes and pipes in chloride and HCl media
Pulp and paper	Digester preheater, evaporators; bleaching pulp storage tanks	Digesters in sulphate and sulphite plants; black and white liquor tanks; oxygen impregnators	Digesters; digester preheaters	Bleaching equipment
Power generation	Feed water heaters; reheaters	Injection pipe in geothermal wells		Heat exchangers and systems in geothermal wells and saline brines
Flue gas desulphurisers		Evaporation plant; centrifugal fans	Liners in evaporator towers	
Oil and gas	Coolers; piping systems; tensioning systems; instrumentation tubing	Flare booms; frame work; slotted oil liners; wirelines; down hole tubing; subsea flowlines	Diving bells; pumps	Heat exchangers and systems in geothermal wells and saline brines; sea water cooling systems; fire water piping; pumps; pressure vessels; valve blocks; down hole tubing; process piping and vessels



12.2 Comparison of the proof stress (R_p) and pitting resistance of duplex and austenitic alloys (after reference 2).

Grade S32205/S31803 has been used also for reactors, heat exchangers and storage tanks in the production of detergent, comprising fatty amines and chlorides; in plastic production, e.g. polypropylene; steam sterilisation of bioproducts and sodium cyanide production.[3]

For many years cast S32550 (J93370) has found applications in phosphoric (and sulphuric) acid production, where chlorides and fluorides are present combined with erosion and wear conditions, such as in pumps, agitator blades and shafts.[3] More recently, this grade has been employed for stud bolts in ammonia injectors; valve internals in urea recycle lines and pumps and valves in sulphuric and nitric acid duties.

12.2 Oil and gas

12.2.1 General

The use of duplex alloys for offshore applications predominantly started in the early days of the North Sea developments. The corrosive conditions which were encountered in this region negated the use of carbon steels and led to the selection of stainless steels. Duplex grades have been supplied for downhole equipment and wellheads, flowlines, umbilicals, process piping and vessels and mechanical components, such as pump parts, compressors and valves (Table 12.1). In particular, due to their high strength and good corrosion resistance, they have become ever more popular in high pressure systems, topside equipment, pipework, and blast walls, which, for offshore facilities, leads to a reduction in the topside weight. Presently duplex alloys are used with thicknesses up to 100 mm and with design temperatures down to −50°C. In general, they have given many years of trouble-free service.

12.2.2 Downhole and wellheads

Duplex steels have been used for downhole tubing with mixed success.[4] The earliest use dates back to the early 1980s with strength levels up to 965 MPa (140 ksi) being applied. Both 22% and 25%Cr grades have been used. For obvious reasons these steels are used primarily in the more corrosive wells and in most cases have been successful.

12.2.3 Flowlines

Duplex stainless steels are used for subsea pipelines and flowlines. Several lines made from S31803 have been in service for many years (Table 12.2) without any problems. It may be argued that these lines are not cold worked like tubing, but they do see a certain amount of deformation during the laying operation and contain residual welding stresses, as well as cathodic protection from sacrificial anodes.

The use of cathodic protection is necessary to protect the material from corrosion by the sea water, but does raise the general question of hydrogen embrittlement. Checks have been made on spools from flowlines and some ingress of hydrogen has been found, though the effect does not seem to be significant. This is probably due to the lower stresses in the pipe wall. In one test, hydrogen was found to have penetrated to a depth of about 2 mm in 2.5 years.[4]

12.2.4 Handling chlorides and H_2S

Duplex grades are used for handling brines and produced water, as well as sea water with chlorine additions. They are highly resistant to 'sweet' CO_2 process systems, even when low pH (2.5), high chloride concentrations (150,000 mg/l) and sand is present[5] with flow rates of up to 30 m/s. Further, duplex alloys are used for more aggressive applications where 'sour' hydrogen sulphide is produced. To this end, specific standards cover these applications such as NACE MR-0175 and EFC Publication No. 17. In the first standard, limits are provided in terms of environmental factors and hardness for different grades (see Tables 1.5 and 1.6), while the second provides an approach to qualify materials for the particular service conditions. The resistance of duplex materials to sour conditions is covered further in Section 7.3.4.

12.2.5 Other piping, vessels and equipment

Duplex stainless steels have also been used for applications which handle de-aerated water and oil/water mixtures such as heat exchangers in refineries.[6] In addition, experience for these steels in sea water applications is accumulating. The longest experience derives from pumps, compressors and valves on water injection systems. Here duplex stainless steels have been used since the initial operations of many fields giving more than 10 years good operating experience.

Duplex grades have been used for casings in water injection compressors and sea water lift pumps. The main reason for these selections was that duplex alloys meet the strength of the replaced ferritic steels. For this reason, it is still to be seen whether the good performance of duplex alloys is due to cathodic protection by the steel pipes or is inherent in the material. It should be noted that no problems have been reported with either fabrication or repair welds, but then most of these welds were heat treated. More recently, some operators have employed superduplex steels for sea water piping on a more general basis. Although little experience has been accumulated, early data are promising.

However, it should be noted that where the same pump has been deprived of cathodic protection it has usually failed by crevice corrosion, even in cold sea water.[4]

12.2.6 Bolting

One promising application for duplex steels is for bolting. Although further data are required, it looks like some of the duplex stainless steels have a significant potential here. Bolts in S32205/S31803 and

Table 12.2 Major duplex stainless steel flowlines

Project	Operator	Land/sea	Length (km)	Nominal dimensions‡	Country	Year
K8FA2–K8FA1	NAM	S	3.8	10″ × 10 mm	NL	1978
K11FA1–K8FA1	NAM	S	10.0	6″ × 6.2 mm	NL	1978
Cov 21–24	NAM	L	4.0	10″ × 6 mm	NL	1983
Cov 5–17	NAM	L	3.0	10″ × 6 mm	NL	1983
Cov 2–24	NAM	L	1.0	4″ × 10 mm	NL	1983
AME1 AWG1	NAM	L	4.0	20″ × 11.6 mm	NL	1984
Egmund–Wimmenum	NAM	L	8.0	2″ × 3.9 mm	NL	1985
Inde M–J	Shell Expro	S	3.3	12″ × 14 mm	UK	1985
Sean R–P	Shell Expro	S	4.8	20″ × 14 mm	UK	1985
K7FA1–K8FA3	NAM	S	9.0	12″ × 9.5 mm	NL	1986
Norg 2–3	NAM	L	4.0	6″ × 4.25 mm	NL	1986
LH/LA–LG	NAM	S	10.0	8″ × 9 mm	NL	1987
Cov 33–24	NAM	L	3.0	10″ × 8.3 mm	NL	1988
Brae A–C	Marathon	S	7.0	6″ × 14.3 mm	UK	1988
Tommeliten A–Edda	Statoil	S	11.5 in two sections of diff.wall thickness	Two 9″ flowlines 15.8 and 24.4 mm 6″ test line 15.4 and 24.6 mm	Norway	1988
Cov 20–21	NAM	L	3.0	10″ × 6 mm	NL	1989
Vries 2–4	NAM	L	4.0	6″ × 4.2 mm	NL	1990
K15FC1–K15FB1	NAM	S	9.0	10″ × 7.3 mm	NL	1990
Gannet	Shell Expro	S	16.0 each	Two 6″ × 14.4 mm and 4″ × 9.5 mm	UK	1991
Scott	Amerada Hess	S	Seven of total 16.0	6″ × 14.3–15.5 mm	UK	1991/2
Embla	Phillips	S	5.5	14″ × 11.1 mm	Norway	1991
Prudhoe Bay	Arco	L	4.5	24″ × 10.0 mm	USA	1992/3
			3.5	6″ × 6.35 mm*		

Point McIntyre	Arco	L	30.5	24" × 6.35 mm	USA	1992/3
			6.1	6" × 6.35 mm*		
Lisburne	Arco	L	3.0	6" × 6.35 mm	USA	1992/3
3C (replacing corroded Carbon steel)	Arco	L	3.0	24" × 6.35 mm	USA	1992/3
Pelican*	Shell Expro	S	17.2	200 mm ID × 11.7 mm	UK	1994/5
South Birch*	Lasmo	S	14.5	282 mm OD × 14.1 mm	UK	1995
Kadanwari	Lasmo	L	22.0	12" × 8 mm	Pakistan	1994/5
Sleipner West	Statoil	S	10.0	20" × 14.5 mm plus riser 20" × 17.4 mm	Norway	1995
	Clyde Petroleum	L	12.0	10" × 8.7 mm	NL	1995
Munnekezijl–Grijpskerk	NAM	L	6.5	18" × 12.7 mm	NL	1995
N'Kossa WHD1–WHD2	Elf Congo	S	3.9	18" × 17.45 and 20.6 mm	Congo	1995

‡Diameter values in inches are *nominal* API pipe dimensions for outside diameter. Correct diameter in inches and metric conversion are given in API 5L 'Specification for Linepipe'.
* = 25Cr duplex.

S32760 are in use,[4] which opens up the possibility of using piping systems at lower temperatures. One problem is the lack of data in the various codes.

12.2.7 Architecture

A considerable amount of duplex has been installed for architectural purposes, such as blast and weather walls. Generally speaking this application tends to favour the use of low alloyed grades like S32304, due to their lower cost. The experience to date is limited, but the indications are that the material fares no worse than S31603. Fortunately, there have been no cases where the properties of duplex stainless steels in fire or blast walls have been relied upon. Actual working experience is therefore thin on the ground.

12.3 Pulp and paper

Duplex stainless steels have been used in the pulp and paper industry since the 1960s, although it took several years before their advantages over austenitic grades became more widely appreciated. One of the first applications involved grade S31500 (3RE60) for suction rolls. Since 1974, it is reported that more than 50 Kraft batch digesters have been built, with either solid or clad duplex to S32205/S31803, with no maintenance required over a six-year period.[7] It seems that the combination of a high chromium, low nickel content stainless steel is beneficial for resisting attack in such media.[8,9] Similarly, superduplex clad plates to S32750 have been used successfully for chip prestreaming vessels in Kraft continuous digesters. Overall, duplex alloys find many applications in this industry sector (Table 12.1), including chemical pulping, bleaching, chemi-thermomechanical pulping (CTMP), pulp storage tanks, paper machines, recovery and steam plant.[10]

12.4 Power generation

Due to the embrittlement of duplex alloys during extended exposure to temperatures above 300°C, their applications are limited to temperatures below this. The main use of duplex in the power generation industry would appear to be where sea water cooling systems are employed or in the handling of geothermal fluids.[11]

Duplex alloys have been utilised in FGD systems, mainly in North America and Europe, which involve scrubbing the SO_2 containing gas with a slurry of lime or limestone in water. Early use of duplex involved grade S32550 (Ferralium 255), as pumps and wall papering (lining) in absorber towers.[12] Applications for the standard 22%Cr S32205/S31803 grade include centrifugal fans[7] and absorbers (after pre-absorption).[13] In addition, flue gas ducting expansion joints and dampers[14] and feed/effluent heat exchangers in waste water heat treatment have all been made with duplex stainless steels.[11]

12.5 Marine transportation

Austenitic stainless steels have been used for transporting chemicals and chemical products since the 1960s. In the early 1980s, duplex stainless steels began to emerge as a viable alternative to 316L(N) and 317L(N),[15–17] particularly as their high strength to weight ratio maximised cargo capacity through a reduction in wall thickness. Today the cargoes carried by duplex chemical tankers range from molasses, fish oil and lubricants to methanol. In addition, the improved corrosion resistance of duplex alloys makes them a common choice for phosphoric acid and chlorinated hydrocarbons.[18] It is estimated that the use of duplex over austenitic grades can save about 10% of the tank system weight. However, candidate materials must be readily available in the required product sizes and have good fabrication properties, including ease of forming and welding at a shipyard without due complications. Grade S32205/S31803 meets these requirements and has been approved by all the main classification societies. (Refer to the listings at the end of this chapter). This grade has been used extensively since 1987 and is now the dominant choice for the construction of advanced chemical tankers.[19]

Duplex grades are also employed in marine applications such as propeller shafts, steering propellers, thrusters, water jet engines and other products subjected to high mechanical load.

12.6 Other applications

12.6.1 Mining/extraction

Superduplex grades (e.g. S32760) have been used successfully for pumps to handle potash at around 80°C and hot bauxite slurry in the Bayer process. Other uses of S32760 pipework include a titanium dioxide refinery for spent HCl acid lines.[20]

12.6.2 Food manufacture

Duplex grades are selected for water heaters, calorifiers and hot water tanks in the brewery and similar industries. For such applications, the low alloy grade S32304 is often the low-cost choice.

12.6.3 Structures

Stainless steels are used in reinforced concrete, in particular for bridges, where corrosion of steel is difficult to avoid. Often these applications cover those constructions which require repair or restoration and are generally located at construction joints or critical gaps between columns and decks. The duplex grade S31803 is suitable for applications in coastal locations[21] and guidance on its use is available.[22] Other structural applications include lamp posts and railings in exposed sites.

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Shipping

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Design/fabrication codes

ASME

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BS

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CODAP

French code for the construction of unfired pressure vessels.

DIN

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13 Service experience

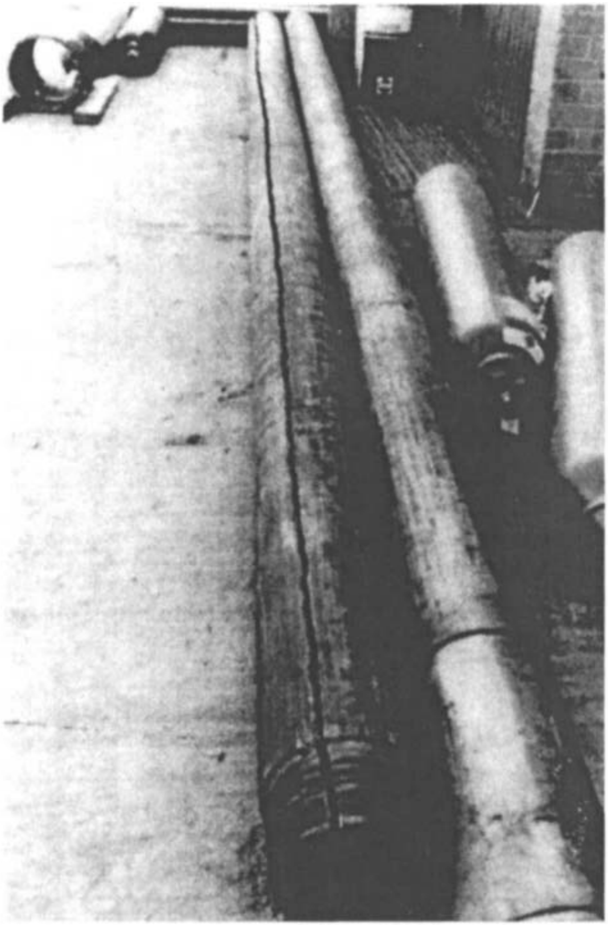
13.1 Cracking of seam welded pipes

In the mid 1980s, early versions of 22%Cr pipe were used by NAM in the Dutch sector and several problems were encountered.[1] One such problem concerned seam welded pipe, which was welded with a PAW root and completed with two passes of submerged arc and a GTAW cap pass. All welding was carried out with Ar+5% H_2 as the shielding gas, to improve the surface condition of the weld. However, small intrusions were detected by radiography in the root, which would have led to rejection. To this end, the root was rewelded using PAW with the same shielding gas.

Hydrostatic tests were undertaken and, after 24 hours under pressure, a leak occurred with a second leak developing after some 76 hours. An investigation of two failed pipes revealed that the microstructure in the root weld metals was almost completely ferritic and contained appreciable amounts of hydrogen[1]. As the leaks were due to hydrogen cracking, it was recommended that any repairs should be given a full heat treatment, to re-establish the phase balance, and that hydrogen containing shielding gases should be avoided.

13.2 Cracking of cold worked tubulars

In 1989, Marathon Oil UK Ltd (Brae field) experienced five cases of longitudinal cracking in 25%Cr duplex stainless steel (S31260) downhole production tubulars[2] (Fig. 13.1). The tubulars did not fail in service, but rather under excessive impact damage during removal in a routine workover. The cause of failure was identified as hydrogen embrittlement, caused by the galvanic couple between the duplex stainless steel tubulars and the carbon steel casing in the downhole conditions. The tubulars were cold worked to a yield strength in the range 965–1103 MPa (140–160 ksi). It was noticed that the failures were in the higher strength tubulars, and so the replacement tubulars, which had a lower degree of cold work



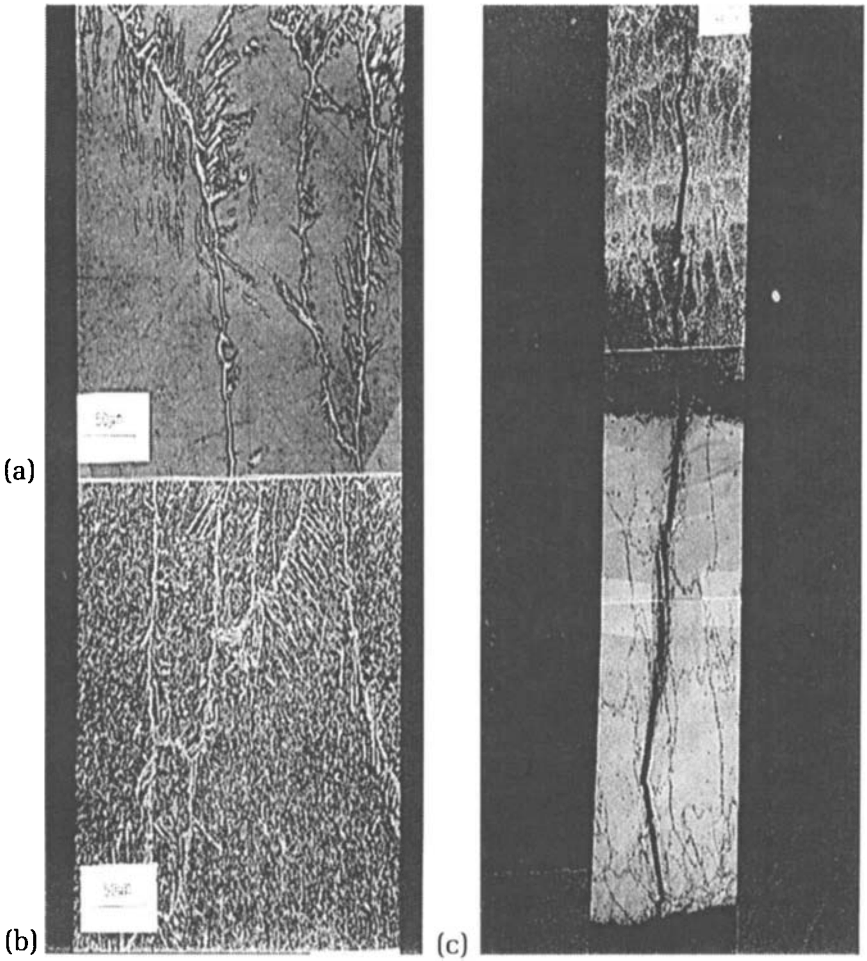
13.1 Cracked oilfield tubular (after reference 2). Courtesy of Marathon Oil UK Ltd.

(S31260 and S31803) performed satisfactorily, i.e. hydrogen entered the tubulars but did not lead to cracking.

It can be concluded[3] that very heavy cold work severely reduces the resistance to cracking under hydrogen charging conditions. It should be noted that manifolds and flowlines would normally use solution annealed material with a yield strength of 550 MPa (80 ksi) and bolting would be lightly cold worked (R_p max 900 MPa (130 ksi)). Under these conditions cracking is less likely to occur.

13.3 Cracking in offshore production piping

During 1991, Esso Production Malaysia Inc. (EPMI) discovered cracks among 2500 UNS S31803 girth welds during fabrication of an offshore production module.[4] All the cracks were transverse to the weld and located solely in the cap weld metal. Initially repairs were attempted, but these recracked in adjacent areas. GTAW was



13.2 Example of (a) cap microstructure (b) fill microstructure and (c) crack path in offshore production pipework. Courtesy of Exxon Production Research Company, Houston.

used exclusively for pipes with a wall thickness of less than 11 mm, while, for larger diameter, heavy section pipes, GTAW was employed for the root and hot passes and SMAW fill and cap passes. In total, some 71 welds had cracked, although limited to those joints with SMAW runs (tending to occur in the thicker wall pipes). The cracks were detected after a range of time periods, sometimes within one day of welding, but mostly between one and two months, and, in one case, after some 153 days.

Field ferrite measurements performed on the cap weld metal gave typical values of 55% to 65% ferrite, although when sectioned the cap pass was found to have significantly higher levels, up to 100% (Fig. 13.2). The cracks appeared to start in this highly ferritic cap pass and propagate through the previous passes of higher austenite content. The fracture faces showed extensive cleavage features. Further, it was revealed that the SMAW field welds contained about 24 ppm H_2. Electrode baking trials were undertaken,[4] but this hydrogen level could only be reduced to 18ppm. It was concluded that the cracks were caused by the composition of the SMAW electrodes (leading to excessive ferrite contents), combined with high hydrogen levels. Based on this conclusion, EPMI removed and replaced all of the SMAW welds, and rewelded exclusively with GTAW.

13.4 The Gyda failure

In January 1992, there was a failure of a 22%Cr duplex stainless steel (S31803) separator by chloride SCC under insulation on the BP Gyda platform in the North Sea. The failure of this vessel was attributed to poor welding practice (presence of hydrogen cracks) and high ferrite content in the weld metal (>70%).[5] In turn this led to chloride SCC due to concentration of sea water beneath the insulation. It is well known that high ferrite contents increase the susceptibility of duplex stainless steels to chloride SCC. No further failures have occurred and no other incidence of cracking on duplex or superduplex has been reported. This is true even though there are many cases of encrusted valves and piping systems operating at temperatures above 100°C.[6]

Following the failure and the reported mechanism, several laboratories investigated the resistance of duplex and superduplex stainless steels to chloride SCC under salt crusts.[3] In one programme, welded bent beam specimens in S31803 were stressed up to and just beyond R_p, with insulation over the specimens. Sea water was regularly sprayed onto the specimens which were placed in an environmental chamber to control the humidity and temperature, such that salt crusts would form beneath the insulation. No cracking was observed on any test specimen up to the maximum test temperature of 90°C. The conclusion was that chloride SCC was not a risk up to this temperature for S31803 duplex grades.

Another programme included C-rings stressed to 72% of the yield stress and heated to 150°C. Sea water was slowly dripped onto the specimens which were regularly inspected for weeks. Specimens of a S31803 duplex, a superduplex and a 6%Mo austenitic stainless steel all cracked inside 30 days. Further tests showed that the S31803 grade tested still cracked at 60%R_p, while the superduplex grade (S32760) was resistant to cracking at stresses up to 68% R_p. This is a very severe test and it has been pointed out that external cracking is not a problem with process pipes in the North Sea. This is possibly because salt crusts on pipes in service form by intermittent wetting rather than by continuous dripping of sea water. Thus, the surface has a chance to repassivate during each dry cycle. Nevertheless, it is recommended that all duplex stainless steels are painted when the parts are subject to wet insulation.

13.5 Cathodically protected bolts

During the mid-1990s, a few failures of cathodically protected 25%Cr duplex bolts (S32550) were reported on one of BP's North Sea platforms.[3] The microstructure comprised about 70% ferrite, with the strength of the bolts achieved by ageing at about 500°C, rather than by cold work. As described in Section 3.4.1, this heat treatment leads to the precipitation of alpha prime, which produces a dramatic drop in resistance to embrittlement in the slow strain rate test, especially with 70% ferrite.[7] It is for this reason that the high strength bolting grade should be achieved by cold work and not by ageing, while maintaining a 50/50 phase balance.

13.6 Acid treatment

Some cases of suspected SSCC have been reported in crude oil producing pipe spools, up and down stream of a test separator, following acid treatment.[6] These seem to be connected to the production of H_2S from the reaction between a ZnS rich film and hydrochloric acid (involving up to 8,000 litres of 10%HCl) used to remove $CaCO_3$-scale build-up in safety valves. In this case, the cracks tended to initiate in the HAZ near the fusion line and propagate preferentially within this area. None of the observed cracks propagated into the weld metal, although several cracks were found to pass into the base material.

Following this experience, laboratory tests and field acidising operations were conducted on a superduplex grade (S32760) with 90%HCl (by volume), 15% + 10% CH_3COOH acid mixture inhibited with a commercial inhibitor package.[8] Acceptable levels of attack were experienced up to 130°C for 5 hours at the worst depth of 5600–5770 m.

13.7 Intermetallic formation in pipe weldments

During the early 1990s, several North Sea operators selected superduplex stainless steel to UNS S32760 for topside hydrocarbon process systems. During procedure qualification of the joints, a high proportion of these operators reported that intermetallic phases were present in the weldments. One example was the Marathon East Brae platform, where 2–3 volume per cent was measured in the HAZ of the pipe welds up to 14 mm thick.[9] The highest volume fractions was observed in thinner/small diameter geometries where the heat flow away from the weld was reduced.

For the particular example cited, an experimental and analytical programme was undertaken which included CTOD, R-curve, tensile and Charpy testing, full scale validation tensile testing of welded pipe, and fracture assessments.[9] The overall conclusion was that for pipe wall thicknesses up to 14 mm, welds containing sigma levels up to 2.5% in HAZ regions were fit for purpose for the design conditions considered. Later work[10] showed that the original solution anneal carried out on the batches of pipe produced during the early 1990s, either had an insufficient heat treatment to remove intermetallic nucleation sites formed during prior processing or that the solution anneal served to provide incipient intermetallic formation. In either case, the subsequent weld thermal cycle induced particle growth, as observed.

13.8 Fatigue of pipework

Some flowlines have been exposed to severe vibrations and the first fatigue failures have occurred.[6] In part, these failures can be attributed to designers taking advantage of the high strength-to-weight ratio of duplex steels, and reducing the wall thickness, without taking consideration of the increased need for supports. In addition, several failures have been associated with poor root bead geometries which have led to fatigue initiation on the internal bore.

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Appendix A

Nominal composition of stainless steels and Ni-base alloys

UNS	Common names	Element, wt%						PRE_N
		Cr	Ni	Mo	Cu	N	Other	
Ferritic grades								
S43000	430	17	–	–	–	–	<0.12C	17
S44700	29–4	29	–	4	–	–	–	42
S44800	29-4-2	29	2.2	4	–	–		42
300-series austenitic grades								
S30403	304L	18	9	–	–	–	–	18
S31603	316L	16	10	2.1	–	–	–	23
S31626	316LN	17	12	2.5	–	0.13	–	27
S31703	317L	18	14	3.1	–	–	–	28
S31726	317LN	17	13	4.2	–	0.15	–	33
High alloy austenitic grades								
N08028	Alloy 28	27	31	3.5	1	–	1.8Mn	38
N08904	904L	21	25	4.5	1.6	–	1.7Mn	36
N08932	UR SB8	25	25	5.2	1.5	0.2	1.8Mn	45
S31254	254SMO	20	18	6.1	0.7	0.2	–	43
S32654	654SMO	24.5	22	7.5	0.4	0.5	3Mn	57
Ni-base alloys								
N06455	Alloy C4	16	66	15.5	–	–	0.3Ti	67
N06625	Alloy 625	21.5	61	9	–	–	3.6Nb, 4Fe	51
N08020	Alloy 20	20	36	2.5	–	–	<4Cu, <1Nb	28
N10276	Alloy 276	15.5	57	15.5	–	–	4W, 5.5Fe, 0.2V	73

Appendix B

Welding consumables for duplex and superduplex stainless steel grades

(Each entry represents the nearest approximation to AWS/CEN designation)

Welding	Process	Filter material classification		
consumable	AWS$^{\#}$	E2209	E2553	–
manufacturer	CEN	X22 9 3 N L	X 25 9 3 Cu N L	X 25 9 4 N L
Avesta Welding, Sweden	SMAW	2205-PW, AC/DC		2507/P100
	GTAW	2205		2507/P100
	GMAW	2205		2507/P100
	SAW*	2205		2507/P100
	FCAW	2205		
Böhler Edelstahl, Austria	SMAW	Fox CN22/9N&22/9N-B	Fox Duplex Cu3.0	Fox CN 26/10 N**
	GTAW	CN 22/9N-1G		
	GMAW	CN 22/9N-1G		
	SAW*	CN 22/9N-UP		
	FCAW	CN 22/9N-FD		
ESAB AB, Sweden	SMAW	OK 67.50	OK 68.53	OK 68.53
		OK 67.53	OK 68.55	OK 68.55
		OK 67.55		
	GTAW	OK Tigrod 16.86	OK Tigrod 16.88	OK Tigrod 16.88
	GMAW	OK Autrod 16.86	OK Autrod 16.88	OK Autrod 16.88
	FCAW	OK Tubrod 14.27		
		OK Tubrod 14.37		
	SAW	OK Autrod 16.86	OK Autrod 16.88	OK Autrod 16.88
		OK Flux 10.93	OK Flux 10.94	OK Flux 10.94
Filarc	SMAW	RS 22.9.3 LCN		RS 25.10.4 LCN
	GTAW	PZ 65.17		
	GMAW	PZ 60.17		
	FCAW	PZ 6447-PZ 6450		

Welding	Process	Filter material classification		
consumable	AWS#	E2209	E2553	–
manufacturer	CEN	X22 9 3 N L	X 25 9 3 Cu N L	X 25 9 4 N L
Kobe, Japan	SMAW			NC-329M
	GTAW			TGS-329M
	GMAW			DW-329M
	SAW			US-329M or PFS-1
Lincoln Electric, USA Lincoln–Smitweld, Netherlands	SMAW	Grinox 62	Grinox 63	
		Grinox 33	Grinox 37	
	GTAW	Grinox T-62		
	GMAW	Grinox S-62		
	SAW*	Grinox UP-23 8 3 NL		
Metrode Products, UK	SMAW	Supermet 2205	Supermet 25.6.2.CuR	2507XKS
		Ultramet 2205		Zeron 100XKS***
		2205XKS	ER225Cu	
	GTAW	ER329N	ER225Cu	Zeron 100X***
	GMAW	ER329N		Zeron 100X***
	FCAW	Supercore 2205		
	SAW*	ER329N, SSB flux		Zeron 100X, SSB flux
Nippon Welding Rod, Japan	SMAW	WEL 329J2L	WEL 25-5Cu	WEL 25-5
	GTAW	WEL (Auto) TIG 329J2L	WEL Auto TIG 25-5Cu	WEL Auto TIG 25-5
	GMAW	WEL MIG 329J2L	WEL MIG 25-5Cu	WEL MIG 25-5
	FCAW	WEL FCW 329J2L		

Welding	Process	Filter material classification		
consumable	AWS#	E2209	E2553	–
manufacturer	CEN	X22 9 3 N L	X 25 9 3 Cu N L	X 25 9 4 N L
Sandvik, Sweden	SMAW	22.9.3.LR		25.10.4.LR
		22.9.3.LB		25.10.4.LB
	GTAW	22.8.3.L		25.10.4.L
	GMAW	22.8.3.L		25.10.4.L
	SAW*	22.8.3.L		25.10.4.L
Smitweld (Lincoln Norweld)	SMAW	Arosta 4462	Jungo 4462 Cu	Jungo Zeron 100X
		Jungo 4462		
	GTAW	LNT 4462		LNT Zeron 100X***
	GMAW	LNM 4462		LNM Zeron 100X***
	FCAW	Cor-A-Rosta 4462		
	SAW*	LNS 4462		LNS Zeron 100X***
Soudometal, Belgium	SMAW	Soudinox S4462	Soudinox S52+	Soudinox S100
		Soudocrom S4462	Soudinox S47+	
		Primanox S4462		
	GTAW	Soudotig 22 9 3L		Soudotig 25 10 4L
				Soudotig S100
	GMAW	Soudor G 22 9 3L		Soudor G25 10 4L
				Soudor G100
	SAW*	Soudor 22 9 3L		Soudor 25 10 4L

Welding consumable manufacturer	Process	Filter material classification		
	AWS#	E2209	E2553	–
	CEN	X22 9 3 N L	X 25 9 3 Cu N L	X 25 9 4 N L
Sumikin Welding Industries, Japan	SMAW	DP-8, DP-8S		DP-3
Thyssen Schweisstechnik, Germany	SMAW	Thermanit 22/09W Thermanit 22/09	Thermanit Cu/W	Thermanit 25/09CuT Thermanit 25/07CuT
	GTAW	Thermanit 22/09		
	GMAW	Thermanit 22/09		
	SAW*	Thermanit 22/09		
T&R Welding Products, UK	SMAW	–	Truweld 25.6.2.CuR	Truweld 25.9.3.LR*** Truweld 25.9.3.CuWB
UTP	SMAW	6808MoKb	6807 MoCuKb	6810MoKb**
	GTAW/ GMAW	A6808Mo	–	A681Mo**
Welding Alloys, UK	GTAW	Tube-S 22.9.3L-G	Tube-S D57L-G	Tube-S D57L-G
	GMAW	Tube-S 22.9.3L-G	Tube-S D57L-G	Tube-S D57L-G
	SAW*	Tube-S 22.9.3L-G	Tube-S D57L-G	Tube-S D57L-G
	FCAW	Tetra-S 22.9.3L-G Tetra-V 22.9.3L-G	Tetra-S D57L-G	Tetra-S D57L-G

* filler wire in combination with appropriate flux

** E 25 10 3 L

*** in addition also parent material matching composition

\# ANSI/AWS A5.4-92 and A5.9-93: ERXXXX designates a solid wire

CEN pr EN1600: 'Welding consumables – covered electrodes for manual metal arc welding of stainless and heat resisting steels – classification'

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Microstructure, properties and applications

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Contents

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

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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	Europaïsche Norm/Norme Europeéne/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 (Ni_{eq} = %Ni + 35 × %C + 20 × %N + 0.25 × %Cu)
PAW	Plasma arc welding
PRE_N	Pitting resistance equivalent number (PRE_N = %Cr + 3.3 × %Mo + 16 × %N)
PRE_W	Pitting resistance equivalent number (PRE_W = %Cr + 3.3 × (%Mo + 0.5%W) + 16 × %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_2S 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