⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 566 814 A1**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **92830586.1**

(51) Int. Cl.5: **C22C 38/42**, C22C 38/44

㉒ Date of filing: **26.10.92**

㉚ Priority: **24.04.92 IT RM920309**

㊸ Date of publication of application:
27.10.93 Bulletin 93/43

(84) Designated Contracting States:
AT BE DE ES FR GB IT SE

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(54) Superduplex stainless steel having high corrosion resistance and high yield strength in the solution annealed condition.

(57) The steel, object of our invention is highly resistant to stress corrosion in acid and alkaline environment, and has furthermore high pitting and crevice corrosion resistance. This steel has a very high yield strength, even in the solution annealed condition.

The steel consists of: (in weight percent)

C	0.025 max
Mn	0.80 max
Si	0.80 max
Cr	24 - 26
Ni	6.5 - 8.0
Mo	3.0 - 4.0
Cu	1.2 - 2.0
W	0.8 - 1.2
N	0.23 - 0.33
S	0.002 max
P	0.025 max
Fe	balance

with the proviso: Pitting Index = Cr + 3.3 Mo + 16N > 42

EP 0 566 814 A1

Rank Xerox (UK) Business Services
(3.10/3.6/3.3.1)

The Austenitic/Ferritic stainless steels presently on the market are those reported in the ASTM A790 specification with the addition of the Zeron 100, equivalent to UNS S32760, which is not yet included in the ASTM specification.

The steel grades which are mainly requested for the oil field applications are the UNS S32750 and UNS S32760.

There are however many other kind of steels which can be included in the same class and which are listed and described in the following publications :

Encl. 1 - Superduplex Stainless Steel : Structure and Properties. by J. Charles
Encl. 2 - Superduplex Stainless Steel : Structure and Properties. by J. Charles
Encl. 3 - The Corrosion Resistance of Duplex Stainless Steel. by S. Bernhardsson

The invention concerns the production of austenitic-ferritic stainless steel of the superduplex class, manufactured by electrical arc melting and A.O.D. refining.

The A.O.D. refining allows a deep deoxydation and desulphurization of the steel as well as to reach the required chemical composition in a repeatable way.

The analytical balancing of the alloying elements Cr, Mo, W, Cu and N is very important for obtaining the mechanical properties and the corrosion resistance on hot forged and/or rolled products in the solution annealed condition.

Our invention has taken advantage of the combined action of Mo, W, Cu, N which allows to reach a yield strength value higher than 620 MPa (90,000 PSI) as well as a generalized resistance to the stress corrosion, to the pitting and crevice corrosions.

The optimized chemical composition is the following :
(weight in percent)

C	0.025 max
Mn	0.80 max
Si	0.80 max
Cr	24 - 26
Ni	6.5 - 8.0
Mo	3.0 - 4.0
S	0.002 max
P	0.025 max
Cu	1.2 - 2.0
W	0.80 - 1.2
N	0.23 - 0.33
Fe	balance

The ferrite on the product solution annealed at the temperature of 1070 - 1100 °C is 40 - 55%

Pitting index = Cr + 3.3 Mo + 16 N > 42

1. Mechanical characteristics of the product solution annealed at 1080 °C :

		Room Temp.	80°C	150°C
Rs 0.2 MPa (KSI)		630 (91)	550 (80)	480 (70)
R MPa (KSI)		865 (125)	800 (116)	750 (110)
A %		40		
HB		270		
KV	°C	-45	-65	-100
	Joule	300	144	38

2. Comparisons with other steels of the same class on the basis of the corrosion resistance :

2.1 Chemical analysis of steel (A = Steel subject of the invention)

	Cr	Ni	Mo	Cu	W	N
A)	25.5	7.4	3.9	1.7	0.9	0.27
B)	25.5	7.1	3.6	0.7	0.7	0.26
C)	25.4	7.0	3.6	0.2	---	0.28

2.2 Pitting corrosion resistance (ASTM G48) at 50 °C - 24 h.

	A	B	C
weight loss (g/m^2)	0.049	0.070	0.76
N° of pitting/m^2	0	0	270
Max pit depth (micron)	0	0	100
Critical Pitting Temp.(°C)	80	60	50

2.3 Corrosion resistance in 5% Na Cl at PH = 4 - 6 at 600 mV :

	A	B	C
CPT (°C)	80	72	63

2.4 Crevice corrosion resistance (ASTM G78 modified) 100 days .

Environment : Aerated sea water containing 20,000 ppm cloride plus 2 ppm residual chlorine with occasional shock dosing up to 10 ppm chlorine ar 35 °C

	A	B	C
N° of crevice (min/max)	Absent	1 / 3	Traces

2.5 Sulfide Stress Cracking Resistance of the steel object of the invention (NACE TM-01-77) at 80 °C - 760 h :

Applied load = 550 MPa no cracking

Allegato 1 - Encl. 1

Super duplex stainless steels : structure and properties

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Abstract - After a historical review of the development of duplex steels since the 1930's, today's commercial grades are presented. The structural changes which occur during both isothermal and anisothermal heat treatments are then described in detail, and the roles of the individual alloying elements are discussed. In particular, nitrogen additions are shown to have a beneficial influence on the stability of the two-phase structure during high temperature annealing (1000-1300°C).

The physical and mechanical properties (tensile characteristics, hardness, impact and fatigue strength) are then considered, with particular reference to the effect of microstructure and phase transformations. The influence of copper additions, which produce substantial hardening during low temperature heat treatment (300-500°C) is described.

Finally, the paper considers the forming of these materials, together with their potential for new applications.

1 - Historical aspects

The origin of austenitic-ferritic stainless steels in France goes back to 1933 when, in the Firminy works of the J. Holtzer Company, an alloying error during the melting of a 18% Cr-9% Ni-2.5% Mo grade led to a 20% Cr-8% Ni-2.5% Mo steel containing a high volume fraction of ferrite in an austenitic matrix [1-4]. This magnetic grade was studied in the Unieux research laboratory, and it was rapidly found that, whatever the heat treatment employed, the two-phase α/γ alloy was not sensitive to intergranular attack in various corrosive media. This property was shown at the time to be due to the fact that carbide formation was discontinuous, in contrast to the continuous precipitation observed in austenitic steels [5-8]. This discovery was patented in 1935 (ref. n° 803-361) and in 1937 (New Stainless Alloys - ref. 49.211) [9]. The latter patent included duplex grades containing copper, in order to improve their corrosion resistance in the most aggressive media. In 1940, another patent (ref. 866-685), concerning copper and molybdenum containing alloys, described a new process, involving heat treatment in the range 400-500°C, which enabled these materials to be hardened, without affecting their corrosion resistance and without causing embrittlement.

During the same period (1930-1940), researchs and industrial productions of duplex alloys were realized in Sweden (forerunners of 3 RE 60 SANDVIK). In the USA works on austenitic stainless steels containing large volume fractions of ferrite was reported [10, 11]. Thus, even before 1940, a new family of stainless steels had been born, and certain compositions were studied, patented and marketed simultaneously in France, Sweden and the USA.

One of the reasons for using austenitic stainless steels with large amounts of ferrite was to increase the mechanical properties of castings. In particular, it was possible to control the austenite grain size by heat treatment. This possibility was not of great interest in the case of hot-rolled plate, because of the poor workability of the duplex grades and the ability to refine the grain size by thermomechanical processing. These alloys still had an austenitic matrix, containing considerably less than 50% of ferrite.

In its 1950 brochure, the "Compagnie des Ateliers et Forges de la Loire" presented the UR 50 grade, with a two-phase α/γ structure, whose high yield strength (> 400 MPa) and excellent corrosion resistance made it a prime contender for applications in fields such as chemical engineering, salt production, oil refining, the food industry, dying, tanning, paper-making, pharmaceuticals, photographic products, etc. At the time, it could already be produced as bars, forgings, castings, and machined and welded components [12, 13]. As early as 1947, the UR 50 grade was standardized by the French navy (IT 47, cat. 16b for the hardened condition and cat. 28b for the annealed condition). This same brochure also proposed a duplex / grade URANUS CH with a nitrogen content of 0.2% ! The latter alloy had a yield strength of 530 MPa in the annealed condition, due to the hardening effect of the carbon and nitrogen additions. The applications quoted at the time were for use in acid media (dilute sulphuric, sulphurous, nitric, nitrosulphuric, and acetic acids), saline solutions (chlorides, hyposulphites, seawater and organic acids), and crude oils (with or without inorganic acids).

A more economic version (UR F1 : 20% Cr-3% Mn-2.5% Ni-1.5% Cu) was also developed at this stage. It was used industrially for applications as varied as gas cylinders,welded 0.8 mm sheet, or 2.2 m diameter propellors [12].

In 1950, J. Hochmann [1] described a duplex grade with a composition particularly adapted for high temperature strength (≈600°C) and not prone to the brittle intergranular failure, which was characteristic of the austenitic grades produced at the time. The applications mentioned were for gas turbine disks or for ammonia synthesis catalyst tubes.

All these steels were produced in high frequency induction furnaces, which served essentially to melt the precisely weighed alloying elements, without any significant refining.
A partial vacuum could be used to ensure carbon removal and a rudimentary deoxidation, and to prevent the bath from being contaminated by oxygen and nitrogen in the air.

In these "glorious" days, it was not possible to respect narrow analytical ranges, corresponding to highly reproducible structures, and very low oxygen, sulphur and carbon levels could not be achieved. The duplex steels, particularly in the form of plates, could be readily identified in the works by their generous proportion of cracks ! [3, 4] .

The effect of nitrogen additions on the structural stability of austenitic-ferritic steels was also as yet unknown.

From 1950 to 1970, extensive studies were carried out on the hot workability, weldability and corrosion resistance of the duplex steels, and on their structural response to thermal and thermomechanical treatments. However, their industrial applications remained limited at first, and it was the nickel shortage in the early 1950's which led to a regain of interest, 25/26% Cr-4/5% Ni-3% Cu grades being used in particular for castings. The lack of understanding of their metallurgy, especially as regards the necessity for rapid cooling, or even solution annealing and quenching, explains the low ductility and toughness of the parts produced.

Towards the end of the 1950's, the grade CD4MCU (25% Cr-5% Ni-2% Mo-3%Cu) was developed by the Alloy Casting Institute. However, because of the brittleness of the castings obtained, the chromium content was reduced to 22-23% and a quench-annealing treatment was adopted to increase the ductility [11].. Nevertheless, a number of original achievements are to be noted in France, with the first submarine diving spheres (UR 50) for COMEX in 1964, the first three ships for the transport of chemicals, Zambeze, Zelande and Zeebrugge, built in the Dunkerque shipyards in 1970 (UR 50), and the first use of clad duplex steel plates in 1969, for Kraft process boilers and a digester at the St. Gaudens works of the Cellulose des Ardennes company. At about this time, a new nickel shortage gave extra impetus to the α/γ steels, whose high mechanical strength and excellent corrosion resistance, particularly in chloride-rich media, was getting to be well known (figure 1).

The introduction of the VOD and AOD refining processes in the 1970's, and their continuous development up to the present time, led to a significant improvement in the properties of the stainless steels, and not least in those of the duplex grades. In effect, it now became possible to obtain simultaneous reductions in the levels of residuals such as oxygen, sulphur, carbon, etc., while at the same time guaranteeing narrow compositional ranges, including that for nitrogen.

As will be seen below, the accuracy and reproducibility of the chemical composition enabled the amounts of α and γ phases to be closely adjusted. Furthermore, increased control of nitrogen levels made it possible to improve the corrosion resistance and the high temperature stability of the duplex structure, particularly in the heat affected zones of welds. Finally, the reduction in the levels of residuals has resulted in a marked amelioration in hot workability, making possible the production of wide-gauge sheets and, more recently, of coils [14, 15].

These improvements have also led to a significant reduction in production costs, adding to that obtained by the introduction of continuous casting technology in 1976 (at Isbergues, in France).

Today,the foundries too are equipped with modern vacuum and/or argon (VOD/AOD) refining units (1 to 20 t capacity). Even for small tonnages, it is thus possible to ensure precise chemical analyses and low residual levels, two characteristics which, as will be seen below, are of particular importance for the functional properties of the duplex stainless steels.

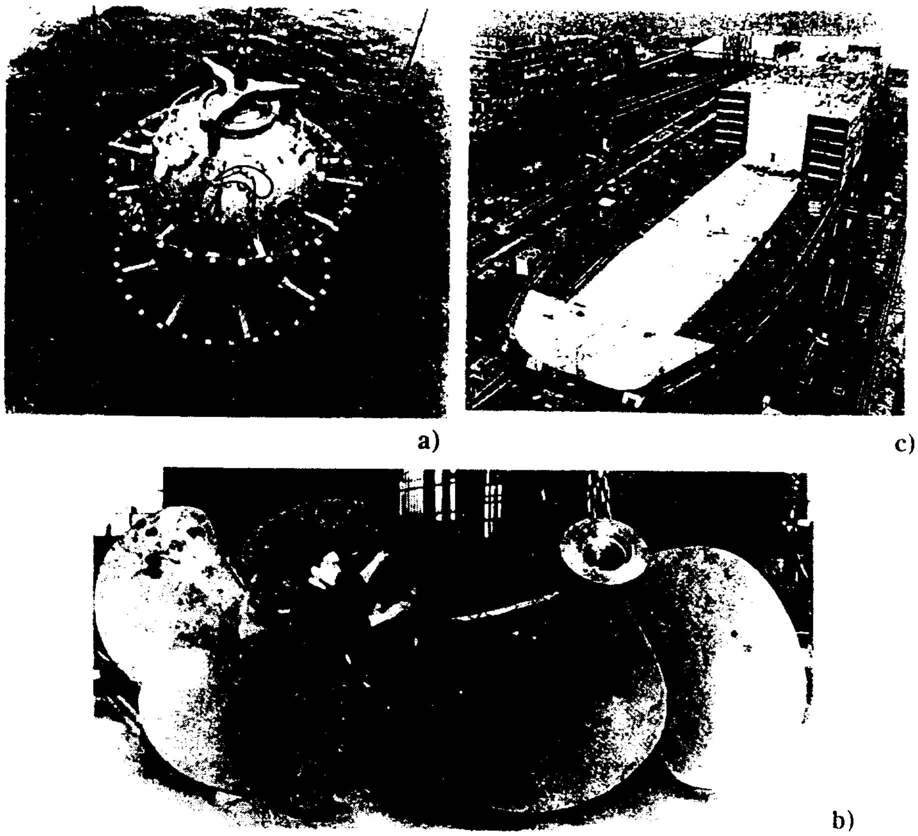


Fig. 1 : Typical duplex stainless steels industrial applications in the 60' and 70'

a) First submarine diving sphere (UR 50) - COMEX 64
b) 2.2 m Ø propellor
c) Chemical tankers

2 - Introduction to the duplex stainless steels

Tables I to III present some of the duplex stainless steels. Although the list is long, it is far from exhaustive ! Table I summarizes the grades marketed in the form of wrought products, whereas table II includes the alloys more particularly designed for castings. Table III includes a number of experimental compositions developed for use in specific media or used in the studies described in the present paper. These tables also give the corresponding values of the pitting resistance index PREN = Cr + 3.3 Mo + 16 N. It should be recalled that the superduplex grades are characterized by a value of PREN > 40.

The large number of grades illustrated in tables I and II is due in part to the gradual optimization of the chemical composition, to meet new property requirements and to take advantage of new technological developments. The following points should be noted :

Table I - Typical chemical composition of some wrought duplex stainless steels

Standard	Trade mark	Typical chemical composition					PREN
		Cr	Ni	Mo	N	Others	
UNS S 32304 WNr 1.4362 Z3CN 2304 AZ	SAF 2304 UR 35 N	23	4	.2	.1	-	25
UNS S 32404 Z3CNDU 2107	UR50	21	7	2.5	.07	1.5 Cu	31
UNS S 31500 W Nr 1 4417	3 RE 60 VEW A903	18.5	5	2.7	.07	1.5 Si	23
UNS S 31803 WNr 1 4462 NFA 36209 Z3CND 2205 AZ	UR45N SAF 2205 223 FAL AF22 VS22 ...	22	5.3	3	.16	-	35
UNS S 32900	10 RE 51	25	4.5	1.5	-	-	30
UNS S 31200 WNr 1. 4460	44LN	25	6.2	1.7	.17	-	33
UNS S 31260	N.A.R. DP-3	25	6.5	3	.16	.5CU.3W	38
UNS S 32550 Z3CNDU2507 AZ	UR52N FERRALIUM 255	25	6.5	3	.18	1.6 Cu	38
UNS (S 32200) Z3CND 2507 AZ	UR47N	25	6.5	3	.18	-	38
	VEW A 905	26	3.7	2.3	.34	6 Mn	39
UNS S32760	ZERON 100	25	7	3.6	.25	.7Cu.7W	41
UNS S32550 Z3CNDU 2506	UR52N^{+}	25	6	3.8	.26	1.5Cu	42
UNS S32750	SAF 2507	25	7	3.8	.27	-	42

Table II - Typical chemical composition of some cast duplex stainless steels

Standard	Trade mark	Typical chemical composition					PREN
		Cr	Ni	Mo	N	Others	(16N)
FISCHER	COR 28	21	8	2.5	.03	1.3 Cu	30
	COR 29	26	7	3	.2	1.2 Cu/3Cu	39
	COR 25	25	7	4.5	.18		43
PLEISSNER	4462	25	5.5	3	.20	1 Cu	38
SCHMIDT + CLEMENS	MARESIST G2205	22	6	2.5	.15	(1Cu-4545)	33
	MARESIST G4468	26	6	3	.2	3 Cu	39
	MARESIST G4460	26	6	3	.2	-	39
	MARESIST G2507	26	7	4.5	.2		43
MATER + PLATT	ZERON 25	24	5.5	2.5	.12	4.5 Mn	34
	ZERON 26	24	6	2.2	.25	.7W .7 Cu	35
	ZERON 100	25	7	3.5	.25		41
FIRTH-VICKERS	FM S	19.5	8	2.8	-	.8 Nb	30
	FM X	23	9	3.4	-		35
	FM N	25	5	2.2	.2		36
MANOIR Ind.	UR 50 M	25	7	3	.15		33
	UR 55 M	26	6	2.5	.2	2.5 Cu	37
LANGLEY ALLOY	FERRALIUM 288	27	8	3	.15	2 Si	39
	FERMANEL	27	8.5	3	.22	1 Cu	41
ATLAS	ATLAS 958	25	7	4.5	.2	-	43

Table III - Chemical composition of experimental heats (research and new applications)

Producer		Chemical composition					Potential Applications
		Cr	Ni	Mo	N	Others	
CLI	A	23	4	.2	.10	1.5-3Cu	Machining
	B	22	2.5	2.2	.4	7 Mn	LowNi,stab.ZAT
	X	25	6.4	4.2	.27		Sea water
	Y	25	6.4	4.2	.27	1.5 Cu	"
	Z	27	7	3.7	.25	1.5 Cu	"
	S	23	8	-	.1	3 Si	Nitric acid
SUMITOMO	28 Cr	27.3	7.3	3.8	.3		Sea water
"	-	22.5	10	-	.1	3.3 Si	Nitric acid
"	D1	25	7	3	.14	.3W.5Cu	Superplasticity
NIPPON STAINLESS STEEL		17.8	4	-	.05	1Cu3Si3Mn	Railway car

1) The change from electric remelting furnaces to AOD/VOD refining has led to lower residual contents (S, P, C, N, O) and closer analytical control, resulting in improved hot workability.

2) Progress in heat treatment furnaces has enabled more uniform heating and more reproducible and homogeneous properties.

3) The demand for higher corrosion resistance has been met by increasing molybdenum, chromium and nitrogen contents.

4) The discovery of the beneficial effect of nitrogen additions (improved resistance to localized corrosion, higher mechanical strength, and stability of the two phase structure, particularly in the heat-affected zones of welds).

5) Continuous improvements in weldability (due in particular to increased nitrogen contents).

6) The development of grades for specific applications, as for the families of austenitic and ferritic steels.

However, in the case of wrought products, there are today essentially only three principal grades :

1) The composition 22% Cr-5% Ni-3% Mo-0.17% N (SAF 2205, UR45N, etc.), which can be considered as the standard duplex stainless steel, and whose nitrogen content has recently been increased to further improve its corrosion resistance in oxidizing chloride-rich acid media (essentially an increase in pitting resistance). Its corrosion resistance lies between those of the austenitic grade AISI 316 and the 5-6% Mo super austenitic alloys.

2) The super duplex grade with a pitting index PREN > 40, containing 25% Cr, 6.8% Ni, 3.7% Mo and 0.27% N, with or without copper and/or tungsten additions (SAF 2507, UR52N+, ZERON 100). This is the most highly alloyed grade for wrought products, and is specially designed for marine, chemical, and oil engineering applications, requiring both high mechanical strength and resistance to corrosion in extremely aggressive environments (chloride-containing acids, etc.).

The corrosion resistance is equivalent to that of the super austenitic steels containing 5-6% Mo.

3) The 23% Cr-4% Ni-0.10% N, molybdenum-free grade, an economical material, which, for the majority of applications, can be used to replace the austenitic grades AISI 304 and/or 316.

Figures 2 and 3 schematically compare the duplex stainless steels and their development to the austenitic and ferritic grades.

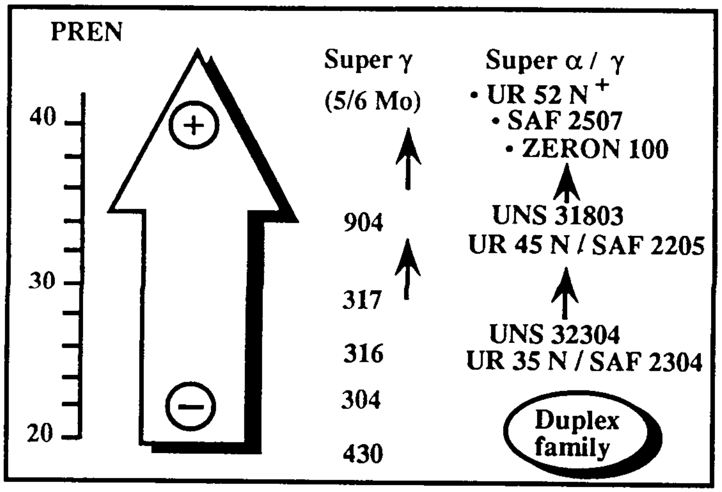


Fig. 2 : Nominal PREN values for different Stainless steels

It is noteworthy in table I that several commercial grades with different analytical balances can be covered by the same specification (e.g. by UNS S32550 for the grades UR52N, FERRALIUM 255 and UR52N+). Figure 4 illustrates the large compositional ranges permitted for a given specification. The corresponding maximum and minimum values of the pitting index PREN = [Cr] + 3.3 [Mo] + 16 [N] are also indicated [16].

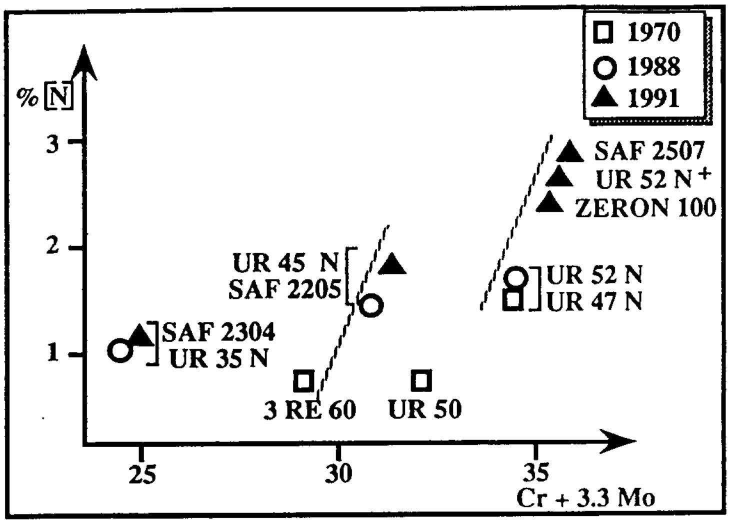


Fig. 3 : Past and present chemical compositions of hot rolled duplex stainless steels .

Typical duplex grades

PREN	min	max.	Δ
S 32304	21.8	28.7	6.9
S 31803	30.5	37.8	7.3
S 32550	35.2	43.9	8.7
S 32750	37.7	47.6	9.9
S 32760	37.1	44	6.9

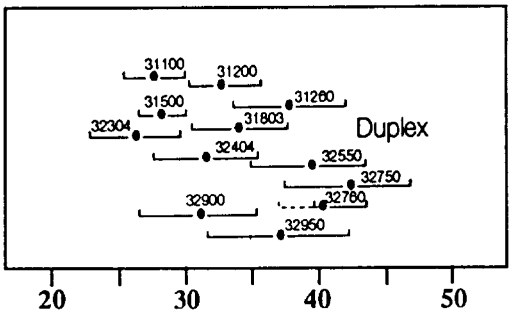


Fig. 4 : UNS numbers and PREN equivalent values of duplex alloys

This example clearly shows that standards such as the UNS specifications are insufficient to define a material with a precise range of properties. It is recommended to apply additional restrictions on chemical composition, and/or complementary acceptance tests, particularly as regards corrosion resistance. This point is of great importance for industrial applications.

Table II illustrates various compositions of duplex steels for castings. The properties of these materials will not be discussed in the present paper, which is devoted essentially to wrought products. Castings, and recently developed duplex steels with high chromium and molybdenum contents, are treated elsewhere, in several excellent papers presented at this same conference. Moreover, it should be emphasized that the cast grades often contain significant amounts of copper, which, with appropriate aging, confer exceptional abrasion-corrosion resistance [11, 17-22].

The alloys presented in table III will be discussed in greater details in the subsequent chapters [23-27].

3 - Microstructure of wrought products

3.1 - Quench-annealed structures

The duplex stainless steels are characterized by a two phase structure comprised of a mixture of f.c.c. austenite and b.c.c. ferrite grains. A rolling texture is usually exhibited (figure 5).

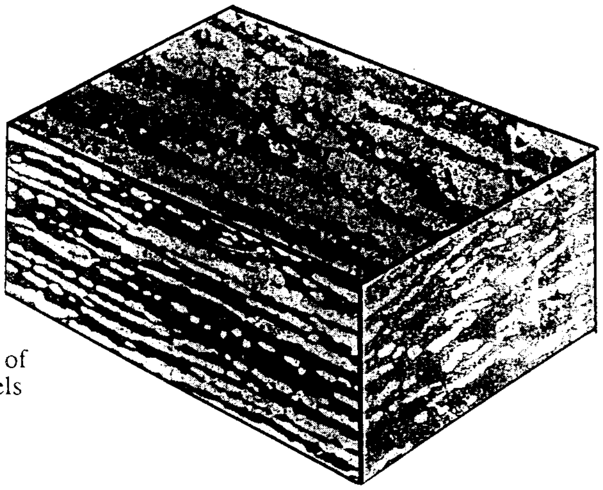


Fig. 5 :Typical microstructure of hot rolled duplex stainless steels plates

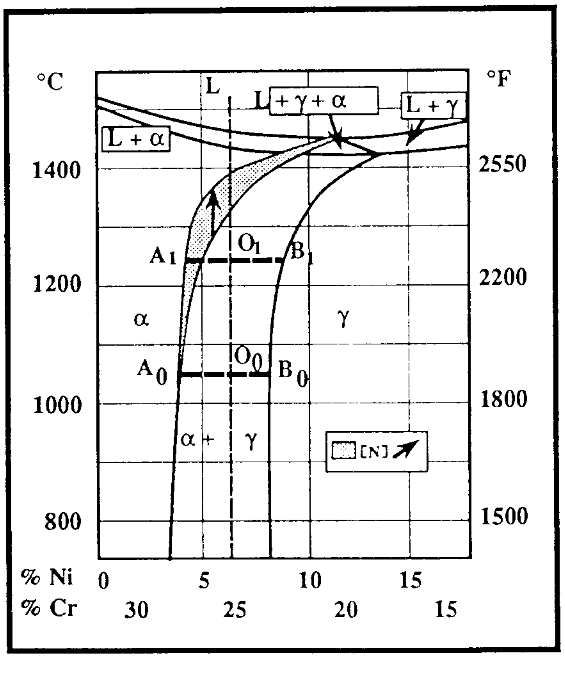


Fig. 6 : Schematic effect of nitrogen additions on the pseudo binary Cr - Ni - 68 Fe phase diagram

The alloys used up to now have roughly equivalent volume fractions of ferrite and austenite. This is obtained by work-hardening, followed by solution annealing and quenching, and involves the simultaneous control of the chemical composition and annealing temperature. Figure 6 shows a schematic isoplethal section of the Fe-Cr-Ni diagram, for an iron content of 68%. The proportions of each of the phases and their respective compositions are indicated for a given alloy analysis and annealing temperature (at temperature To, Ao is the composition of the ferrite and Bo that of the austenite).

The difficulty in predicting the microstructure is due essentially to the effects of the other alloying elements, which modify the phase diagram. Alloy producers use empirical formulae, in which proportionality coefficients are attributed to each element, and the latter are grouped together, depending on their tendency to stabilise either the ferrite,α (Cr, Mo, Si, etc.) or the austenite,γ (Ni, N, C, Cu, etc.). By way of example, figure 7 presents data reported in the literature for some fairly old grades (with relatively low nitrogen contents) [4]. These results clearly illustrate the complexity of the problem, and show why it has been necessary to resort to an empirical approach in the development of today's commercial alloys. The detailed explanation of the effect of nitrogen additions is still the subject of ongoing research. Certain results have been published, but much remains to be done. However, experimentally supported thermodynamic calculations appear to be promising. This approach has been applied to the Fe-Ni-N system by Hertzman, and to the Cr-Fe-Mo-Ni-N system by Frisk. The Physical Metallurgy Division of the Swedish Royal Institute of Technology has applied a computer model "Thermocalc", based on the same principles, to the Fe-Ni-Cr-Mo system [28-31].

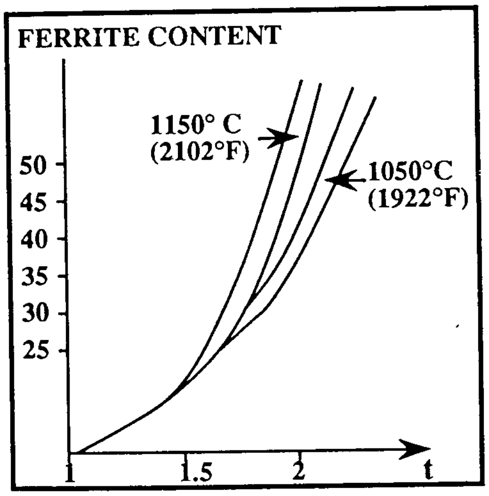


Fig. 7 : Effects of the chemical composition and heat treatment on the ferrite content of water quenched duplex stainless steel alloys.

$$t = \frac{Cr + 2\,Mo + 1.5\,Si + 3\,Al - 5}{Ni + 0.5\,Cu + 15\,C + 2 + X}$$

$$X = (100\,N + 8) \times (N - .3\,V - .3\,Ti - .04\,Nb)$$

In practice, the annealing temperature is chosen as low as possible, but sufficient to take into solution any precipitate phases. The relative amounts of the α and γ phases is then essentially determined by the chemical composition, particularly as regards the balance between α-stabilizers (Cr, Mo, Si) and γ-stabilizers (Ni, N, C).

The accuracy of the melt analysis, particularly the nitrogen content, is then the only guarantee of a controlled microstructure.

Table IV gives the partition coefficient between the ferrite and austenite phases, determined by microanalysis, and includes both data from the literature and results obtained in the author's laboratory. Examination of this table reveals several points : [19, 32-39].

1) The ferrite is enriched in α-stabilizing elements, in the order P>W>Mo>Cr≈Si.

2) The austenite is enriched in γ-stabilizing elements, in the order N>>Ni>Cu>Mn.

Table IV - Partition coefficient $\frac{([\alpha])}{([\gamma])}$ between ferrite and austenite phases for several elements in duplex stainless steels

GRADE	T°	Cr	Ni	Mo	N	Si	Cu	Mn	W	P
AF 22	1000	1.20	.54	1.65	-	-	-	-	-	-
*UR 35 N	960	1.19	.61	1.65	-	1.16	.68	.89	-	2.38
* UR 35N3Cu	975	1.2	.60	1.7	-	1.19	.66	.87	-	-
*UR45N	980	1.1	.61	1.66	-	1.16	.67	.86	-	2.31
SAF 2205	980	1.2	.58	1.72	.2[o]	-	-	-	-	-
DP3 (SEM)	1020	1.1	.74	1.49	-	1.19	-	1.01	2	-
*UR52N	1040	1.15	.65	1.6	-	1.19	.69	.87	-	2.9
*UR52N^{+}	1060	1.11	.66	1.49	-	1.15	.71	-	-	-
SAF 2507	1060	1.13	.70	1.3	.125[oo]	-	-	-	-	-
*SAF 2507	1060	1.12	.60	1.58	-	1.19	-	.95	-	-
*ZERON 100	1080	1.16	.65	1.57	-	1.10	.73	.94	-	-
*X (Table III)	1040	1.12	.61	1.58	-	1.18	-	.86	-	-
*Y (Table III)	1040	1.17	.62	1.61	-	1.21	.60	.82	-	-
*Z (Table III)	1040	1.17	.61	1.66	-	1.21	.63	.88	-	-

o : [N] = .05 in α and [N] = .25 in γ
oo : [N] = .06 in α and [N] = .48 in γ
* : CLI/CRMC results

3) Except for nitrogen, the partition coefficients for a given element vary very little from one alloy to another, in spite of the wide range of compositions investigated. For example, the same values are found for molybdenum and copper in both UR35N and UR52N. This is due to the fact that, for the concentrations and annealing temperatures concerned, the solubility limits for these elements have not been exceeded. This is obviously not the case for nitrogen. However, for the most highly alloyed grades (super duplex steels), the partition coefficients tend slightly towards unity, due perhaps partly to the use of higher solution annealing temperatures. For nitrogen,. the partition coefficient is seen to vary markedly with the total concentration in the alloy. In effect, the ferrite becomes rapidly saturated, and the excess nitrogen goes into solution in the austenite. The equilibrium solubility limit for nitrogen in the ferrite appears to be in the range 0.03-0.05%, for the compositions and annealing temperatures considered.

In practice, any increase in the nitrogen content of the duplex alloy will therefore lead to a marked enrichment of this element in the austenite, without changing the level in the ferrite, provided that the annealing temperature is not modified. A precise knowledge of the nitrogen solubility limits in both phases as a function of temperature is thus of great importance. Some published data are given in figures 8 and 9. [40-42]. It is not surprising that the alloys with the highest chromium content enable the introduction of the highest nitrogen contents, since this element increase its solubility in the austenite. The increase in nitrogen solubility in the ferrite at higher temperatures is also extremely important, and will be discussed later in relation to the kinetics of nitride precipitation under anisothermal conditions, and its effect on corrosion resistance.

As has been pointed out elsewhere, increasing the nitrogen content, particularly in the super duplex grades (PREN = [Cr] + 3.3 [Mo] + 16 [N]), produces a marked

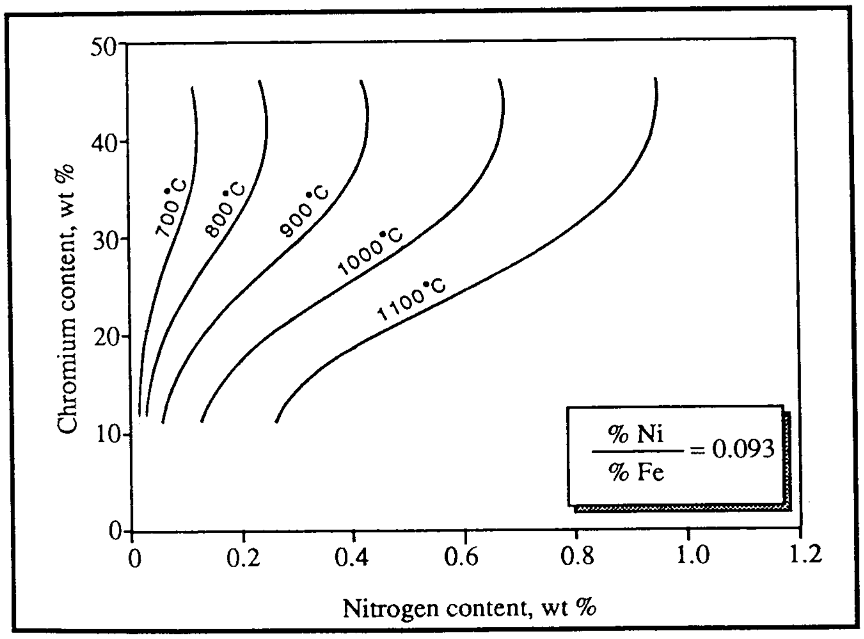


Fig. 8 : Calculated nitrogen solubility for Cr_2N in Cr - Ni austenitic steels with a constant ratio % Fe / % Ni (0.093 corresponding to 18 Cr - 7 Ni)

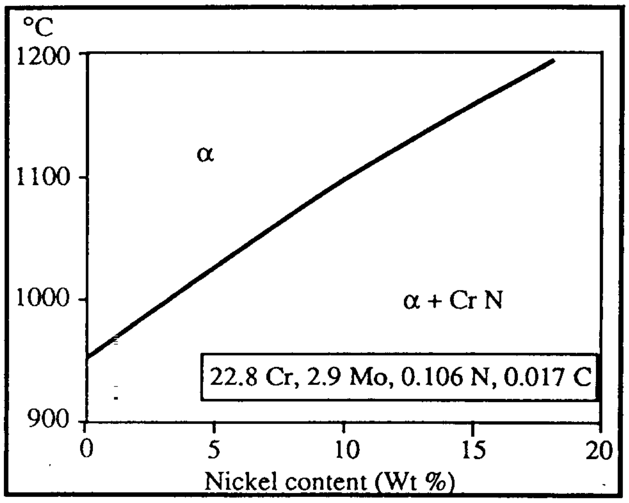
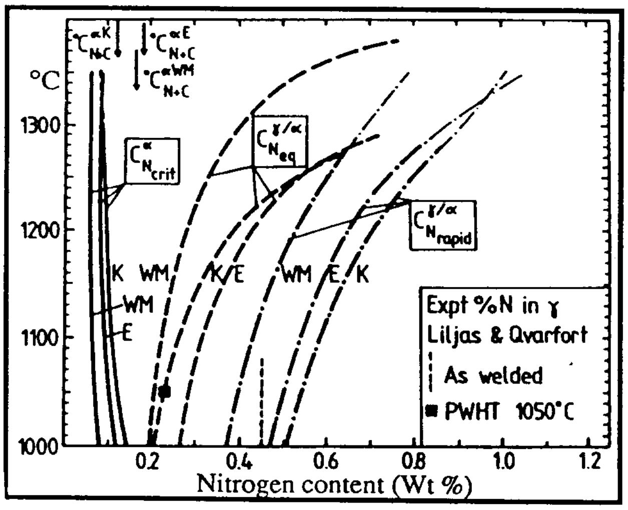


Fig. 9 a : Calculated effect of Ni on the solubility of Cr N in ferrite. Ni additions lead to an increased tendency for Cr N precipitation and Cr N can thus precipitate at higher temperature



Alloys	Cr	Ni	Mo	N
K	22.8	5.6	2.9	.10
E	21.9	5.6	3.1	.17
W.M	22.6	8	3	.15

ig. 9 b : Calculated N-content in first precipitated ustenite, equilibrium N-content in austenite and ritical N-content for rapid transformation of three lloys, low N (K) high -N (E) and W.M.

enrichment of this element in the austenite, which, combined with the high coefficient of 16, largely compensates for the preferential partition of chromium and molybdenum to the ferrite, thus limiting the difference in "pitting index" between the two phases.

3.2 - Structural transformations produced by heat treatment

Numerous structural changes can occur in the duplex stainless steels during isothermal or anisothermal heat treatments. Most of these transformations concern the ferrite, due essentially to the fact that the diffusion rates of the alloying elements in this phase are of the order of 100 times faster than the corresponding values in the austenite. This is principally a consequence of the less compact lattice of the b.c.c. crystal structure. Moreover, as already mentioned, the ferrite is enriched in chromium and molybdenum, which are known to promote the formation of intermetallic phases. Furthermore, the solubilities in the ferrite of the elements nitrogen, carbon, tungsten and copper fall sharply with decrease in temperature, increasing the probability of precipitation during heat treatment.

Several papers at this conference are devoted to phase transformations in duplex steels, for example, those presented by B. Josefsson et al. and by M. Gutmann [43, 44].The present article will therefore be limited to a description of certain experimental results obtained in the author's laboratory, together with a brief summary of the different transformations identified [4, 32-34].

The results presented were obtained on 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 must be remembered that solidification segregation will affect precipitation kinetics and the stability of the phases formed. This is particularly true as regards residuals such as P, Si, Mn and W.

3.2.1 - Transformations at temperatures above 1050°C

The duplex stainless steels solidify completely in the ferrite field, and it is only during cooling of the solid that part of the ferrite transforms to austenite (at least for standard grades and normal cooling rates). This transformation is naturally reversible, so that any large increase in temperature (e.g. 1050°C --> 1300°C) leads to a significant change in the volume fractions and chemical compositions of the two phases (figure 6). [45, 46]. In practice, the volume fraction of ferrite increases and the partition coefficients of the alloying elements decrease. In particular, the ferrite becomes enriched in interstitial elements such as carbon and nitrogen.

Figure 10 shows the variation in ferrite content with temperature for different duplex grades, and some additional results will be presented later. [4, 13, 47-50].The marked influence of chemical composition on the shape of the curves should be noted. This is particularly true for nitrogen additions, 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 remain roughly equivalent, whereas alloys 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, as illustrated in figure 11, which shows the influence of cooling rate on the maximum ferrite content in the HAZ, determined by the grid method at a magnification of x 1000. The addition of large amounts of nitrogen to the duplex steels is clearly seen to stabilize the HAZ microstructure. These aspects are treated in greater detail in an other paper presented at this conference. [50].

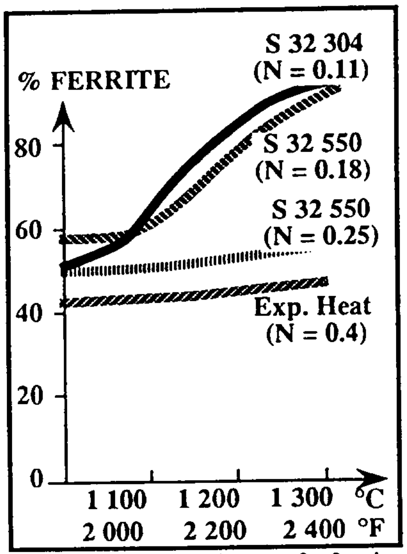


Fig. 10 : Variation of ferrite content with increase of Temperature for several duplex stainless steels

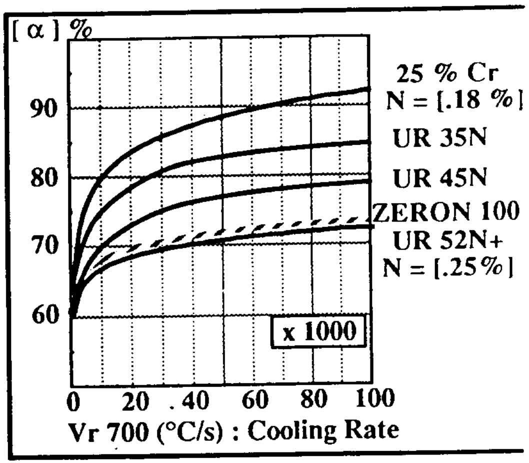


Fig. 11 : Variation of the HAZ maximun ferrite level determined by optica metallography at a 1000 magnification as function of the cooling rate.

It should be emphasized that the extent of the γ-->α transformation and the resulting microstructures depend on the heat treatment cycle. Table V shows the variation of the ferrite volume fraction as a function of temperature and holding time, for the grade UR35N, while figure 12 illustrates different microstructures which can be obtained. The grains can be made equiaxed by prolonged treatment at high temperature, or can be rendered acicular, with a Widmannstätten type structure, by cooling at intermediate rates. A dual structure, consisting of both coarse and fine austenite grains, can be obtained by step quenching, with or without simultaneous mechanical strain. The acicular structures are also encountered in weld deposits. In this case, in order to obtain 50% α and 50% γ, it is necessary to increase the quantity of gamma-stabilizing elements (nitrogen and/or nickel), since the α--> γ transformation is incomplete due to the rapid cooling rates.

Table V - Variation of the ferrite volume fraction as a function of temperature and holding fime for grade UR35N

GRADE	TEMPERATURE	HOLDING TIME (mn)					
		5	10	20	30	60	600
UR35N	1200°C	73	75	80	85	85	85
	1150°C	-	-	68	70	72	74
	1100°C	54	-	58	-	60	65

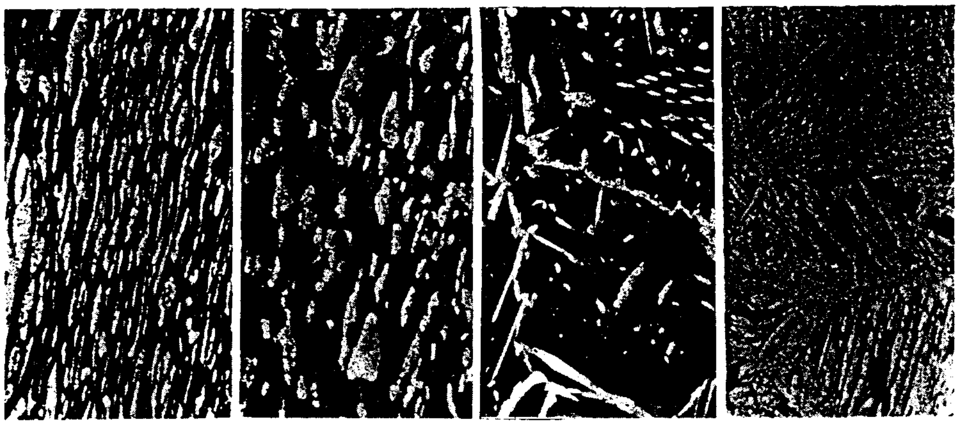


Fig. 12 : Effects of heat treatments on the α / γ microstructure

3.2.2 - Transformations at temperatures below 1050°C

3.2.2.1 - TTT diagrams and the effect of alloying elements

Figure 13 shows TTT diagrams for the grades UR35N, UR45N, UR52N and UR52N+. In the temperature range 600-1050°C, the diagrams are based on optical microscope observations of the time necessary for the appearance of intergranular precipitation, 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. As will be discussed later, this is particularly true for the low temperature ferrite hardening field.

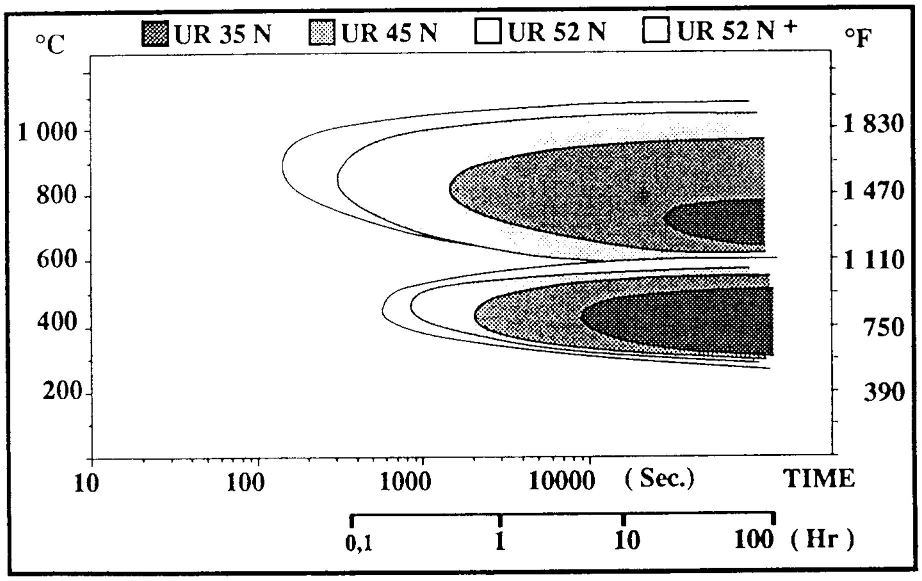


Fig. 13 : T.T.T. diagrams of Duplex Stainless Steels

Examination of figure 13 reveals a number of important features :

A - Temperature range 600-1050°C

1) The UR35N grade is little prone to the precipitation of intermetallic phases. A minimum exposure of 10 to 20 hours is necessary for their formation, and they appear only at relatively low temperatures (<900°C). It should be recalled that this alloy contains 23% Cr, i.e. a higher content than in UR45N. A solution annealing temperature below 1000°C can be chosen for this material.

2) The UR45N alloy is more sensitive to the formation of intermetallic phases than UR35N. The difference is due exclusively to the molybdenum content, which not only increases the rate of precipitation of intermetallic phases in the ferrite, but also extends their stability range to higher temperatures. A solution annealing temperature of about 1000°C is necessary.

3) The grade with the greatest propensity for precipitation of intermetallic phases is naturally the alloy with the highest chromium and molybdenum levels. A more detailed study of the influence of Cr, Mo, W and Cu additions on the constitution of duplex stainless steels is presented elsewhere, [49]. However, it must be emphasized that the precipitation kinetics in UR52N and the other more highly alloyed duplex steels are slower than, or at the most, equivalent to those in the super austenitic or super ferritic stainless grades (figure 14). [4, 49, 51-59]. As is the case for the latter materials, by taking certain precautions during heat treatment, the super duplex alloys can be used satisfactorily in industrial applications. Solution annealing must be performed at or above 1050°C for these grades.

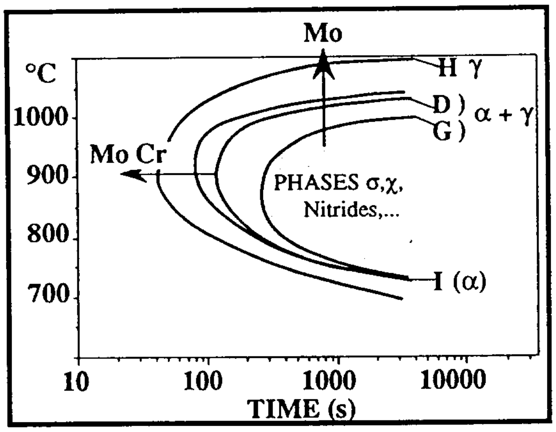


Fig 14 : TTT Diagrams

D • Super duplex UR 52 N +
H • Super austenitic steel 5/6 Mo
I • Super ferritic steel 29.4

	Cr	Mo	N	Cu
D	25	3.7	.25	1.5
G	25	3	.18	
H	25	5	.20	
I	29	4	-	

B - Temperature range 300-600°C

1) The start of low temperature hardening is observed only after a minimum of 3 hours exposure at 400°C for the UR35N grade containing 23% Cr.

2) A much shorter incubation time is found for UR45N, containing only 22% Cr, but with an addition of 3% Mo. Unless some additional strengthening

mechanism is involved, molybdenum thus apparently accelerates the transformation of the ferrite, which is the cause of hardening.

3) The grades UR52N and UR52N+ show the largest range of low temperature hardening, with both shorter incubation times and extension to higher and lower temperatures. This is the result both of the higher chromium and molybdenum contents and of the addition of copper, a new hardening mechanism which will be discussed later.

In order to complete these observations on industrial heats, additional investigations were carried out on a number of experimental compositions (table III). Figure 15 shows the TTT diagrams determined for a modified UR35N containing 3% of copper. [32, 60]. The hardening range can be seen to lie between those of the UR45N and UR52N grades. The addition of copper has widened the hardening range, particularly towards the higher temperatures. Furthermore, the precipitation kinetics are markedly accelerated. In contrast, the precipitation of intermetallic phases in the ferrite at 700°C remains unaffected by the presence of copper.

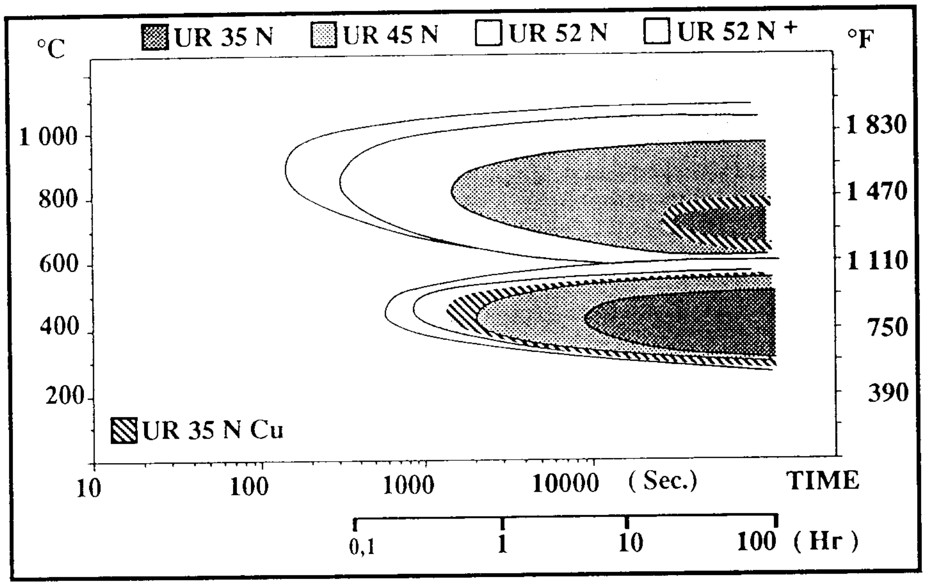


Fig. 15 : T.T.T. diagrams of Duplex Stainless Steels

Similar studies have been carried out on both experimental and industrial heats of super duplex alloys. The results obtained are illustrated partly in figure 16, and are described in detail in a separate paper presented at this conference. [49]. The following points can be made :

-the intermetallic phases are more stable at high temperature in the presence of W, Mo and Si, making higher solution annealing temperatures necessary (≈1100°C);

-the rate of precipitation of intermetallic phases is accelerated by increasing additions of W, Mo, Cr and Si. Copper has no effect on the TTT curve in this temperature range (700-1050°C).

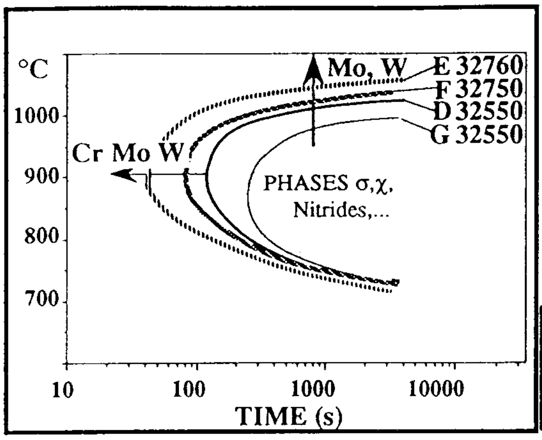


Fig 16 : TTT Diagrams

	Cr	Mo	N	
D	25	3.7	. 25	1.5 Cu
E	25	3.7	. 22	.6Cu.7W
F	25	3.8	. 28	-
G	25	3	. 18	1.5 Cu

3.2.2.2 - 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. It is therefore difficult to avoid phase transformations, such as sigma precipitation, during the reheating of heavy section products (e.g. ingots, castings, thick plate, etc.). It is thus necessary to perform solution treatment at a sufficiently high temperature to redissolve any such phases formed during heating. On the contrary, 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.

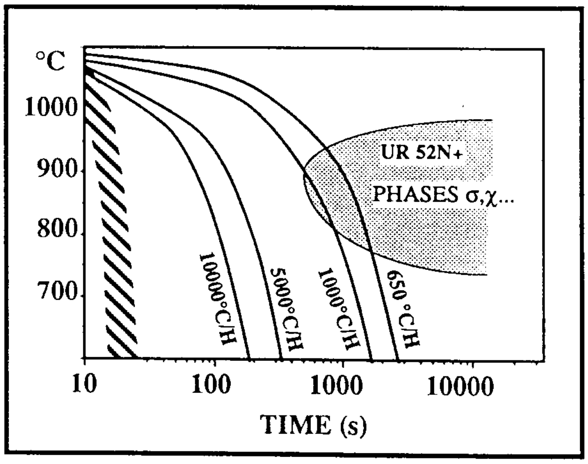


Fig. 17 : Continous cooling diagram (heating at 1080°C)

▨ Typical HAZ cooling rates

Figure 17 shows the example of CCT diagram for the UR52N+ grade. A considerable shift can be seen in the position of the precipitation 'nose' between the TTT (Fig. 13) and CCT (Fig. 16) diagrams. [43, 49, 61, 62]. 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 risks of nitride precipitation are then increased. The cooling rates measured in the heat affected zones of welds are generally much higher than the above limiting value.

3.2.2.3 - Nature and morphology of the precipitate phases

A - Carbides and nitrides

The earliest duplex steels (UR50, etc.) were characterized by low nitrogen contents and relatively high residual carbon levels (≈0.03%). The first phases to form were M7C3 carbides at high temperatures (900-1050°C) and M23C6 at lower temperatures. As already indicated, because of its discontinuous nature, this precipitation did not necessarily affect the mechanical properties or the corrosion resistance.

Today's alloys have carbon contents which are often less than 0.015%, while the nitrogen content is adjusted as a function of the chromium and molybdenum additions (0.10% for UR35N, 0.17% for UR45N, 0.26% for UR52N+), since its solubility is increased by these two elements.

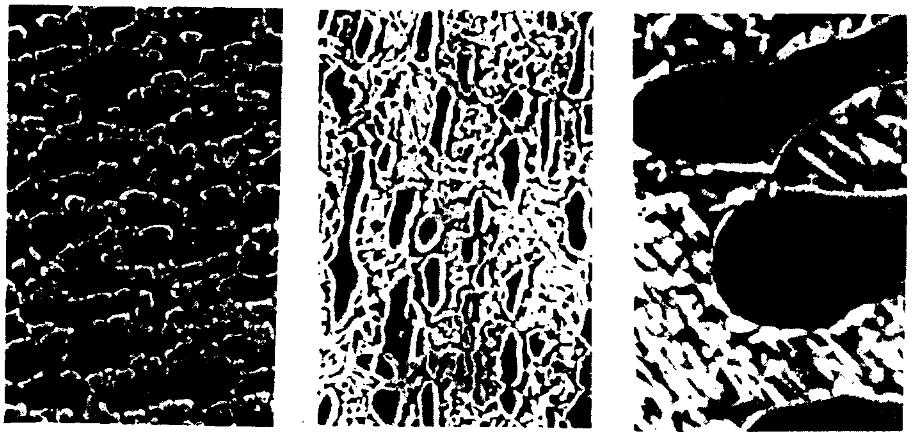
The Cr2N precipitates have a hexagonal structure, and their enthalpy of formation at 900°C is similar to that of the M23C6 carbides, so that the two phases may form simultaneously, as has been observed for UR35N (figure 18a - 18b).

It is to be noted that the kinetics of nitride precipitation depend strongly on the solution treatment conditions. A high temperature treatment (1200-1300°C) can lead to greater dissolution of interstitials (C, N) in the ferrite. Consequently, abundant precipitation of nitrides can occur during cooling, or during subsequent heat treatment. Even in the duplex grades, it is reported that nitride formation will precede precipitation of intermetallic phases (σ,χ, etc), which is retarded due to the reduction in the partition coefficients of the elements concerned (between and) after the high temperature treatment. [35, 36, 43, 46, 63-65]. However it is to be noted that it may be difficult to identify the nature of such small pricipitates. (Nitride, γ_2, σ, χ ?).
Nitride precipitation can affect the functional properties of the duplex steels, especially the pitting corrosion resistance, due to local chromium depletion.

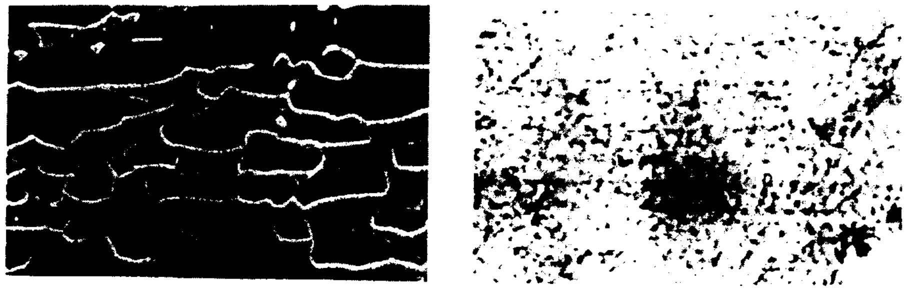
B - Intermetallic phases (σ,χ , R, etc.)

Depending on the chemical composition of the alloy and the heat treatment conditions, various intermetallic compounds can form in the ferrite, principally in the range 600 to 1000°C (figures 18a and 19). [31, 43, 66, 67].

Among these, the most commonly observed is the σ phase, which is known for its particularly harmful effect on the mechanical properties, especially the ductility and toughness. Several analyses have been reported for different grades and various heat treatments. The chemical composition is typically close to Fe-30% Cr-4% Ni-4 to 7% Mo, and its crystal structure is P42/m n m , with a ≈ 0.88 nm and c ≈ 0.45 nm.
In practice, this compound is often confused with the χ phase (I43m, with a ≈ 0.89 nm), with a typical composition Fe-25% Cr-3% Ni-14% Mo (e.g. in SAF 2205 and



(1) UR 52 N / 900°C / 10 H (2) UR 52 N / 800°C / 100 H (3) UR 52 N / 600°C / 100 H



(4) UR 52 N /1040°C /WATER QUENCHED (5) UR 35 N / 500°C / 425 H x 100.000

(6) UR 52 N / 700°C / 10 min (7) UR 52 N / 500°C / 1 H (8) UR 35 N 3 Cu/ 600°C / 1 H

Fig. 18 a : Typical microstructures of aged duplex alloys
1-2-3-6) σ and χ intermetallic phase precipitations
4) water quenched microstructure free of precipitates
5) long term aging of α phase (α')
7) some ε Cu precipitates, 8) ε Cu, M23 C6 and Cr_2N precipitat

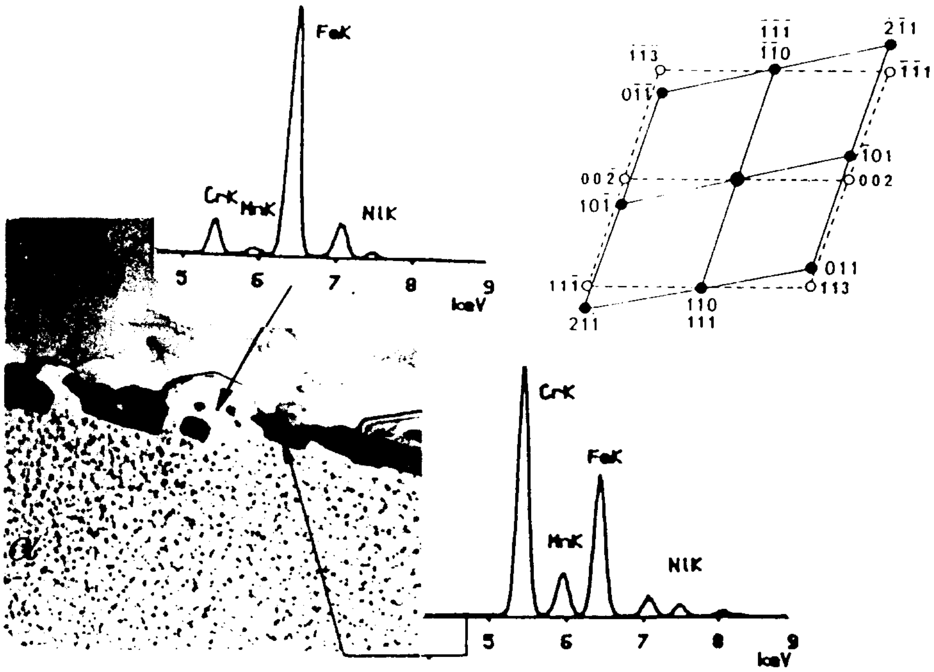


Fig. 18b : Electron microscope investigation on an UR 35 N 3 Cu duplex alloy aged at 500°C for 100 hours

Identification of ε Cu in α grains M23 C6 andCr 2 N on grain boundaries chromium depletion zone between the grain boundaries precipitates.

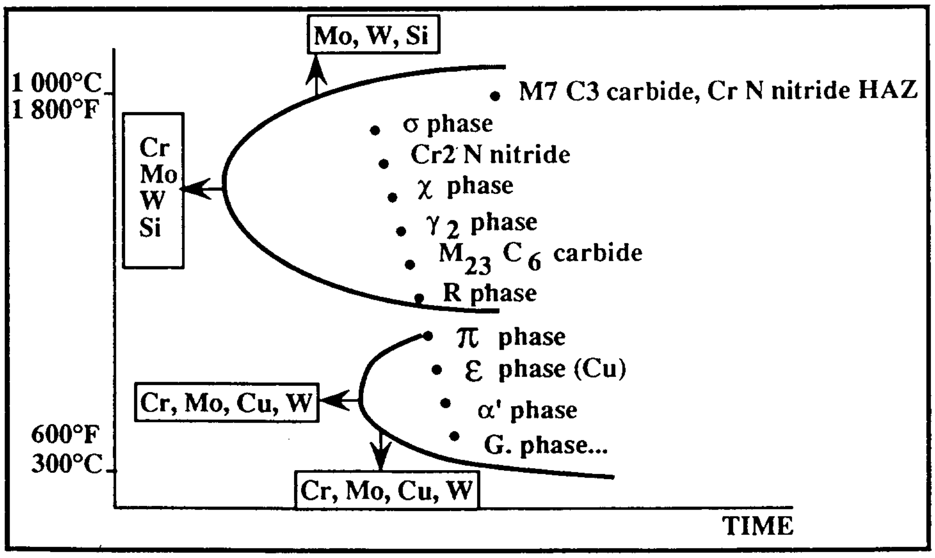


Fig. 19 : Possible precipitations in duplex stainless steels.

UR45N). In fact, the two phases often occur together. The χ phase is generally observed in the range 700-900°C, and may represent an intermediate stage in the formation of phase.

More recently, a 'P-nitride' has been identified, with a P4132 crystal structure (a ≈ 0.65 nm) and a composition Fe-35% Cr-3% Ni-34% Mo (type Fe7Mo13N4), while Laves phases and R phase (R3 structure; a ≈ 1.09 nm, c ≈ 1.93 nm) have also been reported. All these compounds, together with others, such as the G phase, tend to appear after exposures of several hours at relatively low temperatures (550-650°C).

C - Variation of the austenite volume fraction and morphology

As illustrated in figure 6, the volume fractions of ferrite and austenite depend on the temperature. During cooling, an increasing amount of ferrite transforms to austenite. In the case of slow cooling, this can occur by displacement of the grain boundaries. Step cooling,(for instance at 700°C), with or without mechanical deformation, can lead to the precipitation of numerous small acicular austenite grains (γ_2), presenting a $\{111\}_\gamma // \{110\}_\alpha$ Kurdjumov-Sachs type orientation relationship. [68]. At lower temperatures, an even finer structure is formed, by a mechanism similar to a martensitic transformation. A $\{123\}_\alpha$ habit plane, with a Nishyama-Wasserman orientation, has been identified. [69, 70].

Finally, as previously mentioned, the precipitation of carbides, nitrides, and/or intermetallic phases can lead to the formation of austenite, due to local chromium and molybdenum depletion (α--> ($M_{23}C_6$ +γ); α--> σ+γ, etc.), figure 18 .

The formation of the γ_2 phase, particularly in heat affected zones, can sometimes be mistaken for the precipitation of intermetallic phases or nitrides. Due to the accompanying variation in chemical composition, it can also lead to a reduction in the corrosion resistance, especially in HAZ's, and can be a preferred site for the nucleation of nitrides or intermetallic compounds.

D - Transformations involved in low temperature hardening (<550°C)

As for the high chromium ferritic stainless steels, the ferrite of the duplex alloys can be hardened by heat treatment between 300 and 550°C. This hardening can be caused by numerous transformations :

-the formation of α' phase by spinodal decomposition or by conventional nucleation and growth;

-the precipitation of intermetallic phases, nitrides or carbides;

-the precipitation of copper or tungsten rich phases.

The hardening of the ferrite is generally attributed to the formation of the chromium rich α' phase by spinodal decomposition. The ferrite spontaneously separates into zones which are alternately enriched or depleted in chromium (figure 18). However, at higher temperatures, or for lower chromium contents, it cannot be excluded that the transformation may occur by a normal nucleation and growth process. In either case, because of the fine scale of the constituents, the structure can only be revealed by high resolution TEM or Mössbauer spectroscopy investigations.
Studies have shown that the formation of the α' phase is facilitated by increased

chromium and interstitial contents, and to a lesser degree, by the addition of titanium, aluminium and copper. The role of molybdenum remains uncertain, although it is known to cause a sharp acceleration in the hardening rate (figure 13).

Prolonged exposures at 400°C also lead to the formation of complex carbide and nitride phases, which contribute to the hardening of the ferrite due to their small size.

Finally, for alloys containing copper and/or tungsten, other hardening mechanisms can occur. In the case of copper, the supersaturation of the ferrite due to the decrease in solubility at lower temperatures leads to the precipitation of extremely fine particles highly enriched in this element, and significantly extends the low temperature hardening range of the duplex steels. Figure 18 illustrates this type of precipitation for the grades UR52N and UR35NCu. The ε Cu phase was identified by transmission electron microscopy.

4 - Physical properties

Table VI shows some of the physical properties of the stainless steels. The most interesting characteristics of the duplex alloys include :

Table VI - Typical physical properties of stainless steel alloys

GRADES		TEMPER.		YOUNG'S MODULUS GPa	THERMAL EXPANSION $10^{-6}K^{-1}$	SPECIF. HEAT $J\,kg^{-1}\,K^{-1}$	THERMAL CONDUCTION $Wm^{-1}K^{-1}$
		°C	°F				
α	A 516	20	70	205	12,5	450	60
	S 43000	20	70	205	10	480	22
	S 44700	20	70	205	10	480	21
γ	S 30400	20	70	205	16	520	16
	S 08904	20	70	205	16	544	15
α+γ	S 32550	20	70	205	13,5		17
		100	200	195	14	500	18
		200	400	185	14,5	530	19

-Low thermal expansion coefficients, similar to those of the ferritic grades. This limits the requirement for expansion joints, and makes these materials suitable for use in thermal cycling conditions.

-Thermal conductivity higher than in austenitic steels, which, associated with low expansion and the thinner sections rendered possible by their high mechanical strength, makes the duplex grades choice candidates for heat exchanger applications.

-Strongly magnetic behaviour, due to the presence of 50% of ferrite, enabling the use of magnetic clamps during machining.

5 - Mechanical properties

5.1 - Tensile characteristics

Table VII shows typical tensile properties obtained on hot-rolled duplex steel plate. They should not be extrapolated to thin section products, such as cold-rolled sheet, or to forgings or castings. Like all other metals and alloys, their mechanical properties depend on factors such as the grain size, texture and degree of segregation. [18, 71].

TABLE VII - Typical tensile properties of hot rolled duplex stainless steels alloys

GRADES		.2 % YS MPa	U.T.S. MPa	ELONG %	HARDNESS HV 5
α	S44700 -	500	630	18	210
γ	S08904 - UR B6	280	600	50	250
$\alpha + \gamma$	S32304 - UR 35N	450	650	35	240
$\alpha + \gamma$	S31803 - UR 45N	510	730	32	255
$\alpha + \gamma$	S32750 - UR 52N$^+$	650	840	30	270

The major characteristic of the duplex stainless steels is their extremely high yield stress, twice that of austenitic grades of equivalent PREN index (figure 20). The ultimate tensile strength is also high, while the elongation is greater than 25%. These property levels allow the use of thinner sections, leading to considerable savings in weight and capital investment, as will be indicated in other presentations at this conference.

The high mechanical strength is the result of several simultaneous mechanisms :

-interstitial solid solution hardening (C, N);
-substitutional solid solution hardening (Cr, Mo, Ni, etc.);
-strengthening by grain refinement, the presence of two phases preventing their mutual growth during heat treatment;
-possible hardening due to the formation of γ_2 phase;
-strengthening due to the presence of ferrite, since, for a similar composition, this phase is harder than the austenitic structure.

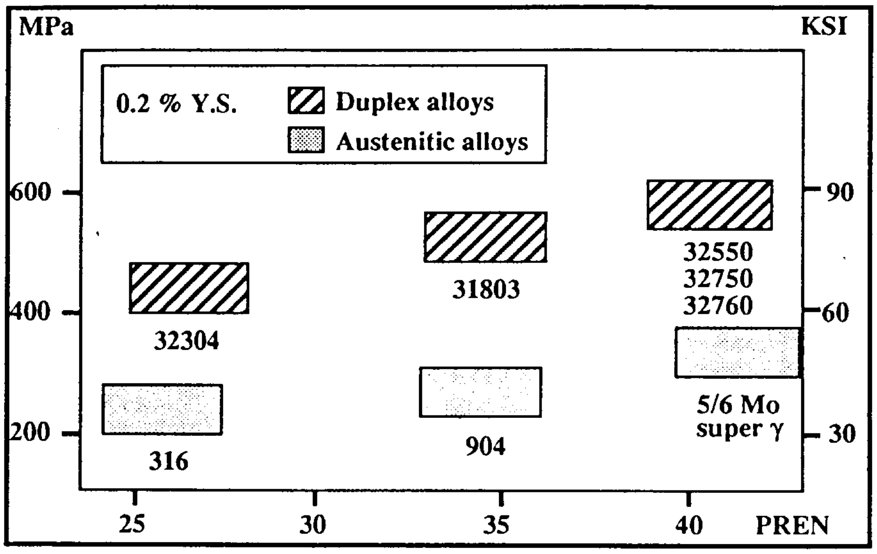


Fig. 20 : Typical . 2 % yield and ult. tensile strengths of hot rolled stainless steels

The combination of these different mechanisms explains the remarkable mechanical properties of the duplex stainless steels. However, it is important to emphasize 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. [72]. Indeed, for small nitrogen additions (<0.1%), it is the austenite which has the lowest yield stress, whereas at higher levels (>0.2%), the ferrite becomes the weaker phase. This explains why the macroscopic hardening effect of nitrogen is observed mainly for the initial small additions, whereas beyond a certain level, found to be equal to 0.12% for the SAF 2205 grade (figure 21), only

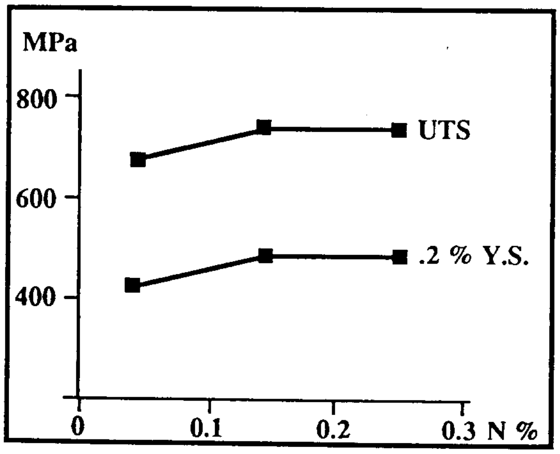


Fig. 21 : Effect of nitrogen additions on the .2 % yield strength and ultimate tensile strength of 22 Cr 3 Mo duplex stainless steels

moderate hardening occurs. A similar effect has been found in the super austenitic grades, no significant further increase in yield strength being obtained when the nitrogen content was raised 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.

W. Hutchington et al. [71] have studied the influence of plate thickness on the tensile properties of a duplex grade. The mechanical characteristics were found to become increasingly anisotropic as the alloy hardened with reducing thickness, figure 22a. Both the hardening and the anisotropy are due to refinement of the structure, the ferrite and austenite grains being elongated parallel to the principal strain axis, figure 22b. There is no "fibre-strengthening" effect, since the two 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)[0$\bar{1}$1] to (211)[0$\bar{1}$1] for the ferrite fibres and (1$\bar{1}$0)[2$\bar{2}$3] for the austenite fibres. The microstructural aspects of the mechanical interaction between the phases merit further study.

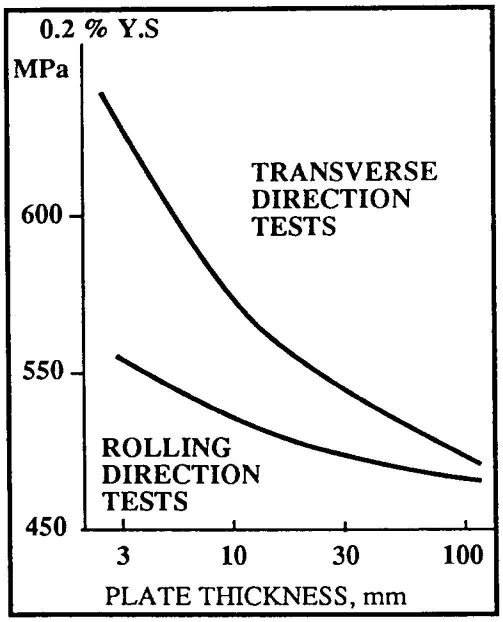


Fig. 22 a : Representative yield stresses for tensile specimens from rolling and transverse directions as function of plate thickness

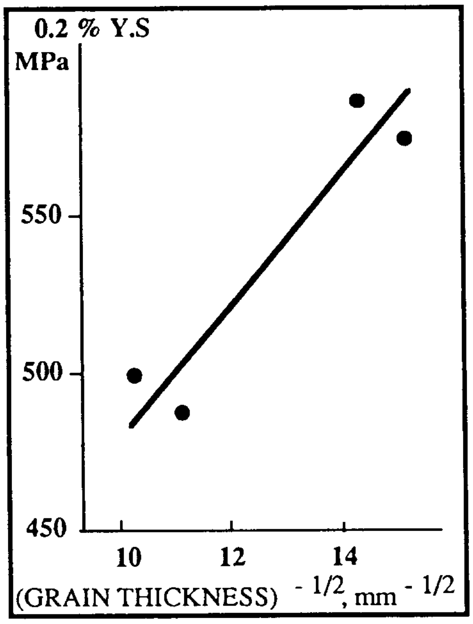


Fig. 22 b : Petch plot relating yield stress (average of O° and 90° tests) to average grain thickness.

Figure 23 shows the influence of temperature on the tensile properties of various duplex grades, and of single phase austenitic or ferritic alloys with compositions close to those of the austenite or ferrite in the two phase materials. The variation of the mechanical strength in the duplex alloys can be seen to be controlled essentially by the ferrite, particularly at low temperatures. Strengthening is thus accentuated at low temperatures, and the room temperature level is maintained over the range 100-300°C.

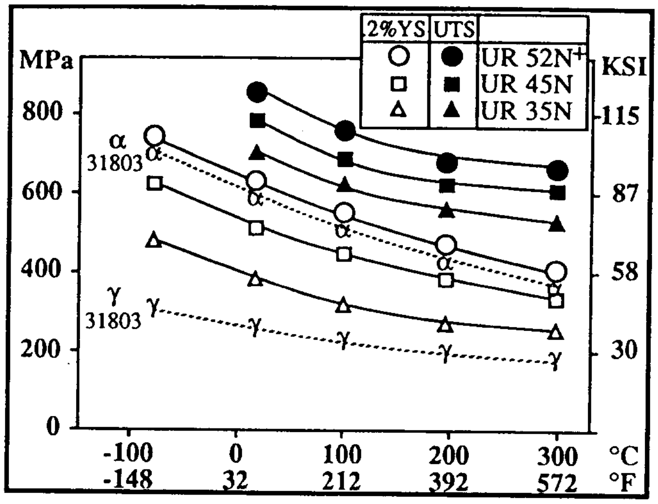


Fig. 23 : Temperature dependance of mechanical properties of several stainless steels

Figure 24 illustrates the effect of cold work on the tensile properties of a number of duplex alloys. [73, 74]. The work hardening rate can be seen to be similar to that of the other types of stainless steel. Only the AISI 304 grade shows a higher work hardening rate, but this alloy undergoes a strain-induced martensite transformation (this could also be partly true for the lowest alloy duplex grade UR35N or SAF 2304). This capacity to work harden up to yield strengths of more than 1200 MPa is exploited in the manufacture of wirelines, surgical prostheses, etc.

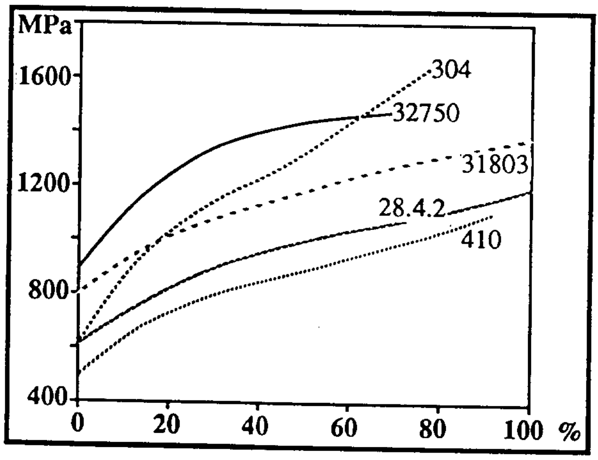


Fig. 24 : UTS of different stainless steels as function of cold deformation by wire drawing

Figures 25 and 26 show the influence of structural transformations during heat treatment on the tensile properties and hardness. [32, 75, 76]. The intermetallic phases σ and χ, formed in the range 700-950°C, clearly have a marked effect on ductility, and, as will be described below, this is confirmed by toughness measurements. The

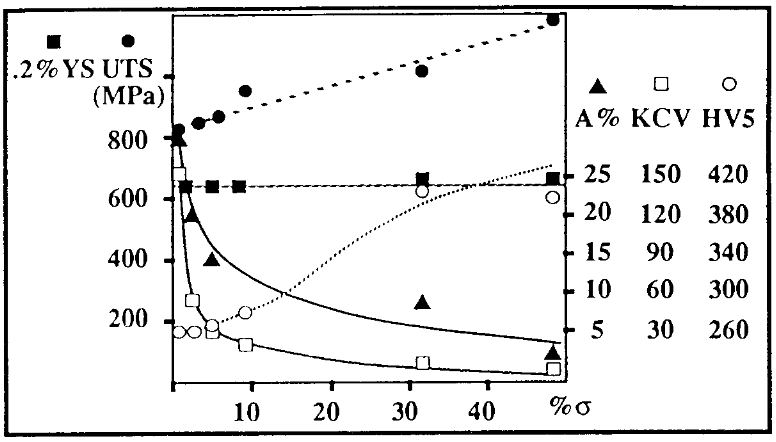


Fig. 25 : Mechanical properties of UR 52N duplex alloy as function of sigma phase precipitation by thermal ageing

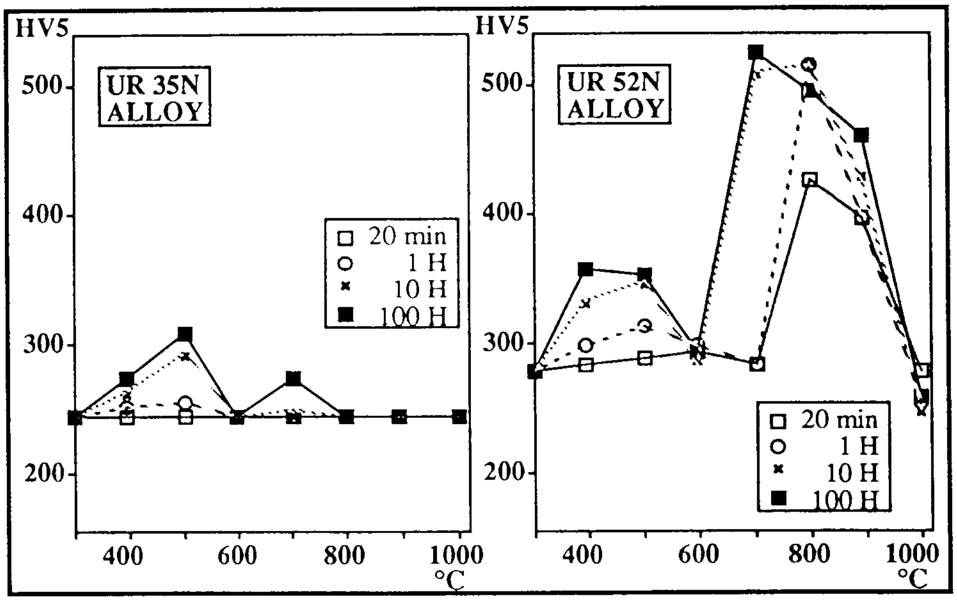


Fig 26 : Effect of thermal aging on the HV5 hardness of UR 35N and UR 45N alloys

presence of intermetallic phases, even in small amounts, is to be avoided. On the contrary, the addition of copper enables considerable hardening to be obtained in the duplex steels, without excessive loss of ductility, provided that the heat treatment has been optimized. It is therefore 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). (Figures 27 and 28).

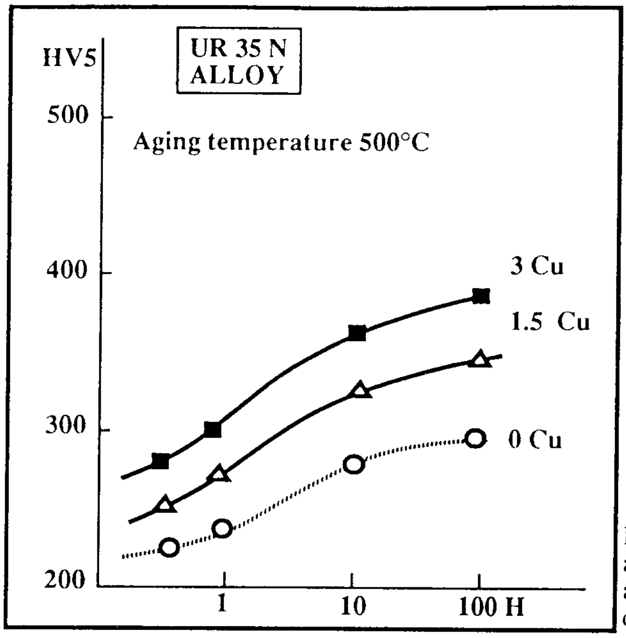


Fig. 27 : Effect of copper additions on the thermal aging behavior of UR 35 N duplex alloy

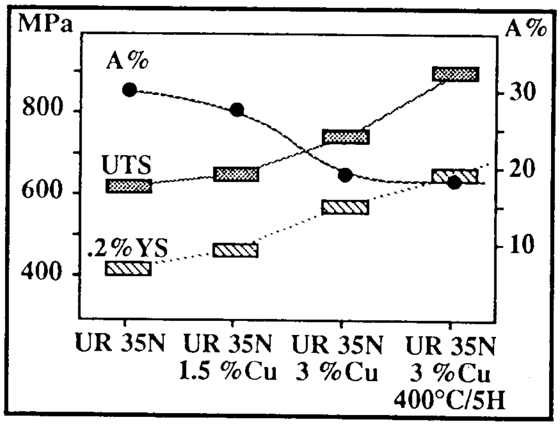


Fig. 28 : Effect of copper additions and 400°C aging on the mechanical properties of UR 35N alloy

5.2 - Impact strength

Figure 29 shows the variation of impact strength with temperature for the different families of stainless steel. The behaviour of the duplex alloys is seen to fall between those of the austenitic and ferritic grades. It is important to note that the toughness of the duplex materials remains satisfactory down to temperatures as low as -60°C. However, the superduplex steels appear to have a slightly lower toughness than the other two-phase grades. Also, a certain scatter in the toughness values is observed at room temperature. This can probably be explained by texture variations, but could also

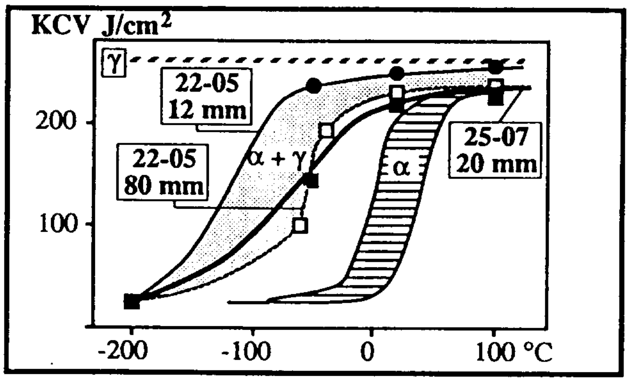


Fig. 29 : Impact Charpy energy versus testing temperature measured for several stainless steels

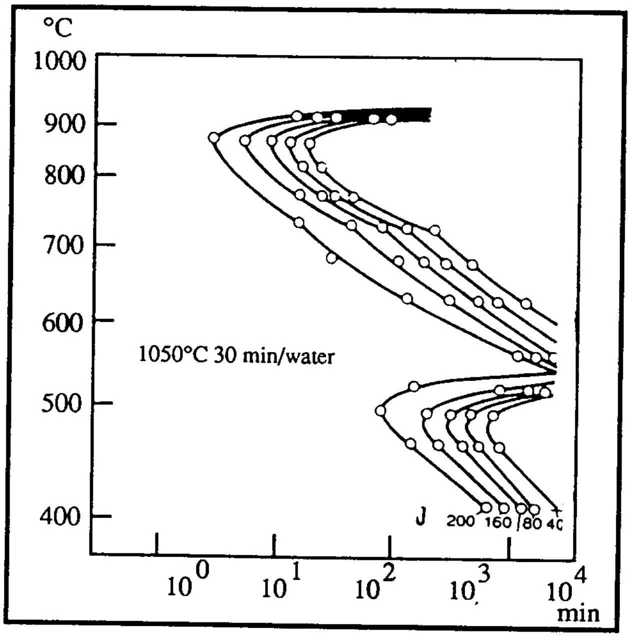


Fig. 30 : Impact Charpy energy versus aging temperature/time treatment for duplex 2205 type alloy (Remanit 4462)

be due to differences in residual elements. Indeed, the impact strength can be improved by reducing the oxygen content, and by controlling the aluminium level to avoid the formation of AlN.[47, 50, 77, 78, 79].

Figures 30 to 33 illustrate the effects of heat treatment on impact strength. The major features to be noted are as follows : [80- 85].

> -Any precipitation of intermetallic phases, such as σ, χ, etc., leads to a sharp decrease in toughness, which rapidly falls to a level which is inadequate for industrial applications. This phenomenon is particularly important in the superduplex grades, in which the transformations are the most rapid. A high temperature solution annealing treatment is recommended (1050-1100°C), followed by rapid cooling (e.g. a water quench). [86].

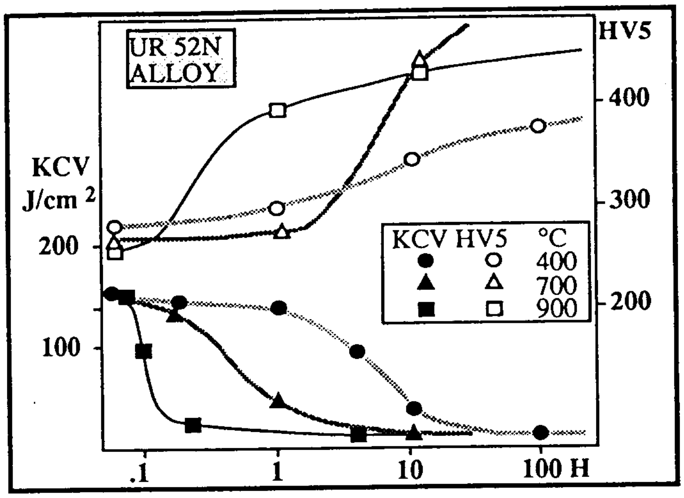


Fig. 31 : Influence of aging treatment on the Impact Charpy energy and HV5 values of UR 52N alloy

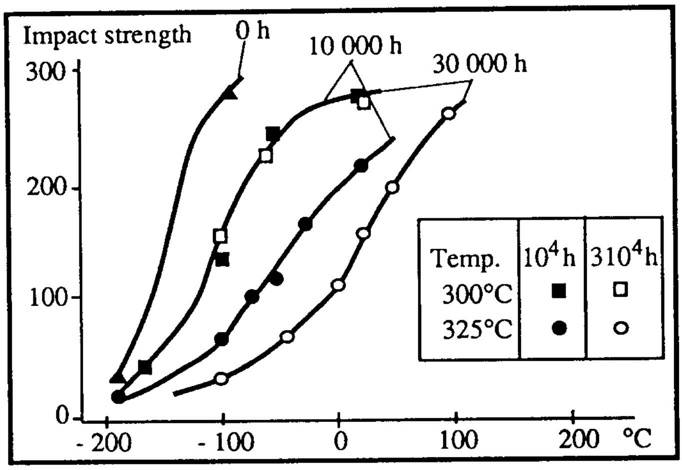


Fig. 32 : Charpy V - notch impact curves for quench annealed SAF 2507 alloy aged at 300°C or 325°C

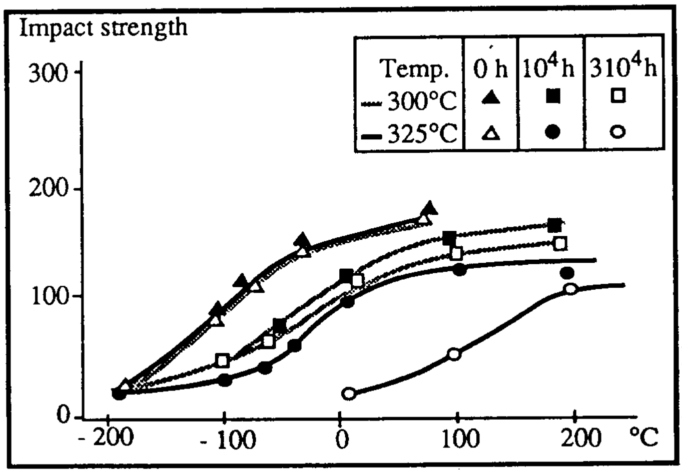


Fig. 33 : Charpy V - notch impact curves for 45 % cold worked SAF 2205 alloy aged at 300 or 325°C.

-The low temperature hardening treatments also lead to a reduction in impact strength. However, particularly in alloys containing copper, it is possible to optimize the treatment conditions (e.g. a few hours at 400-500°C) so as to obtain appreciable hardening, while maintaining satisfactory toughness.

-Prolonged aging in the range 280-350°C can also produce a marked decrease in room temperature toughness, while the ductile to brittle transition is shifted to higher temperatures. Additions of copper and molybdenum appear to accentuate the drop in impact strength due to treatment in the range 260-320°C.

-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 aging in the range 300-400°C leads to an even greater drop in the room temperature impact strength, and in a UR45N/SAF 2205 grade, the ductile to brittle transition can be raised above ambient temperature !

These various observations clearly demonstrate that the use of duplex steels must be strictly limited to a temperature range from -50 to 300°C. For numerous applications, this range must be even further restricted. Thus, the NFA 36.219 standard limits the use of duplex steels to service temperatures between -50 and 280°C for copper-free grades, and between -50 and 260°C for copper-containing alloys. Furthermore, particular attention must be paid to welds, where the initial impact strength should be sufficiently high to accomodate the drop which occurs during ageing. The oxygen content must be kept low and the volume fractions of the two phases must be correctly balanced.

5.3 - Fatigue strength and crack propagation resistance

Figures 34 to 36 have been constructed from data available in the literature, and are based particularly on the review papers of A.G. Haynes and P. Combrade. The following points are to be noted : [16, 87-90].

-The results of rotational bending tests in air on smooth specimens (figure 34) indicate the occurrence of a fatigue limit for all types of stainless steel, situated at about 50% of the ultimate tensile strength. However, for materials with a UTS higher than 1000 MPa, the value is generally found to be less than 50%.

-Similar results obtained in a seawater environment show an extremely large scatter. The fatigue limits vary between 25% and 50% of the UTS for the austenitic and duplex grades, whereas they lie in the range from 10% to 25% of the UTS for the martensitic (12-17% Cr) and precipitation hardened alloys.

-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 seawater type environments, the ratio between the fatigue limit in the corrosive medium and the fatigue limit in air can be correlated to the PREN value. The ratio is 1 for austenitic and duplex steels with PREN values greater than 40.

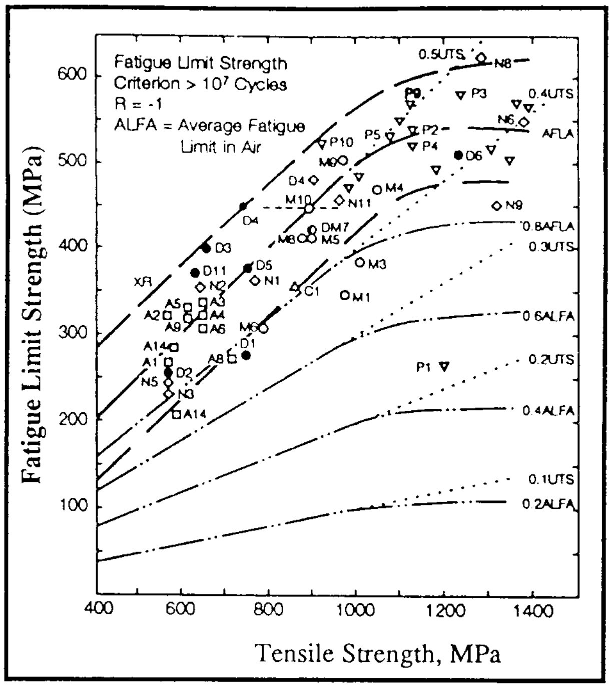


Fig. 34 : Unnotched rotating bend fatigue strength limits versus tensile strength for various types of stainless steel and higher nickel alloys.

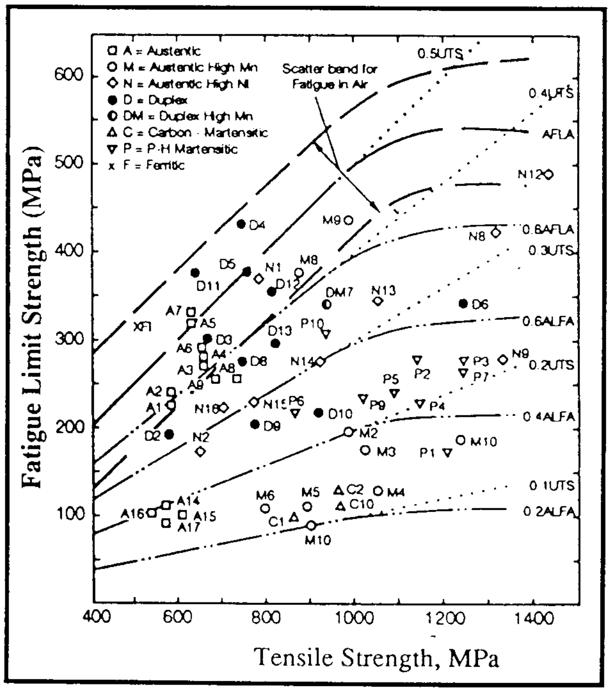


Fig. 35 : Unnotched rotating bend fatigue strength limits versus tensile strength for various types of stainless steel and higher nickel alloys.

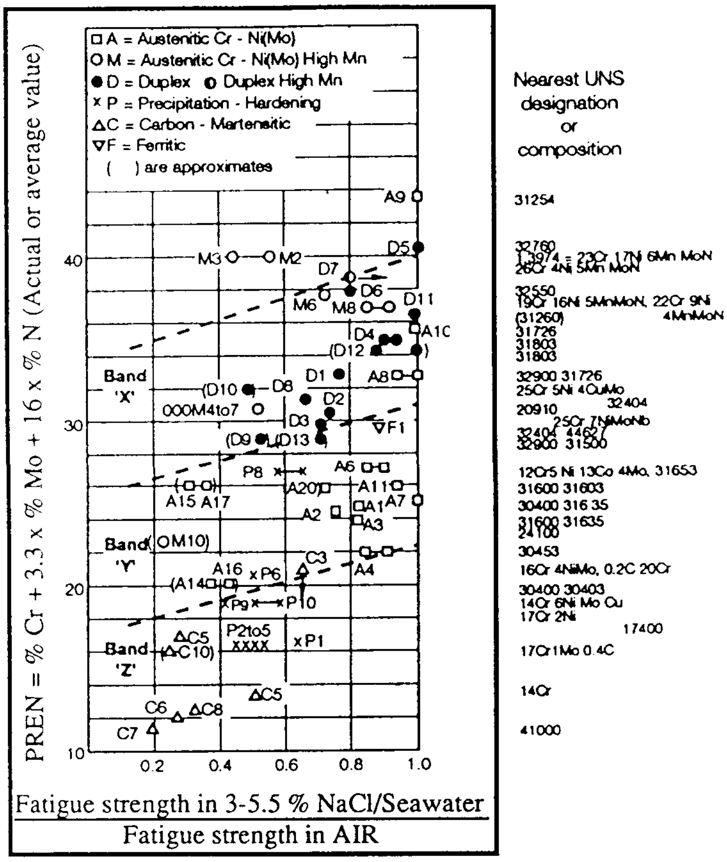


Fig. 36 : PREN versus the ratio of unnotched fatigue strength in sea water type solution to that in air, for various stainless steels.

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

Figures 37 confirms the major influence of the test parameters (particularly the nature of the solution and the imposed oxidation/reduction potential) on the fatigue-corrosion properties. Some crack propagation rate data are shown in figure 38. Those data demonstrate the difficulty of predicting values without performing tests which closely simulate industrial conditions. In effect, the influence of the aggressivity of the environment becomes paramount at low loading frequencies. Moreover, the conditions at the crack tip (composition of the solution and oxidation/reduction potential) can be markedly different from those at the free surfaces. This can affect matter transport and the possibility of repassivation during accelerated propagation.

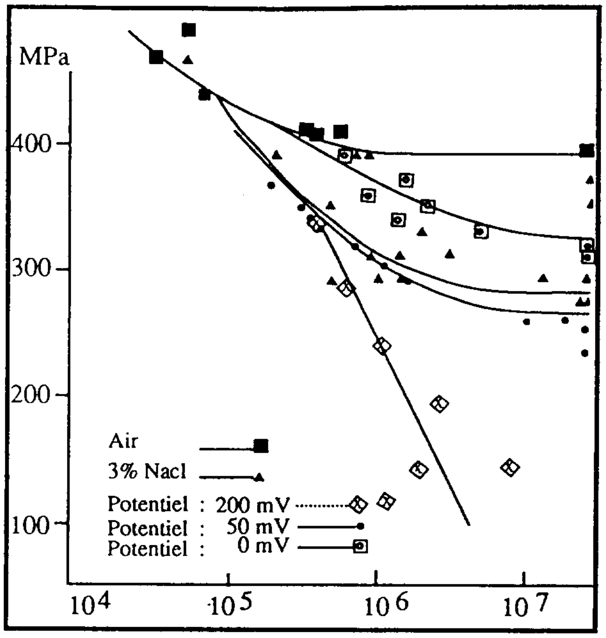


Fig. 37 : Fatigue corrosion tests results on Z3 CND 21-7 duplex alloy

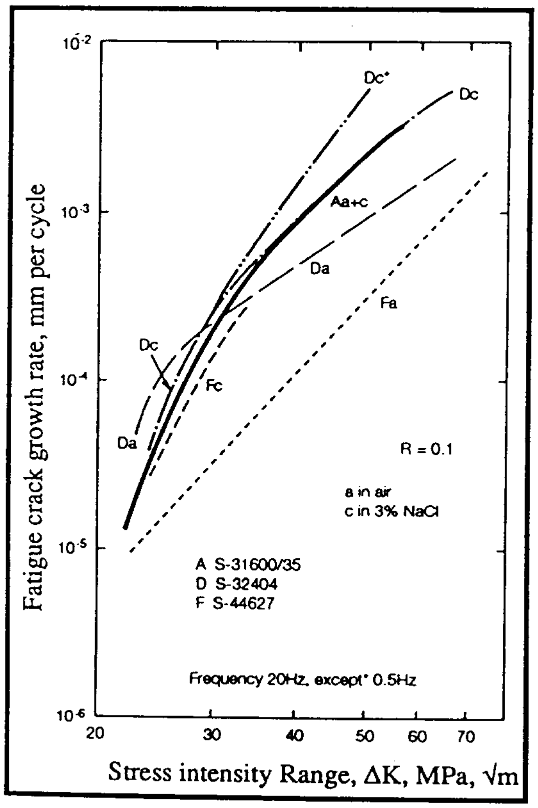


Fig. 38 : Fatigue crack growth rates in air and 3 % NaCl for two austenitic (UNS S31 600 ans S 31 635) a duplex (UNS S32 404) and a ferrite (UNS S44 627) type steels

In conclusion, the fatigue and fatigue-corrosion behaviour of the duplex stainless steels can be seen to be 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 (presence of hydrogen). However, such conditions are rare, and in the majority of cases, the duplex stainless steels have excellent fatigue and fatigue-corrosion properties.

6 - The forming of duplex steels

6.1 - Cold forming

Because of the higher mechanical strength of the duplex steels and their lower ductility compared to the austenitic grades, it is important to study their cold formability. Table VIII shows some cold bending and cupping values determined on thick annealed and quenched sheets.

The behaviour appears to be very similar to that of high molybdenum and nitrogen austenitic steels. Consequently, high forming pressures are required, greater than those for the AISI 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 optimized by controlling the oxygen and hydrogen contents, and by ensuring the absence of intermetallic phases. [50].

Table VIII- DUPLEX STAINLESS STEEL COLD FORMABILITY COLD FORMED CAPS FROM 7 MM PLATES

GRADE	CALCULATED MAXIMAL STRAIN %	$\frac{\text{DISC. DIAM.}}{\text{INSIDE CAP DIAM.}}$	RESULTS
AUSTENITIC ICL 170 HE AISI 317 LMN	71	2,03	SUCCESS
	79	2,20	CRITICAL
	86	2,37	RUPTURE
AUSTENO-FERRITIC UR 52 N	67	1,95	SUCCESS
	71	2,03	SUCCESS
	75	2,12	RUPTURE

A common practice is 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.

6.2 - Hot forming and superplasticity

Because of their two-phase α/γ structure, with 50% of ferrite, the duplex steels can be readily hot-formed ($T > 950°C$). Indeed, they deform so easily at high temperatures that certain precautions are necessary to avoid creep during homogenization treatments. An elegant way to overcome this problem in the case of tubes is to use induction heating, which prevents ovalization, due to its rapidity and its local nature.

Superplastic behaviour (elongations of several hundreds of % before failure) has even been shown to be possible in duplex steels deformed above 900°C. [91, 92]. This phenomenon requires slow strain rates (a few mm/mn), 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 (>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 subsequently σ, produces the required fine structure.

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

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 take advantage of this exceptional hot formability. However, in the future, it is not impossible 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. [93].

7 - Future prospects for duplex stainless steels

As was the case for the austenitic stainless steels, after a somewhat disorganized development period, the duplex steel family now requires a greater degree of standardization. The grade SAF 2205 or UR45N appears today to be the reference alloy for this category of materials. It is gradually becoming recognized that its composition should be centred on 22% Cr, 5% Ni, 3% Mo and 0.17% N, i.e. high molybdenum and nitrogen contents, compared to the alloys produced a few years ago. Further increases in the chromium, molybdenum and nitrogen levels do not seem to be advisable. This composition can be considered to be well balanced, and its acceptance and generalization should help to solve the problems associated with complementary products, packaging and stock management.

On either side of this alloy, the grades UR35N/SAF 2304 and UR52N+/SAF

2507/ZERON 100 harmoniously complete the range of duplex steels, so as to cover the same range of corrosion resistance as the austenitic alloys, ranging from AISI 304 to the super austenitic grades containing 5-6% Mo. Although slight differences remain for the super duplex steels as regards the contents of copper, tungsten and residuals, their compatibility no longer needs to be demonstrated. Nevertheless progress is necessary in order to improve further the corrosion resistance of welds. The use of a non-homogeneous, niobium-free nickel base filler metal could be a possible solution. (625 modified ; Hastelloy C 22 type...).

It is relatively improbable that the chemical composition of these three grades will be significantly modified in the future. However, progress continues to be made in the control of residuals during melting, with the production of "superclean" steels, and in the range of available products (shaped sections, coils, etc.).

Apart from these three alloys, which should become reference grades, what then will be the future developments ?

Upward or downward extensions of the Cr-Mo-N base appear to be unrealistic, without departing from the two-phase α/γ structure, since lower alloy contents would lead to the formation of martensite, while higher levels would enhance the tendency to precipitate intermetallic phases, at least for products obtained by the conventional melting route. A certain potential could still remain in this area, by the use of powder metallurgy techniques. The possibility of the direct casting of thin sheet also remains to be demonstrated. However, it is probable that these processes would offer only a limited gain in alloying capability.

The most probable future developments in the field of duplex steels are twofold :

1) The simple substitution of austenitic grades or non metallic materials due to the cost effectiveness in numerous applications, some of which may remain to be identified, where their combination of physical and mechanical properties and corrosion resistance are highly attractive. Detailed analyses of all stages of fabrication, including welding, with evaluation of material savings, infrastructure costs, etc., will reveal the great potential for cost reductions offered by these alloys. This question is treated by a number of papers at the present conference. Operating expenses, such as maintenance costs, must be integrated in the analysis. Furthermore, the fluctuations in service conditions with time should not be forgotten, since, in general, they become more aggressive, due to the tendency to increase temperatures and pressures in order to improve yields, together with the trend towards a stricter control and a reduction in the volume of industrial wastes, leading to an enrichment of the effluents in corrosive elements (Cl-, F-, etc.). The interest of higher alloy contents, which will reduce service risks, will be gradually recognized.

2) The development of new alloys for specific applications, as has occurred for the austenitic stainless steels. Thus, studies are already under way on duplex steels with improved machinability, on high silicon grades for use in nitric media, on optimized manganese and cobalt additions for applications requiring increased weldability, on alloys with very high nitrogen contents, etc. - this is a field where creativity has a free rein. [23-25, 60, 73, 87, 88, 94, 95].

8 - Conclusions

The first observation is the existence of a family of duplex stainless steels, situated mid-way between the austenitic and the ferritic grades, and combining the best aspects of both. They are characterized by high mechanical strength, due to their fine two-phase structure. The yield stress is double that of austenitic steels with an equivalent PREN index. This represents a potential for substantial economic savings, due to lighter structures. Furthermore, the thermal expansion and thermal conductivity make them particularly suited for use in heat exchangers, and make them readily compatible with low alloy or plain carbon ferritic steels, even under thermal cycling conditions. These advantages are combined with an excellent corrosion resistance, due to their high chromium, molybdenum and nitrogen contents. Their range of properties, for service temperatures between -50 and +300°C, is at least equivalent to that of the austenitic stainless steels, extending from the AISI 304 grade through to the super austenitic alloys containing 5-6% Mo.

It is often an advantage to use them in the place of austenitic grades, when the application requires a corrosion resistance equal to or greater than that of the AISI 316 alloys. However, as has been described, particularly for the duplex steels with the highest chromium and molybdenum contents, their use requires certain precautions, especially with regard to heat treatment. In fact, the same is true for the super austenitic and super ferritic alloys.

The principal variations in the chemical composition of the duplex steels have also been indicated, particularly the progressive increase in the nitrogen content. Today, three grades with narrowly defined chemical compositions emerge as commercial materials : UR35N/SAF 2304, UR45N/SAF 2205 and UR52N+/SAF 2507/ZERON 100. The recognition of these standard alloys should facilitate stock management and improve the availability of complementary products (sheet, tubes, bars, forgings, castings, etc.).

Finally, new duplex steels are undergoing development for specific applications, and will extend the potential range of these materials.

It is hoped that, through the present paper, the duplex stainless steels will gain still more "desciples", for, while their scientific interest no longer remains to be demonstrated, the economic savings which they can procure for the user should continue to extend their popularity.

Aknowledgments :

I would like to express my thanks to all members of the stainless steel team of CLI / CRMC research center and P. CHEMELLE (IRSID). Most of the original results here presented are issued from their works.

Allegato 2

Encl. 2

DUPLEX STAINLESS STEELS

Super duplex stainless steels: structure and properties

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Abstract - The article reviews the latest research in the field of austenitic-ferritic stainless steels with a pitting index PREN > 40, familiarily known as the super duplex grades. Aspects covered include the effects on structure of both isothermal and anisothermal heat treatments, physical and mechanical properties, certain types of corrosion behaviour, and examples of applications. Particular attention is given to the super duplex grades UNS S 32550, S 32750 and S 32760 in the form of hot-rolled and quench-annealed plate (approximately 12 mm thick). These new alloys, developed in 1990 and 1991, are shown to offer an exceptional combination of mechanical properties and corrosion resistance, and have already found applications in a variety of fields. The beneficial effect of high nitrogen additions is emphasised.

1 - Introduction

The so-called "duplex" stainless steels receive their name from the fact that they possess a two-phase microstructure, comprising approximately equivalent volume fractions of austenite and ferrite. The most widely used alloy, which has now become a veritable standard, is UNS S 31803, a dual phase steel containing 22% Cr, 5% Ni, 3% Mo and 0.17% N. The composition of this steel has recently been optimised [1,3] by slightly increasing the molybdenum content, and especially, by increased nitrogen additions (0.12 --> 0.17%). The principal properties of this grade are :

- a high yield strength (460 MPa), twice that of 18-10 type austenitic grades, due to a fine-grained pseudo-composite α / γ structure.

- a corrosion resistance significantly higher than either ferritic (13-17% Cr) or austenitic (18-10-2) grades, particularly as regards to local attack (pitting and crevice corrosion) and stress corrosion, due partly to the high chromium, molybdenum and nitrogen contents (PREN = 35).

- a reasonable cost, due to the relatively low level (5%) of the expensive alloying element, nickel.

All these aspects, and many others, are treated by S. Bernhardsson [3] in the keynote lecture to be presented at this conference.

The present paper will be devoted to the more highly alloyed duplex grades, developed for applications requiring even higher corrosion resistance. A typical feature is a chromium content of about 25%.

The earliest alloys of this type were developed in the 1940's, initially as castings, and subsequently in the form of wrought products. From the outset, increased chromium contents were used to improve corrosion resistance. However, the concentrations were rarely higher than 26-27%, due to the increased tendency to form undesirable intermetallic phases [4-7]. It is only fairly recently that the advantages of nitrogen additions have been shown, as regards :

- the high temperature stability of the duplex structure,
- increased stability of the austenite with respect to the formation of intermetallic phases (σ,χ etc.) in the range 800-1000°C,
- resistance to corrosion, particularly to local attack (pitting and crevice corrosion), in chloride-containing neutral or oxidising acid media.

This positive contribution of nitrogen additions to the corrosion resistance of stainless steels has led to the definition of a pitting index of the type PREN = Cr + 3.3 Mo + 16 N, the nitrogen coefficient is still being the subject of debate, which enables different grades to be ranked rapidly with respect to their resistance to pitting and crevice corrosion in chloride-containing oxidising acid media, based simply on their chemical composition [8,9].

The present article discusses recently developed two-phase stainless steels, with PREN values greater than 40, obtained by 25 % chromium high nitrogen (0.22-0.30%) and molybdenum additions (> 3.5%).

2 - Chemical composition

Table I gives the chemical compositions of a number of duplex stainless steels containing a minimum of 25% of chromium. The only steels which warrant the designation "super duplex", i.e. with a pitting index PREN = Cr + 3.3 Mo + 16 N > 40, correspond to the grades UNS S 32550 (UR 52N+), UNS S 32750 (SAF 2507) and UNS S 32760 (ZERON 100). Their chemical compositions are closely similar. However, the differences in residual copper and tungsten levels should be noted.

It should be emphasised that, in the form of wrought products (hot-rolled plate), these grades are extremely recent. For other products, such as castings or seamless tubing, a more limited experience has existed for a certain time. However, as regards the present compositions, and the wide range of products now available (including hot-rolled plate), none of these grades were presented at the 1986 Duplex Stainless Steels conference in The Hague. The alloy Zeron 100, derived from a casting grade, was however undergoing development for wrought products. Since then, the grades SAF 2507 and UR 52N+ have been developed and marketed in the form of hot-rolled plate, essentially from 1990-1991 [10-12].

Table II gives the chemical compositions of the experimental heats and industrially

TABLE I - LIST OF DUPLEX STAINLESS STEEL GRADES CONTAINING AT LEAST 25 % Cr.

	TRADE MARK		STANDARD	Cr	Ni	Mo	N	Other
WROUGHT ALLOYS	CLI	UR 47N	UNS S32200	25	6.5	3	.18	
	SUMITOMO	S.M.D.P.3	UNS S31250	25	6.5	3	.16	.5Cu .3W
	VEW	A905	-	26	3.7	2.3	.34	6 Mn
	VEW	44LN	WRN 1.4460	25	6.2	1.7	.17	
	CLI	UR52N	UNS S32250	25	6.5	3	.18	1.6Cu
	LANGLEY FERRALIUM ALLOY	255	UNS S32250	25	6.5	3	.15	2 Cu
	JESSOP	2507	UNS S32550	25.5	6	3.5	.18	1.8Cu
	SANDVIK	SAF 2507	UNS S32750	25	7	3.8	.28	
	CLI	UR52N+	UNS S32550	25	6.5	3.6	.26	1.6Cu
	MATER + PLATT	ZERON 100	UNS S32760	25	7	3.4	.25	.7Cu .7W
CAST ALLOYS	FISCHER	GOR 25	WN r 1.4469	25	7	4.5	.18	
		GOR 29	WNr 1.4515	26	7	3	.2	1.2Cu
	PLEISSNER		WNr 1.4462	25	5.5	3	.20	1Cu
	LANGLEY ALLOY	FERMANEL		27	8.5	3	.22	1Cu
	MATER + PLATT	ZERON 100		25	7	3.5	.25	.7Cu .7W
	SCHMIDT + CLEMENS							
	MARESIST 4515		WNr 1.4515	26	6	3	.2	1Cu
	MARESIST 4460		WNr 1.4460	26	6	3	.2	3Cu
	MARESIST G 2507			26	7	4.5	.2	

☐ Super Duplex wrought stainless steels alloys (PREN > 40) produced plates used for a more thorough study of structural stability and corrosion resistance. Most of the present paper concerns super duplex grades in the form of hot-rolled plate.

TABLE II : CHEMICAL ANALYSIS OF INVESTIGATED HEATS

	TRADE MARK	STANDARD	Cr	Ni	Mo	N	Other
A	CLI	exp. Heat A	25	6.4	4.2	.27	
B	CLI	exp. Heat B	25	6.4	4.2	.27	1.5 Cu
C	CLI	exp. Heat C	27	7	3.7	.28	1.5 Cu
D	CLI UR52 N+	UNS S32550	25	6	3.7	..25	1.5 Cu
E	WEIR ZERON 100	UNS S32760	25	7.7	3.7	.22	.6 Cu .7W
F	SANDVIK SAF 2507	UNS S32750	25	6.8	3.8	.27	
G	CLI UR52 N	UNS S32550	26	6	3	.16	1.5 Cu

3 - Microstructure

3.1 - Isothermal heat treatments

3.1.1 - Heat treatment at T > 1050°C

The duplex stainless steels solidify Liquid + ferrite field, and it is during cooling of the solid that part of the ferrite transforms to austenite in order to have the $50\alpha / 50\gamma$ structures. The structure of wrought products is therefore determined both by the chemical composition of the alloy and the quench-annealing temperature (figure 1). Heat treatment at a temperature above 1050°C will then lead to a modification of the volume fractions of the two phases and of their chemical compositions. Figure 2 shows the variation with temperature of the ferrite content (determined by optical microscopy, using the grid method), for the different α / γ steels studied, including in particular a range of nitrogen contents [13].

As regards the high temperature stability of the duplex structure, it is important to note the marked effect of nitrogen compared to those of chromium and molybdenum. The gamma-stabilising action of nitrogen is clearly revealed, since, in spite of larger additions of ferrite-stabilising molybdenum, for about 0.25% N, the volume fraction of ferrite at 1050°C is close to 50%, compared to nearly 60% in the 25% Cr heat containing only 0.18% N.

Furthermore, the reversion to ferrite increases more slowly with rise in temperature. As will be discussed later, this stabilisation of the duplex structure at high temperatures by the addition of nitrogen is of particular interest in the heat-affected zone (HAZ) of welds.

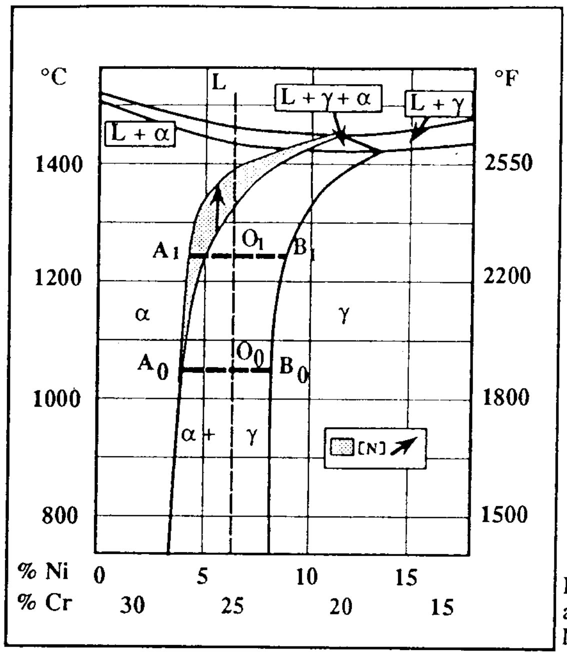

Fig. 1 : Schematic effect of nitrogen additions on the pseudo binary Cr - Ni - 68 Fe phase diagram

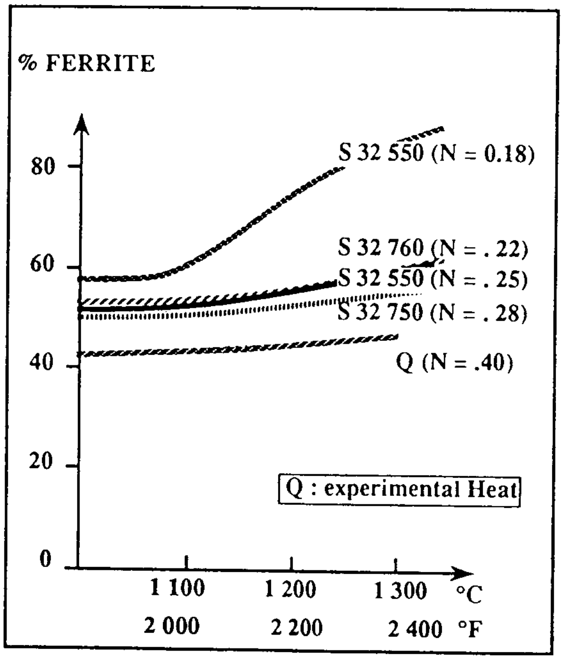

Fig 2 : Variation of ferrite content with increase of Temperature for 25 Cr Duplex Stainless Steels

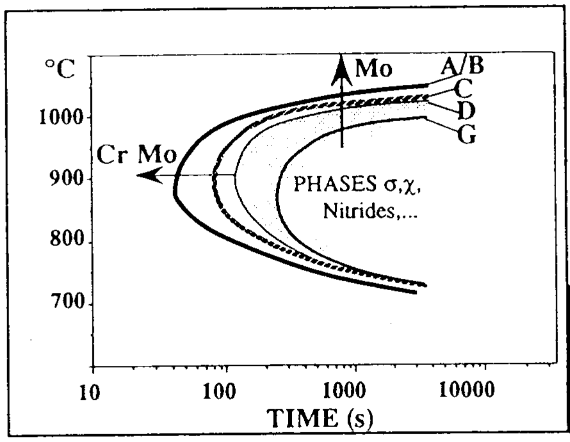

Fig 3 : TTT Diagrams

	Cr	Mo	N	Cu
A	25	4.2	.27	-
B	25	4.2	.27	1.5
C	27	3.7	.28	1.5
D	25	3.7	.25	1.5
G	25	3	.18	1.5

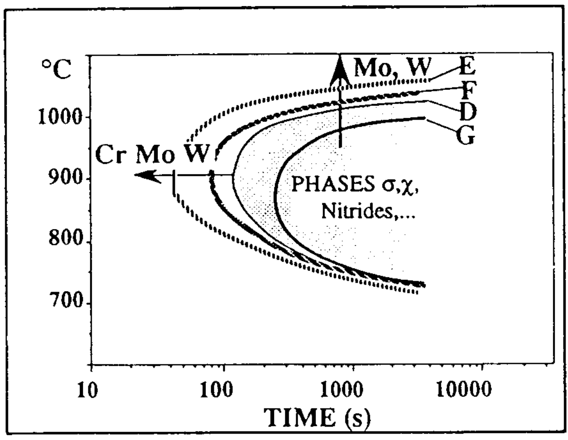

Fig 4 : TTT Diagrams

	Cr	Mo	N	
D	25	3.7	. 25	1.5 Cu
E	25	3.7	. 22	.6Cu.7W
F	25	3.8	. 28	-
G	25	3	. 18	1.5 Cu

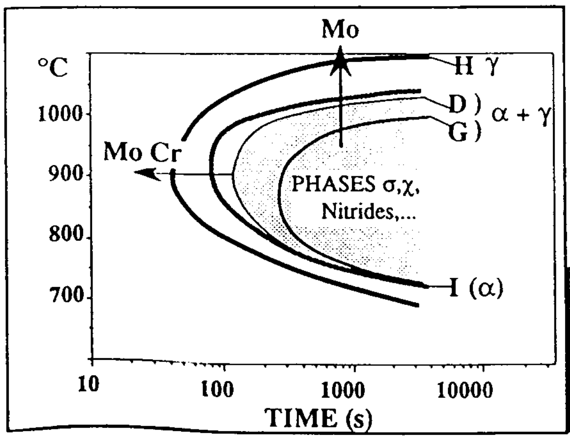

Fig 5 : TTT Diagrams

D • Super duplex UR 52 N$^+$
H • Super austenitic steel 5/6 Mo
I • Super ferritic steel 29.4

	Cr	Mo	N	Cu
D	25	3.7	. 25	1.5
G	25	3	. 18	
H	25	5	. 20	
I	29	4	-	

3.1.2 - Heat treatment at T < 1050°C

The TTT diagrams in figures 3 and 4 show the kinetics of precipitation in the duplex alloys investigated. The curves were plotted on the basis of optical microscopy observations. The results clearly indicate that precipitation is accelerated by increasing additions of tungsten and chromium. The precipitation range is extended to higher temperatures in alloys rich in molybdenum and tungsten. Copper has no effect on the precipitation of intermetallic phases between 800 and 1020°C. In fact, the solubility limit for copper is not exceeded, either in the ferrite or in the austenite. This is confirmed by the fact that the partition coefficient between the two phases remains approximately the same for additions of 1.6 or 0.2% Cu [1,14].

Figure 5 [15,16] compares the precipitation kinetics in super duplex, super austenitic and super ferritic grades. It is clear that the precipitation rate in the super duplex alloys is lower than in the other types of stainless steels. Nevertheless, the three grades require particular attention to be paid to heat treatment cycles, with rapid removal from the furnace, followed by water quenching, in order to conserve a precipitate-free structure in the hot-rolled sheet. High-performance industrial equipment is particularly recommended for heavy-section components, in order to avoid precipitation. At Creusot-Loire Industrie, 60 mm thick plate has been produced in super duplex steel.

It should also be pointed out that re-solutioning of precipitate phases is extremely rapid in α/γ alloys. A few minutes at 1050-1070°C are sufficient for grades UR 52N+ and SAF 2507. A slightly higher temperature, 1100°C, is necessary in the UNS S 32760 grade, due to the effect of tungsten. It should be noted that higher temperatures would also be required in the case of welds, since the segregation associated with higher levels of residuals, such as silicon, can lead to the formation of more stable intermetallic phases (Si and Mo enrichment). This tendency should be counteracted where possible by a tighter control of sigma-promoting elements, such as manganese, silicon and phosphorus.To high solution annealing temperatures (1120°C ...) will be avoided in order to limit the nitrogen content of the ferrite and in this way reduce the kinetics of nitride precipitations, detrimental for the corrosion resistance.

In the case of the super austenitic grades, heat treatment at temperatures ≥ 1120°C is required.

The nature of the precipitate phases varies widely in the different super duplex grades, all of which have not yet been fully investigated. Figure 6 summarizes results taken from the literature and observations made in the author's laboratory. More detailed information is to be presented elsewhere at this conference [1,17,18].

Precipitation at lower temperatures (300-600°C) is also discussed in these papers. However, it is noteworthy that the high chromium and molybdenum contents can lead to hardening of the ferrite by spinodal decomposition and/or by conventional precipitation. Quench-annealed products are not affected, but the phenomenon may occur in heavy-section parts such as certain castings or forgings [19].

Copper and tungsten additions can accelerate hardening and widen its range, particularly for temperatures higher than 400°C. This hardening effect has long been exploited for improving the abrasion-corrosion resistance of duplex steels for pump castings. The phenomenon is well understood and does not lead to any significant reduction in corrosion resistance, while the toughness remains at a good level [20].

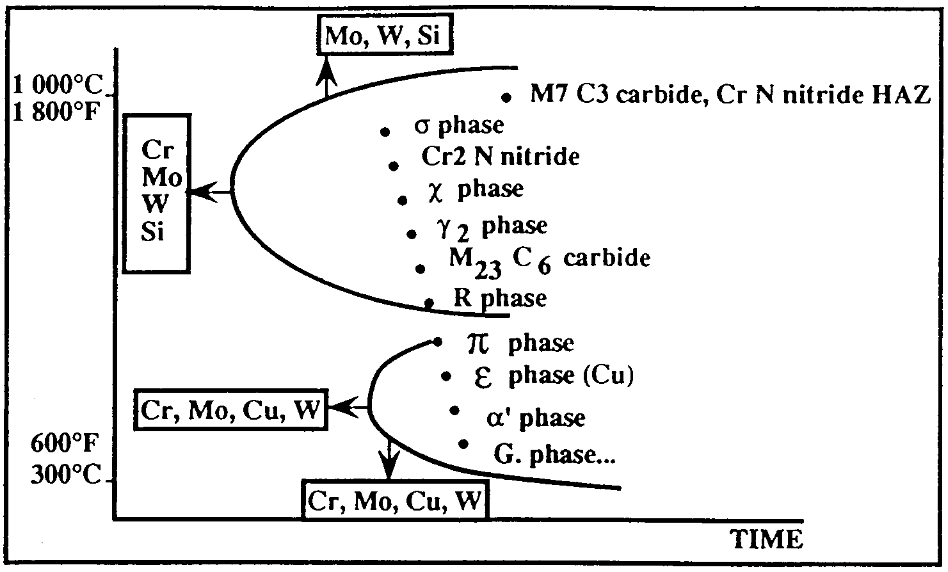

Fig. 6 : Possible precipitations in Super duplex stainless steels.

3.2 - Anisothermal heat treatment

3.2.1 - Variation of ferrite content during Heat treatment at T>1050°C

Figure 7 shows the variation in the maximum ferrite content in the HAZ after TIG melting with different cooling rates (obtained by varying the welding power for a given plate thickness). Measurement of the ferrite content was performed by optical micrography at a magnification of x1000, so that the values are conservative. Note that it is the maximum ferrite content which is plotted as the ordinate. Nitrogen is without question the element which has the most marked effect. An increase in its concentration considerably attenuates the reversion to ferrite in the HAZ, for a large range of cooling rates. As has already been seen, this effect can be explained by retardation of the austenite to ferrite transformation on heating, and not by an accelerated inverse

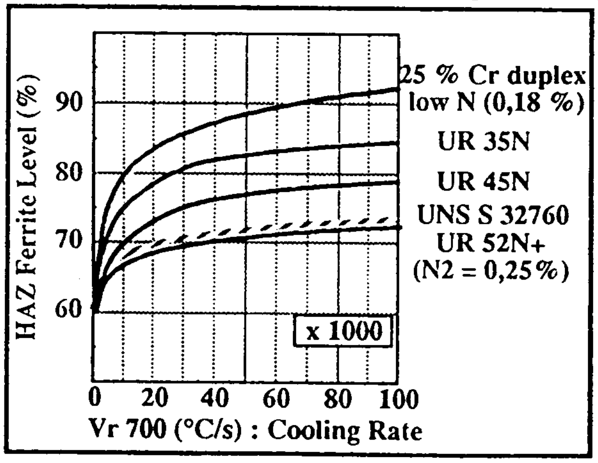

Fig. 7 : Variation of the HAZ maximum ferrite level determined by optical metallography at x 1000 magnification as a function of the cooling rate.

transformation to austenite of the ferrite formed at high temperature (reversed austenite). This is of particular interest, since it significantly reduces the structural transformations in the HAZ of super duplex steels, which thus conserve properties similar to those of the base metal. In effect, in addition to the volume fractions of ferrite and austenite, the compositions of the phases also remain virtually unchanged during the heat treatment [21,22].

3.2.2 - Precipitation during cooling

The isothermal TTT diagrams are conservative, since the minimum time required to initiate the precipitation of a phase is shorter than that observed in the case of continuous cooling. A few results obtained under conditions of continuous cooling are available in the literature. Figure 8 shows those obtained for the UNS S 32760 and S 32550 plates whose compositions are given in table II. Representative constant cooling rate curves have been superimposed.

The UNS S 32760 grade can be seen to be more prone to phase precipitation than UR 52N+. The deleterious effect of tungsten on the stability of the austenite and ferrite phases has already been emphasised.

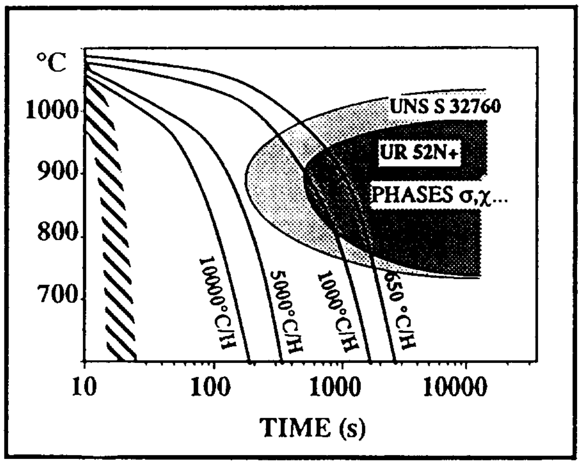

Fig. 8 : Continous cooling diagram (heating at 1080°C)

▨ Typical HAZ cooling rates

The limiting cooling rate for precipitation, after treatment at 1080°C appears to be 5,000°C/hour for UNS S 32760 and 1,000°C/hour for UR 52N+. These rates are much slower than those measured during the water quenching of ≈20 mm thick plates (≈100,000°C/hour). The limiting thickness for water quenching is greater than 100 mm for UR 52N+.

During welding, particularly for a single-pass seam, the cooling rates are much higher. By ensuring a maximum inter-pass temperature of 120-150°C, there is no risk of precipitation in the HAZ [23]. Paradoxically, the old grades containing 25 % Cr and only 0.15-0.18 % N, in spite of a lower molybdenum content (3 %), are more prone to HAZ precipitation, due to the changes in the volume fractions of α and γ, and therefore in the chemical compositions of these phases [24,25].

4 - Physical and mechanical properties (base metal)

Tables III to V give some physical and mechanical properties, for 12 mm thick plate in alloy UR 52N+. Figure 9 shows these results schematically, and compares them to the properties of super ferritic and super austenitic grades. Figure 10 illustrates the effect of cold work on the room temperature mechanical strength of the SAF 2507 grade, and figures 11 and 12 present some fatigue results for the same alloy [26].

TABLE III - TYPICAL MECHANICAL PROPERTIES OF HOT ROLLED ANNEALED 12mm THICK PLATE OF SUPER DUPLEX STAINLESS STEEL

	20°C	100°C	200°C	70°F	200°F	400°F
.2 % Y.S.	650 MPa	525 MPa	470 MPa	94 KSI	76KSI	68 KSI
U.T.S.	840 MPa	720 MPa	700 MPa	104 KSI	104 KSI	101 KSI
Elong.	30 %	30 %	30 %	30 %	30 %	30 %
	20°C	-20°C	-50°C	70°F	0°F	-60°F
KV	120 J	100 J	80 J	88 ft lb	74 ft lb	59 ft lb
Hardness	HV : 270		HRC : 25		HB : 260	

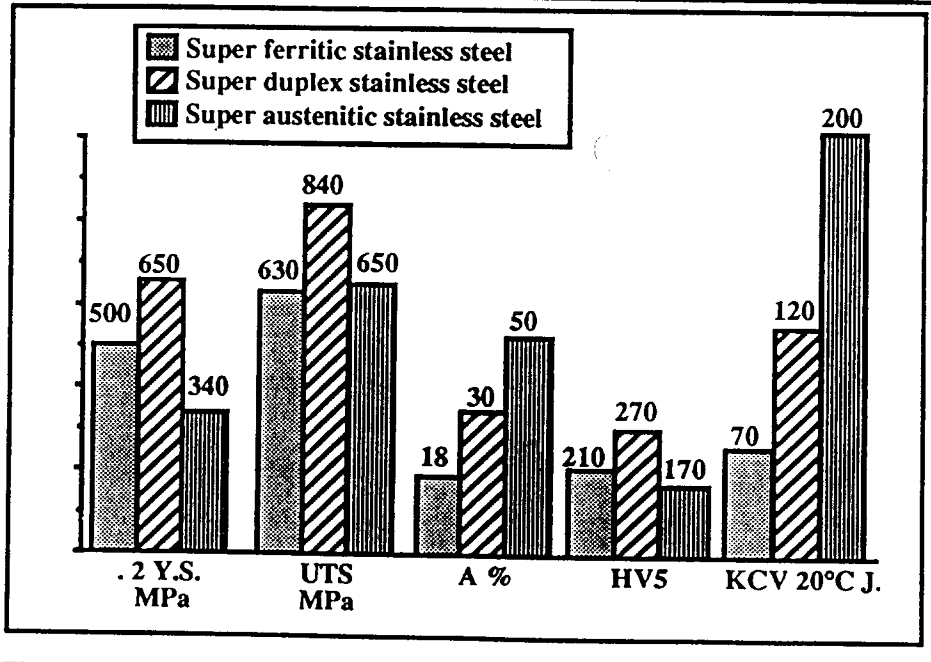

Fig 9 : Typical Mechanical Properties of highly alloyed stainless steels

TABLE IV - TYPICAL PHYSICAL PROPERTIES VALUES OF SUPER DUPLEX STAINLESS STEELS (UR52N+ ALLOY)

Temperature		Young's Modulus (GPa)	Thermal expansion 10-6K-1	Specific heat J.Kg-1.K-1	Thermal conduction W.m-1.K-1
°C	°F				
20	70	205	13.5	450	17
100	200	195	14	500	18
200	400	185	14.5	530	19

TABLE V - EFFECTS OF HEAT TREATMENTS ON THE MECHANICAL PROPERTIES OF UR 52 N ALLOY

Temp. °C	Time H.	2 % Y.S. MPa	U.T.S. MPa	Elong. %	KCV J/cm2	HV5	α % into σ, χ...
1050	0.2	665	820	28	130	260	0
900	0.2	670	1000	3	5	390	50
700	2	660	855	20	55	260	2
700	2.5	620	840	18	30	270	5
700	3	640	880	14	25	278	8
700	4	620	900	12	10	419	33
600	100	640	1000	14	10	309	-
450	5	905	1068	17	58	340	-
400	1	770	900	24	96	301	-
400	5	785	938	21	90	293	-
400	100	990	1128	20	10	362	-

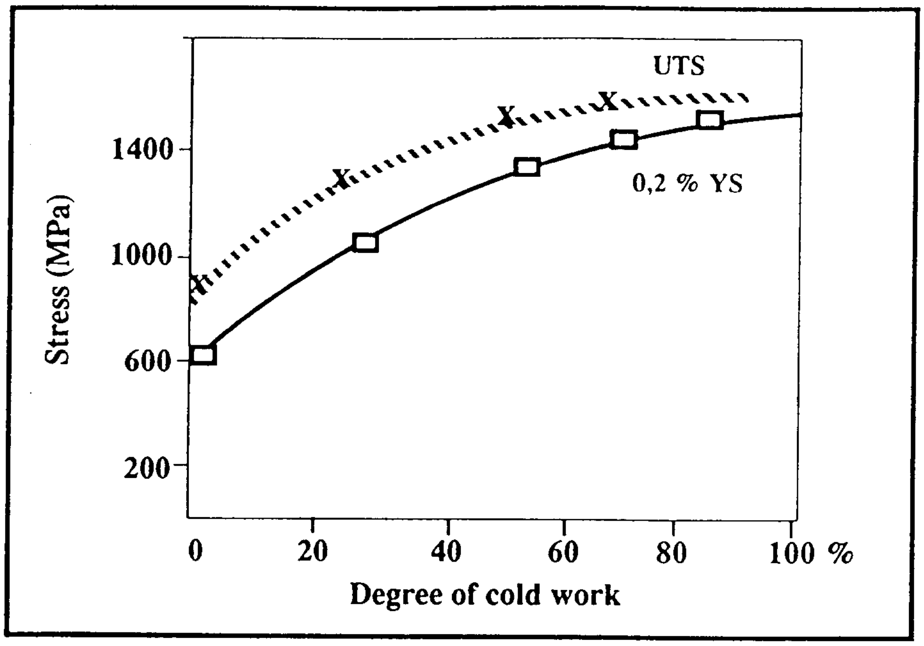

Fig. 10 : Ultimate tensile and .2 % yield strengths as a function of cold drawing

The following observations can be made concerning the super duplex grades :

-the yield strength is very high (≥ 550 MPa for quench-annealed sheet) ;

-the impact strength remains good even at -50°C However, this is likely to vary with the type of product (cast or wrought) ;

-the thermal expansion coefficient is similar to that of a C-Mn steel ;

-the mechanical properties are affected by intermetallic phase precipitations

-the thermal conductivity is higher than those of austenitic stainless steels ;

-strengthening can be obtained by heat treatment or cold working ;

-the fatigue strength is extremely high.

These steels thus enable considerable weight gains to be achieved, for instance, in off-shore engineering equipment, in heat-exchangers, etc.

The specific case of welded joints will be treated in other papers. However, it is important to emphasise that, in order to obtain good low temperature mechanical properties (toughness), the oxygen content must be carefully controlled, so that any fluxes should preferentially be of the basic type [27,28].

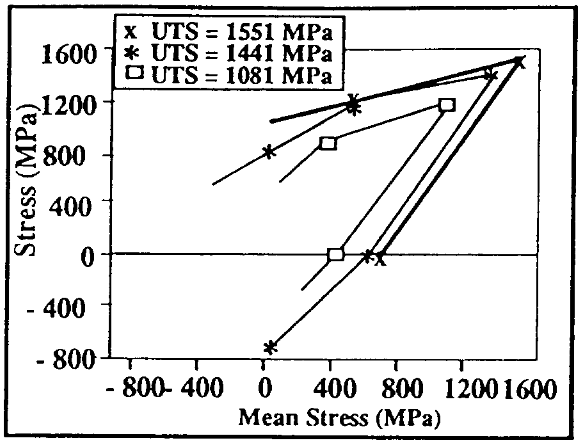

Fig. 11 : Fatigue limits in the Smith's diagram for 25 Cr - 7 Ni - 4 Mo - 0.3 N steel

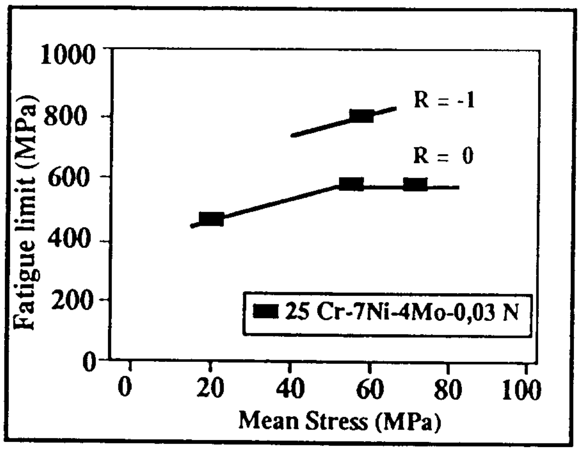

Fig. 12 : Summary of the fatigue tests as a function of the cold drawing degree

5 - Corrosion resistance

Figures 13 to 18 illustrate certain types of corrosion behaviour, and suggest the following comments [10, 11, 24, 29, 30, 31].

-The behaviour of the three super duplex grades investigated (all in the form of 10/15 mm thick quench-annealed hot rolled plate) is very similar, no significant difference being revealed. The PREN value seems to be a good ranking criterion for chloride-containing neutral and acid media, whereas the addition of copper apears to be beneficial in sulphuric environments.

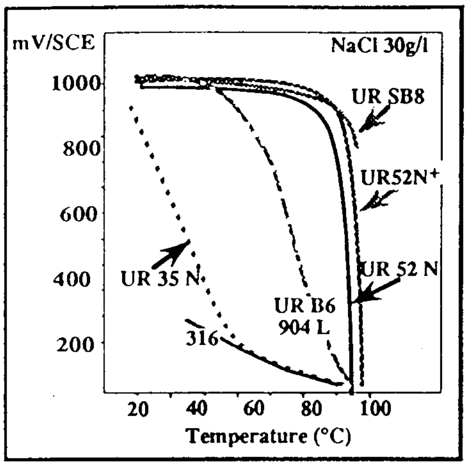

Fig. 13 : Pitting potential determined by polarization curves for different stainless steels

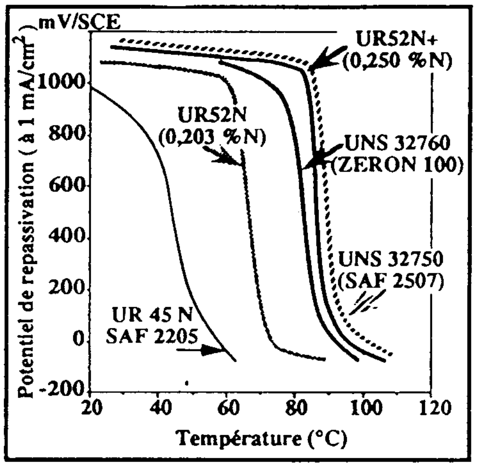

Fig. 14 : Repassivation potential in 15 % NaCl solution saturated CO $_2$

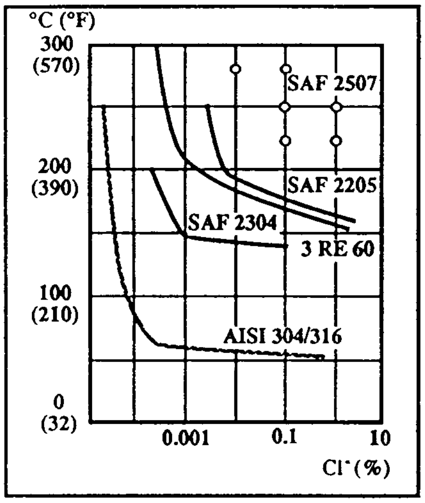

Fig. 15 : Constant-strain tests in autoclave. Above the curve, SCC occurs. Open circles means no SCC for UNS S 32 750 / SAF 2507.

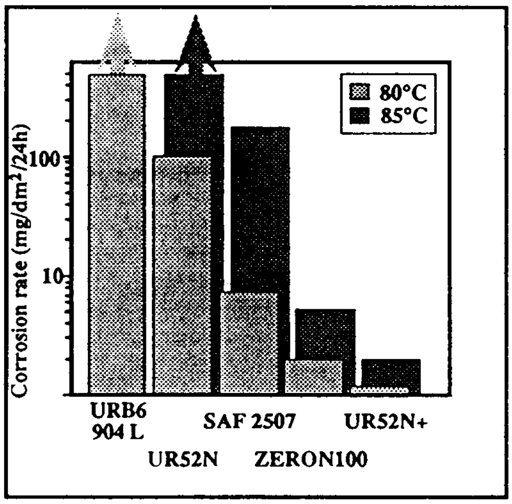

Fig. 16 : Corrosion rate in 10% H2SO4 + 500 ppm Cl-, aerated, at 80°C and 85°C

-The resistance of the super duplex grades is considerably better than that of the duplex grade UNS S 31803, and is also superior to that of the 25% Cr grades with lower molybdenum (3%) and nitrogen (0.18%) contents.

-The behaviour of the super duplex steels is equivalent to that of the super austenitic alloys (5-6% Mo).

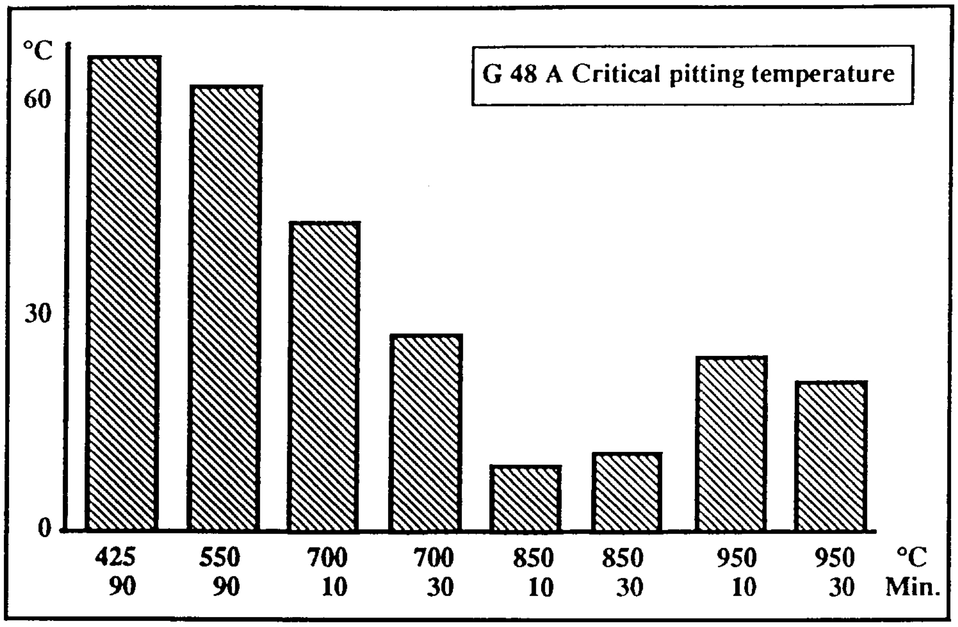

Fig. 17 : Alloy UR 52 N + : effects of heat treatments on the critical pitting temperature determined by G 48 A test method.

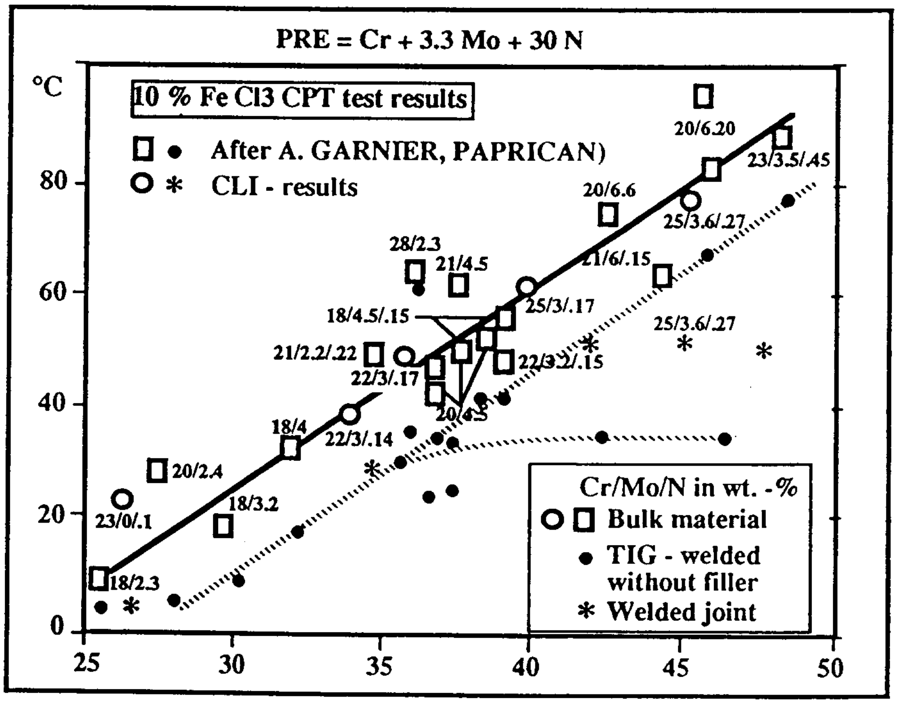

Fig. 18 : Influence of PRE on critical pitting temperature of stainless steels

-In the ASTM G48 test, any precipitation in the super duplex steels
-heat treatments between 900 and 600°C- leads to a marked reduction in the critical pitting temperature. This is not the case of the grades hardened by aging at ≈425°C and containing copper (UR 52N+).

-The weld metal has lower corrosion resistance than the base metal, due to its segregated structure. "Overalloying" is therefore desirable. However, the scope for increasing the alloy content is limited in super duplex steels, due to the two phase structure and the already high levels of molybdenum, chromium and nitrogen. There is a strong risk of promoting the precipitation of unwanted phases, particularly in the presence of sigma-stabilising elements such as silicon, phosphorus, tungsten and molybdenum, leading to a simultaneous reduction in ductility and corrosion resistance. Progress remains to be made as regards the choice of filler metal and optimization of the nitrogen. Some work concerning heterogeneous filler metals are also under way (625 without niobium type...).

6 - Applications

The numerous applications which already employ super duplex steels include those in the oil industry, particularly off-shore drilling equipment, and marine engineering : platform heat exchangers (seamless tubing), fire circuits, two-phase pumps (Posseidon forging), wirelines (wrought), manifolds (welded tubes), various pumps (castings), oilfield effluent extraction circuits, marine propellors, etc.

More recently, a resulphurized grade with improved machinability (UR 52NRS) has been produced for the manufacture of aircraft-carrier catapult rails for the United States Navy (marine corrosion and abrasion).

Other industrial sectors are also concerned, particularly chemical engineering, for the transport of hot chloride-rich solutions, phosphoric acid (fertilizer) production, sulphuric acid handling (hydrometallurgy), purification (scrubbers - sulphuric media with abrasion, where copper additions are highly beneficial), and the food industry, including breweries ! [32-34].

7 - Conclusions

The super duplex stainless steels, characterized by a pitting index PREN > 40, are new materials, developed essentially in 1990 and 1991, particularly as regards hot-rolled plate.

They possess high mechanical strength, with a yield stress twice that of austenitic stainless alloys. They thus enable considerable weight savings to be achieved.

These grades have exceptional corrosion resistance, equivalent to that of the super austenitic steels, due to high chromium (25%), molybdenum (3.8%) and nitrogen (0.26%) contents (PREN > 40).

The nitrogen additions also stabilise the duplex structure in the heat affected zone of welds, helping to maintain the corrosion resistance.

The excellent resistance to localized corrosion is due partly to the very low inclusion contents, which are a characteristic feature of the AOD/VOD melting route employed.

These processes also offer increased control of residuals, leading to improved hot workability.

Finally, considerable effort is being expended in order to improve the weldability of these materials and to extend the range of products available.

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Allegato 3

Encl. 3

The corrosion resistance of duplex stainless steels

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Abstract

The corrosion resistance of duplex stainless steels is reviewed. Special attention is given to their resistance to corrosion in acids and caustics and their resistance to pitting, crevice corrosion and stress corrosion cracking. It is concluded that duplex stainless steels have excellent corrosion properties and can replace many other types of materials in various applications.

1. Introduction

Duplex (ferritic-austenitic) stainless steels in cast and wrought production forms have been manufactured and used in the industry since the 1930'ies (e.g. 1-4). The reasons for the early use of this group of alloys were:

- Excellent high temperature oxidation resistance
- Improved resistance to intergranular corrosion
- High strength
- Low nickel content (especially during the second world war)

In the 50'ies and 60'ies it was also observed that the duplex stainless steels have an improved resistance to stress corrosion cracking (SCC) (2, 6-9).

The last two decades of development, testing and use of DSS have accelerated. While today only limited amounts of DSS are used in high temperature applications, the major reason for the use of DSS is their excellent resistance to wet corrosion, especially localized corrosion, as well as their high mechanical strength.

In this paper, a review of the corrosion resistance of the DSS intended for wrought products is made. Focus has been more on facts related to the practical use of these alloys, rather than the fundamental understanding of the mechanisms of corrosion. Furthermore, since Dr Trevor Gooch at this conference will make a similar review for welded joints in DSS, this paper will be limited to the corrosion properties of the base metal of wrought DSS alloys.

2. Chemical composition and microstructure

The chemical composition and the ferrite content of the most common DSS wrought alloys are listed in Table 1. The designations according to different standards and steel manufacturing companies are also given.

Table 1. Chemical composition (wt-%) and ferrite contents of various duplex stainless steels.

Alloy	Standards	Trade names	C max	Si	Mn	Cr	Ni	Mo	N	Cu	W	%α
Low alloy DSS	UNS S32304 W.Nr 1.4362 SS 2327 NFA 36219	SAF 2304 UR35N	0.03	0.5	1.2	23	4	0.2	0.1	0.2	-	45
Medium alloyed DSS	UNS S31803 W.Nr 1.4462 SS 2377	SAF 2205 UR45N	0.03	0.5	1.5	22	5.5	3	0.15	-	-	45
	UNS S31500 W.Nr 1.4417	3RE60 A903	0.03	1.6	1.5	18.5	5	2.7	0.1	-	-	45
	UNS S32900 W.Nr 1.4460 SS 2324 AISI 329	10RE51	.08	.6	0.8	25	4.5	1.5	-	-	-	70
		UR50	.06	1	2	21	7.5	2.5	-	1.5	-	35
	UNS S32950	Carp 7Mo$^+$	.03	.5	1.5	27	4.8	1.75	.25	-	-	50
High alloyed DSS	UNS S32550	Ferralium 255	.05			25	6	3	.18	1.8	-	50
	UNS S31250	SM 25Cr (DP3)	.030	≤.75	≤1.1	25	6.5	3.0	.16	0.5	0.3	45
		A905	.03		5.8	26	3.7	2.3	.34			
		UR 47N	.03	.3	1.2	25	6.5	3	.17	.2	-	45
		UR 52N	.03	.3	1.2	25	6.5	3	.17	1.5	-	45
		VS 25	.03			25	6.5	3	.18			
Super-duplex stainless steels	UNS S32760	Zeron 100	.03	<1.0	<1.0	25	7	3.2	.25	.7	.7	45
	UNS S32750 SS 2328	SAF 2507	.03	<1.0	<2.0	25	7	4	.27	-	-	45
		UR 52N+	.03	.3	1.0	25	6	3.3	.24	1.5	-	45

One can divide the DSS alloys in four different groups:

- Low alloy, essentially molybdenumfree DSS, i.e. SAF 2304/Uranus 35N.
- Medium alloyed DSS, e.g. SAF 2205, 3RE60, Uranus 45 and Tp 329.
- High alloyed DSS, e.g. Ferralium 255, DP3, Uranus 47N/52N.
- So called superduplex stainless steels, i.e. SAF 2507, Uranus 52N$^+$ and Zeron 100.

The chemical composition of these alloys are balanced to give desired corrosion, mechanical, welding and physical properties, to make them suitable construction materials for general or specific purposes.

The alloying elements are, however, not evenly distributed in these materials; Ferrite-stabilizing elements tend to enrich in the ferrite while austenite-stabilizing elements tend to enrich in the austenite phase, see Figure 1 and Table 2 for a specific example. This partitioning of the alloying elements can mean different corrosion properties of the two phases, a fact which will be discussed in the following.

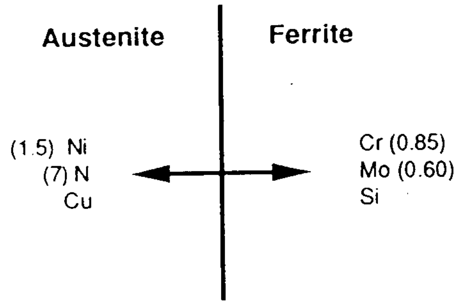

Figure 1. Partitioning of the major alloying elements in duplex stainless steels. Partitioning coefficients (wt-% in γ/wt-% in α) for SAF 2205 within brackets (10).

Table 2. PRE-value calculated for the average composition and the composition of the two phases of SAF 2205 (11)

	wt-% Cr	wt-% Ni	wt-% Mo	wt-% N	PRE
Average composition	21.9	5.5	3.0	.14	34.0
Ferrite phase	24.3	4.1	3.8	.05	37.6
Austenite phase	20.2	7.1	2.2	.24	30.6

PRE = %Cr + 3.3 x %Mo + 16 x %N

3. Selective dissolution and galvanic effects

Selective dissolution of and galvanic effects between the ferritic and austenitic phase in DSS and in weldments of austenitic stainless steels have been studied by a number of researchers (e.g. 11-15). The conclusions from these studies are:

- that selective corrosion (the ferritic phase being more unnoble) can occur when the material corrodes in the active state, i.e. in very aggressive environments or when a localized attack, accompanied by acidification due to hydrolyzes of metal ions in that localized attack, has occurred.
- that no or very limited selective corrosion occurs when the material is in the passive state
- that there is some evidence of galvanic effects between the two phases, when the material is in the active state.

Looking at failures due to corrosion of components made in DSS and used in the chemical process or oil and gas industry, very few of these cases can be attributed to selective corrosion being the primary reason for the corrosion attack though exceptions exist (17).

However, in localized corrosion attacks, rather often one observes selective corrosion in pits and stress corrosion cracks. In the latter case, that selective corrosion occurs behind the crack tip. Depending on the local environment and on the outer corrosion potential, either the austenitic or the ferritic phase can be selectively dissolved.

Thus, the conclusion is that when a proper selection of a DSS with regard to a specific application has been made, selective corrosion will not occur.

If the material selection is improper, active corrosion in aggressive acids or localized attacks in e. g. chloride environments will take place. In connection to the propagation of these attacks, selective dissolution due to differences in chemical composition between the two phases, can occur.

4. Corrosion in acids and caustics

In this part, the corrosion behaviour of DSS in various acids, acid mixtures and caustics is reviewed.

4.1 Sulphuric acid

In Figures 2–4, iso-corrosion diagrams in pure sulphuric acid are shown. As can be seen, the DSS alloys perform well at H_2SO_4-concentrations less than about 40% and at above some 85%. The copper addition, 1.8%, in Ferralium, however, extends the applicability range to intermediate concentrations of sulphuric acid, up to temperatures of 45°C and more.

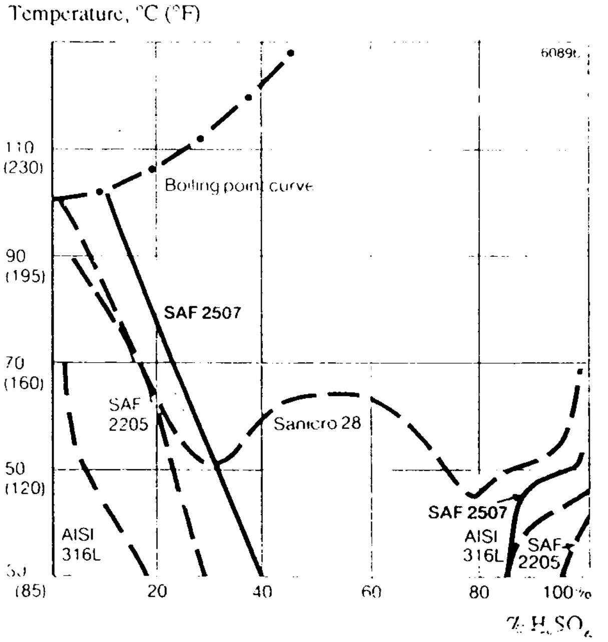

**Figure 2. Isocorrosion diagram in sulphuric acid (p.a) in contact with air.
The curves represent a corrosion rate of 0.1 mm/year (4 mpy) in stagnant test solution.
Testing time: 7 days. (18)**

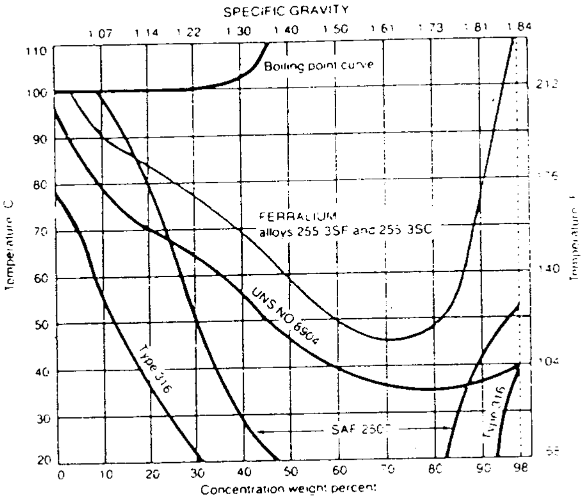

Figure 3. Isocorrosion diagram in sulphuric acid. The curves represent a corrosion rate of 0.1 mm/year in a stagnant test solution. (20)

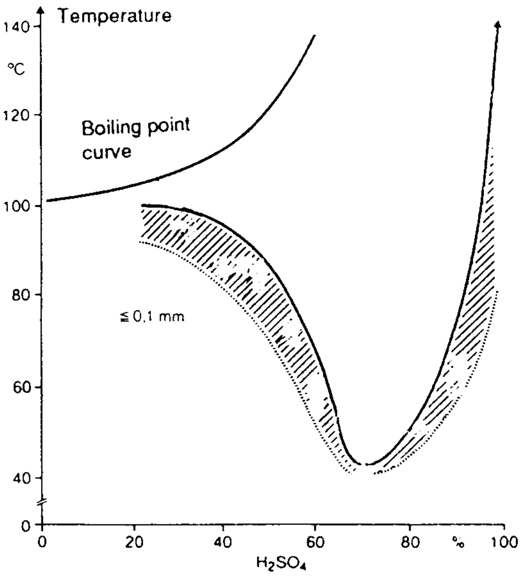

Figure 4. Corrosion diagram of the cast DSS Noridur (25Cr, 7Ni, 2.5Mo, 3.2Cu, .15N) alloy in aerated H_2SO_4 at a flow rate of 10 m/sec. (16)

While Figures 2–3 show results obtained in stagnant solutions, Figure 4 shows the result for a cast alloy, Novidur (25Cr, 7Ni, 2.5Mo, 3.2Cu, .15N) tested at a flow rate of 10 m/s. The result is similar to that of Ferralium in a stagnant solution. In fact, Horn et al found (16) that a flow rate of 10 m/s tended to stabilize the passivity of this alloy. This result can be understood if the anodic processes are potential controlled processes while the cathodic process (which is oxygen reduction) is mass transfer controlled.

In some applications, the sulphuric acid is contaminated with chlorides. Results from tests in such an environment are shown in Figure 5 (21).

4.2 Hydrochloric acid

Hydrochloric acid is extremely aggressive and stainless steels are therefore only resistant at lower concentrations, see Figure 5. While SAF 2205 has a slightly better resistance than Tp 316, SAF 2507 is as resistant as superaustenitics like the 6Mo+N austenitics and Sanicro 28 (27Cr, 31Ni, 3.5Mo, 1.0Cu).

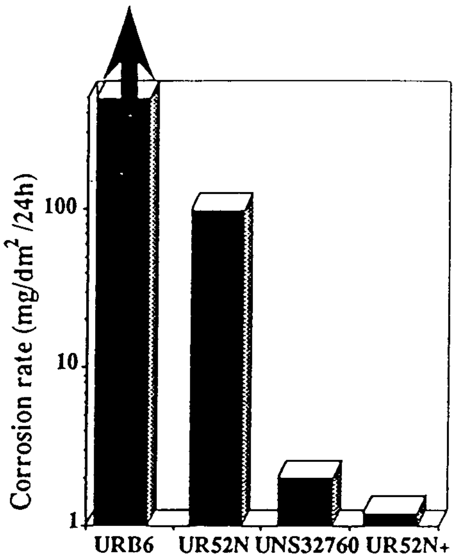

Figure 5. Corrosion rate in 10% H_2SO_4 + 500 ppm Cl^-, aerated, at 80°C (21).
URB6 = 20Cr 25Ni 4.5Mo 1.5Cu

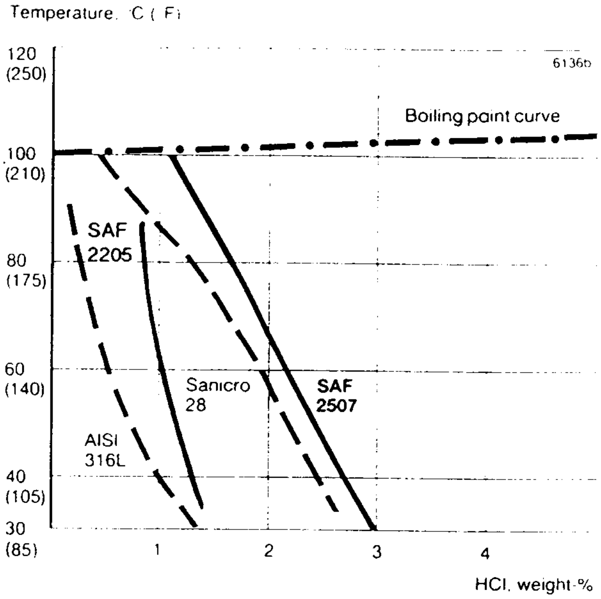

Figure 6. Isocorrosion diagram in hydrochloric acid. The curves represent a corrosion rate of 0.1 mm/year (4 mpy) in stagnant test solution.

4.3 Phosphoric acid

Pure phosphoric acid is not very corrosive. It is the impurities, chlorides and fluorides, in wet process phosphoric acid which cause the high corrosivity of such acid.

A large amount of the Tp 2205 alloy is used in chemical tankers. The most aggressive chemical these tankers transport is wet process phosphoric acid. The steel manufacturers have therefore performed a lot of testing to define safe use limits for the 2205 alloy in wet process phosphoric acid. One example of such data is shown in Figure 7 (22).

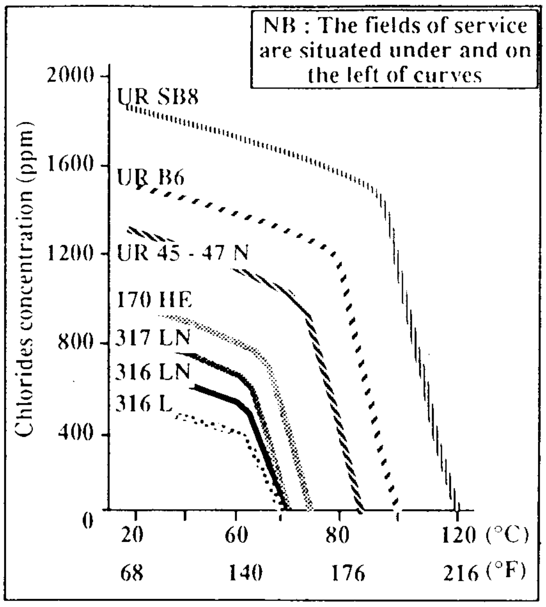

Figure 7. Safe use limits for the chloride content and temperature in 54% P_2O_5. (22)

Similar results have been published by others (23, 24). High-alloyed DSS like Ferralium are since many years used in the phosphoric acid industry in the cast form, as pumps and valves (20).

Quite some work has been performed to investigate the effect of alloying elements on the corrosion resistance of DSS in wet process phosphoric acid (25).

4.4 Organic acids and acid mixtures

While the DSS can be inferior to some superaustenitics in sulphuric acid, they usually have superior corrosion resistance in organic acids, weak or strong. This is exemplified in Figures 8-9 (18, 19). More data can be found in e.g. (3, 20, 26).

4.5 Nitric acid

Even if Tp 329 has been used fairly extensively in nitric acid plants in USA, the problems with intergranular corrosion of welded joints have been frequent. The modified Carpenter 7Mo+ probably has an improved resistance to this type of corrosion (27).

In general, DSS with more than some 2% Mo should not be used in nitric acid. Such alloys are very sensitive to intergranular/interfacial corrosion in this environment.

Extensive testing has, however, shown that the 2304 alloy has excellent corrosion resistance in nitric acid, comparable to that of Tp 304L nitric acid grade (19, 28, 29).

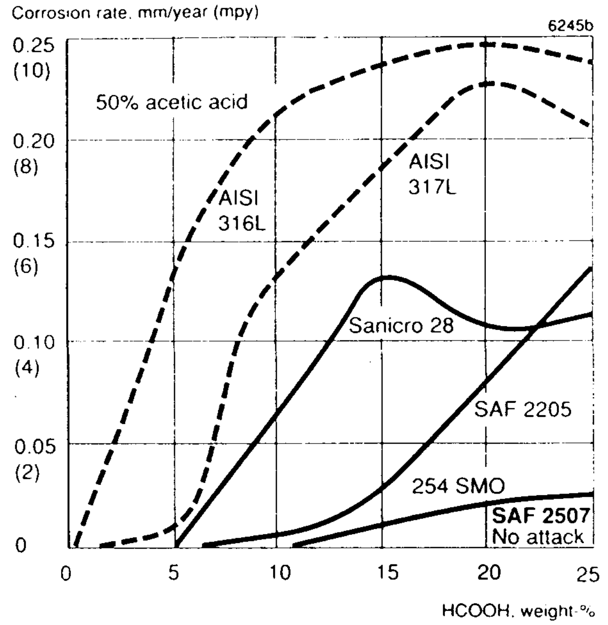

Figure 8. Corrosion rate in boiling mixtures of 50% acetic acid and varying proportions of formic acid. Test time 1+3+3 days (18).

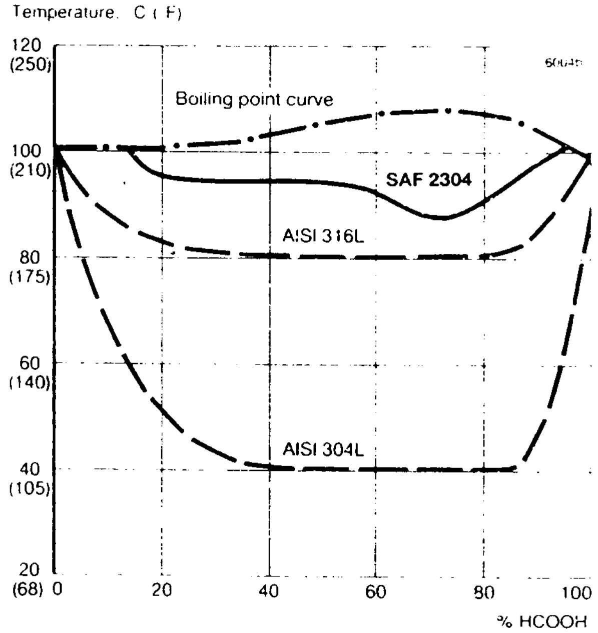

Figure 9. Isocorrosion diagram in formic acid. The curves represent a corrosion rate of 0.1 mm/year (4 mpy) (19).

4.6 Caustic environments

Corrosion testing in a caustic environment has shown that chromium and nickel have strong effects on the corrosion resistance, see Figure 10 (30). As Figure 10 shows, DSS with some 25% Cr (= alloys with 5-10 wt-% Ni) has a high resistance to general corrosion as compared to the standard austenitics (= the alloys with 10-12% Ni). Similarly have tests in boiling white liquor, which is a caustic environment with Na_2S, Na_2SO_4, Na_2CO_3 and NaCl present, shown that the SAF 2304, Uranus 47N and Uranus 52N alloys are superior to the 316L type of material (31, 32).

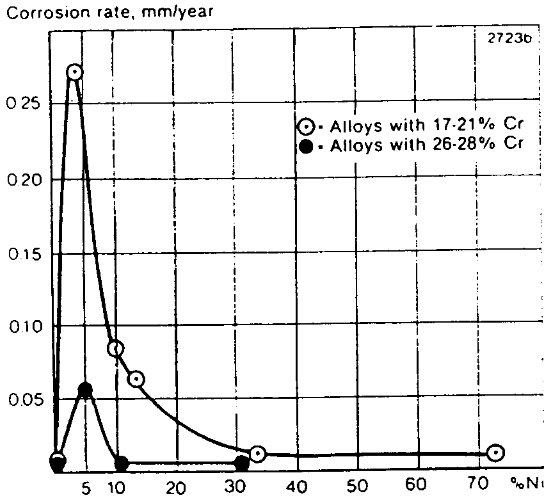

Figure 10. Corrosion rate of FeCrNi alloys as a function of Ni content in 28% NaOH plus 8% NaCl at 99°C (30).

5. Pitting and crevice corrosion

Since the pitting and crevice corrosion resistance of this type of alloys usually are closely related, both these corrosion phenomena are treated together in this review.

In Table 3, a summary of the effect of alloying elements on the pitting and crevice corrosion resistance of duplex stainless steels is given.

To understand the comments made in Table 3, one must realize the fact that the austenitic phase, as illustrated in Figure 1 and Table 2, is less resistant to pitting than the ferritic phase. The reason is the partitioning of alloying elements causing the austenitic phase to have significantly lower contents of chromium and molybdenum. This is true for all DSS with few exceptions. The only way to make the austenitic phase as resistant as the ferritic phase is to alloy the material with high amounts of nitrogen, see Figure 11 (33).

Table 3. Influence of different alloying elements and the microstructure on the pitting and crevice corrosion resistance of the base metal of duplex stainless steels.

Alloying elements	**Effect**	**Reason**	**Practical limitation**
C	Negative	Causes precipitation of chromium carbides with accompanying chromium depleted zones	Abt 0.03% maximum
Si	Positive	Si stabilizes the passive film of the alloy	Abt 2% maximum due to its effect on structural stability and on nitrogen solubility
Mn	Negative	Mn-rich sulphides act as initiation points for pitting. Mn may also destabilize the passive film	Abt 2%. Higher amounts might also increase the risk for precipitation of intermetallics
S	Negative	Sulphides, if not Cr-, Ti- and Ce-rich, tend to initiate pitting attacks	Abt 0.003% if maximum pitting resistance required. If reasonable machinability required, up to say 0.020% allowed
Cr	Positive	Cr stabilizes the passive film	Abt 25-28% maximum depending on the Mo-content. Higher Cr-content increases the risk for precipitation of intermetallics too much.
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 stabilizes the passive film, either directly or through enrichement beneath the film	Abt 4-5% maximum depending on the Cr-content of the alloy. Mo enhances the precipitation of intermetallics.
N	Positive	N increases the PRE-number of the γ phase dramatically, both by increasing the N-content of that phase, but also by increasing the Cr- and Mo-contents through their partitioning coefficients.	Abt 0.15% in Mo-free DSS, abt 0.3% in 25Cr high-Mo ones, and some 0.40% in 25Cr high-Mo, high-Mn alloys
Cu	Disputed	Marginal positive or negative effect	Abt 2.5% maximum more than that reduces hot workability and causes undesired hardenability.
W	Positive	Probably the same as for Mo	Increases the tendency to precipitation of intermetallics.
Volume fraction ferrite	Positive	Increased ferrite content increases the N, Cr and Mo contents of the γ phase	Too high ferrite content can cause precipitation of chromium carbides and nitrides in a coarse microstructure.
Intermetallic phases (σ, χ, ...)	Negative, if any	Precipitates with accompanying depletion of alloying elements (Cr, Mo)	If steel manufacturers recommendations are followed, precipitation of intermetallics will not occur during heat treatment or welding.
Chromium carbides and nitrides	Negative in oxidizing and corrosive chloride-containing environments	Precipitation of carbides/nitrides causes Cr-depleted zones which are selectively attacked in certain corrosive environments.	In older generations of DSS, nitrides have frequently been present in welded joints and in the base metal of material with a coarse microstructure. This has rarely been the reason for a corrosion failure.

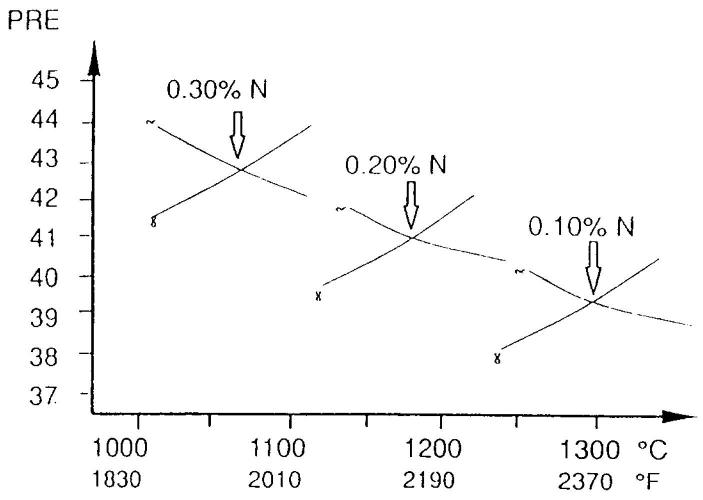

Figure 11. Theoretical calculations based on alloys with 25% Cr and 4% Mo. Ni was varied to keep a constant ferrite content. PRE = Cr + 3.3Mo + 16N. (33)

Figure 11 displays the results of phase diagram calculations using the software and database developed by Hillert et al (34), and shows that for all duplex stainless steels with less than some 0.25% nitrogen, the PRE-number of the austenitic phase is less than the PRE-number of the ferritic phase at quench annealing temperatures less than 1100°C.

Thus, one of the few alloys having similar PRE-values for both phases are SAF 2507, see Table 4.

Table 4. Chemical compositions and PRE-numbers of individual phases of SAF 2507 quench-annealed at 1075°C.

	Cr	Ni	Mo	N	PRE
Ferrite	26.5	5.8	4.5	0.06	42.5
Austenite	23.5	8.2	3.5	0.48	42.5

(PRE = %Cr + 3.3 x %Mo + 16 x %N)

Nitrogen has shown to very strongly improve the resistance to pitting of duplex stainless steels (e.g. 35-38).

Lorenz and Medawar found many years ago the following relationship between the Wirksumme (Pitting Resistance Equivalent) and the alloy composition (39):

$$PRE = \%\,Cr + 3.3 \times \%\,Mo + 16 \times \%\,N \qquad [1]$$

While this relationship is relevant for austenitic stainless steels and the austenitic phase in DSS, it should not be valid for DSS. The reasons are that:

- Nitrogen is nearly completely enriched in the austenitic phase in DSS.
- The austenitic phase in DSS is usually the weak phase with regard to the pitting resistance.
- Nitrogen addition changes the partitioning coefficients for chromium and molybdenum (10).

The relationship between the PRE-number and the alloying content of DSS is therefore more complex than for austenitic stainless steels. In a first approach, however, it is reasonable to nearly double the coefficient for the nitrogen content, viz;

$$\mathrm{PRE} = \%\,\mathrm{Cr} + 3.3 \times \%\,\mathrm{Mo} + 30 \times \%\,\mathrm{N} \qquad [2]$$

PRE-numbers for a large number of duplex stainless steels have been calculated using both [1] and [2] and the results are shown in Table 5.

Table 5. PRE-values for the average composition of various duplex stainless steels.

Alloy	Cr	Mo+1/2 W	N	PRE_1	PRE_2
SAF 2304	23	0.2	0.1	25.3	26.9
3RE60	18.5	2.7	0.1	29.0	31.6
Uranus 50	21	2.5	-	29.3	29.3
10RE51	25	1.5	-	30	30
SAF2205	22	3	0.15	34.3	36.7
Carp 7Mo+	25	1.75	0.25	34.8	38.8
DP3	25	3.2	0.16	38.2	40.8
VEW A905	26	2.3	0.34	39.2	44.6*
Ferralium 255	25	3	.18	37.8	40.7
Uranus 47N	25	3	.17	37.6	40.3
Uranus 52N	25	3	.17	37.6	40.3
Vallourec VS25	25	3	.18	37.8	40.7
Zeron 100	25	3.5	.25	40.6	44.6
Uranus 52N+	25	3.3	.24	39.7	43.5
SAF 2507	25	4	.27	42.5	46.8

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*) This alloy contains 5.8% Mn, which probably lowers the pitting resistance.

$\mathrm{PRE}_1 = \%\mathrm{Cr} + 3.3 \times \%\mathrm{Mo} + 16 \times \%\mathrm{N}$
$\mathrm{PRE}_2 = \%\,\mathrm{Cr} + 3.3 \times \%\mathrm{Mo} + 32 \times \%\mathrm{N}$

The pitting and crevice corrosion resistance of DSS have been extensively studied. Only some of these results can be commented on in this review;

Critical pitting temperatures, CPT, have been determined in neutral aqueous solutions containing different amounts of NaCl, see Figure 12. These results rank the 2304 alloy in comparison to Tp 316L and 304L. They also rank the different duplex stainless steels.

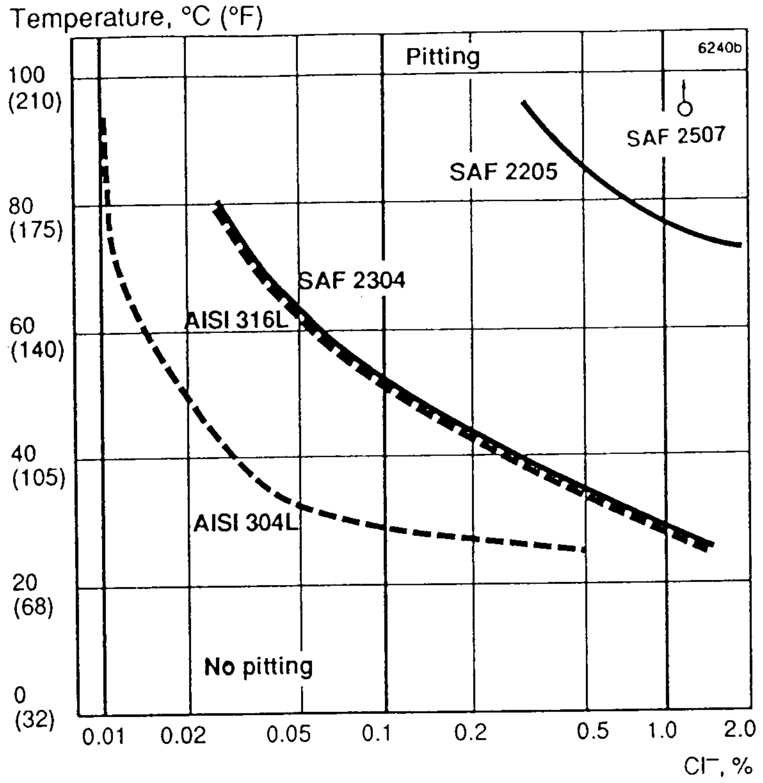

Figure 12. CPT (Critical Pitting Temperatures) of different grades in neutral aqueous chloride solutions. Potential = +300 mV SCE.

In Figures 13-15, similar comparisons are made between different duplex and austenitic stainless steels with regard to their pitting and crevice corrosion resistance (40). The 25Cr DSS tested is of type UNS 31250, the 6Mo+N austenitic grade has a Cr content of 20% and 18% Ni, 0.20% N. The 904L alloy is similar to UR B6, i.e. is an austenitic alloy with 20Cr25Ni4.5Mo1.5Cu. The results show that DSS have excellent resistance to pitting and crevice corrosion as compared to the superaustenitic stainless steels.

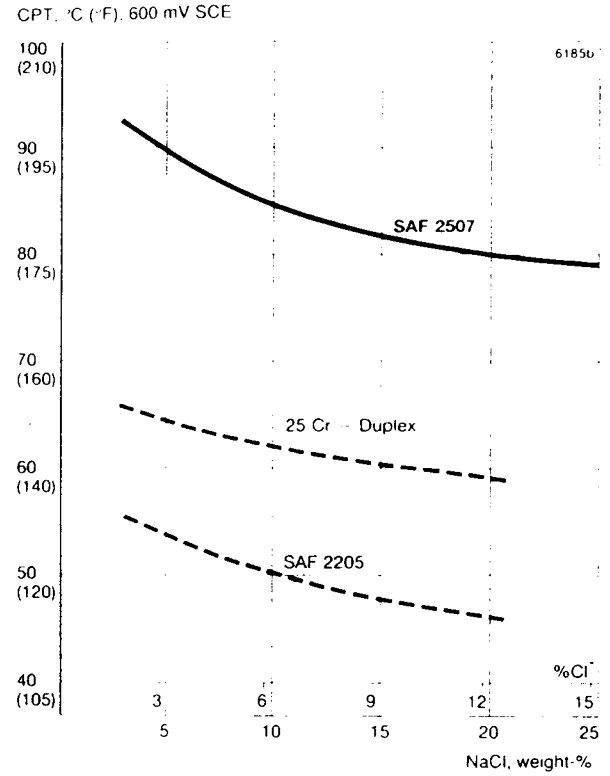

Figure 13. Critical pitting temperatures (CPT) at varying concentrations of sodium chloride, from 3 to 25% (potentiostatic determination at +600 mV SCE with surface ground to 600 grit paper)(40).

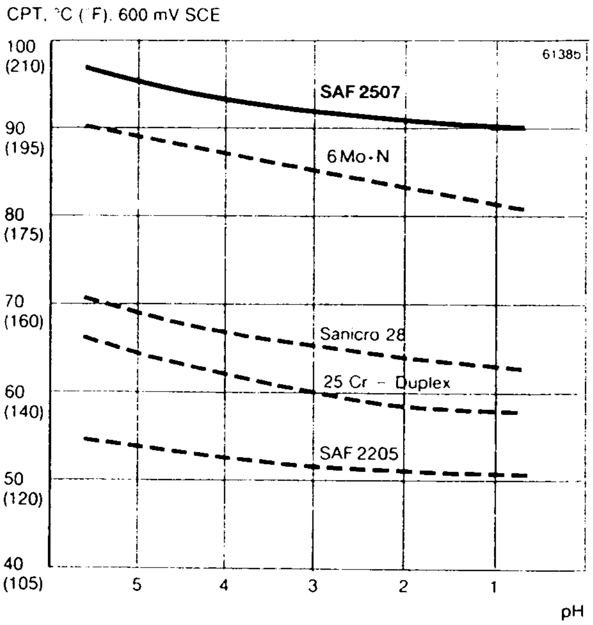

Figure 14. Critical pitting temperatures (CPT) in 3% NaCl with varying pH potentiostatic determination at +600 mV SCE with surface ground to 600 grit paper) (40).

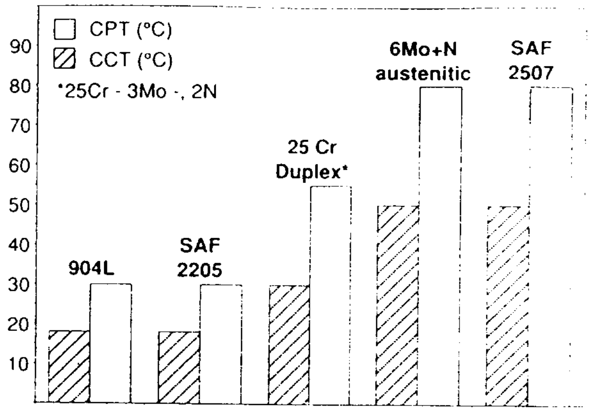

Figure 15. Critical pitting and crevice temperatures in 6% $FeCl_3$, 24 h (similar to ASTM G48) (40).

Other test results are shown in Figures 16-18 (41-43). However, there exist also many other publications, where DSS have been exposed to pitting and crevice corrosion testing (e.g. 44-50). The general conclusion from these reports as well as from service experience (51) is that DSS have as good or better resistance to pitting and crevice corrosion as the austenitic standard and special stainless steels.

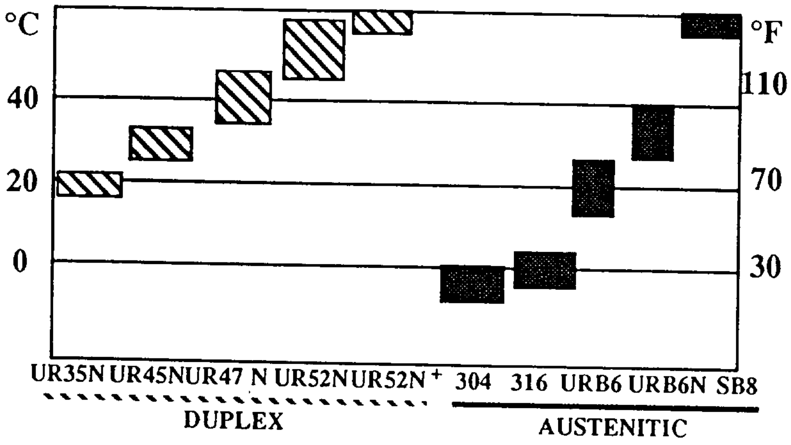

Figure 16. Typical crevice temperature determined for several stainless steels (6% Fe Cl_3 solution, 72 h) (41).

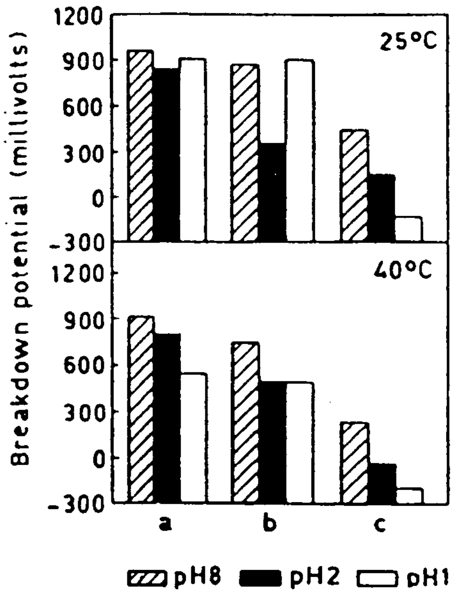

Figure 17. Breakdown potentials (versus the saturated calomel electrode) of a. 25Cr7Ni4Mo, b. 20Cr18Ni6Mo, and c. 25Cr6Ni2Mo obtained in simulated crevice solutions at 25 and 40°C (42).

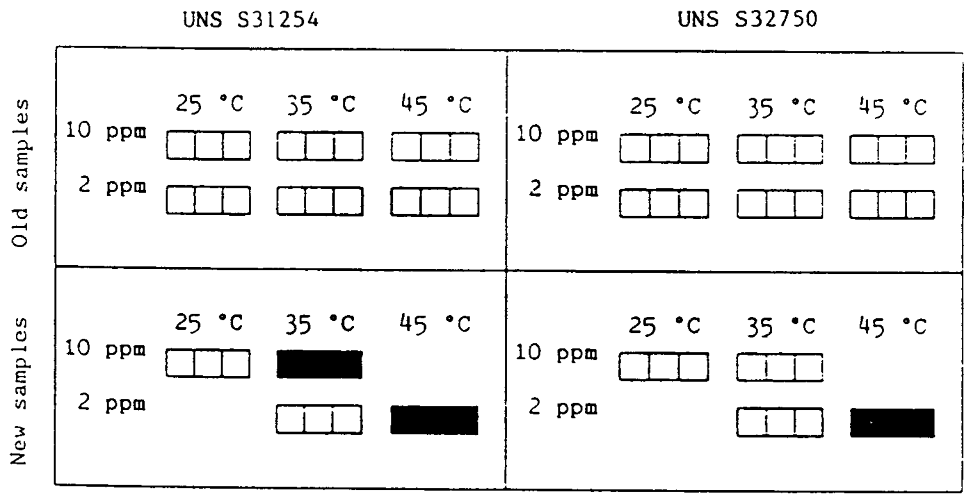

Figure 18. A summary of crevice corrosion test results in chlorinated seawater. An open square means a non-corroding sample while a filled square means a corroding sample (43).

6. Stress corrosion cracking (SCC)

Service experience has proven, beyond any doubt, that DSS have a superior SCC resistance as compared to the standard austenitic stainless steels (e.g. 3, 5, 17, 51, 52). However, still there is reluctance in various types of industries to select and use DSS more broadly. Some reasons for that are probably:

- Also the DSS have their limitations with regard to environmental variables, e.g. the oxygen, chloride and sulphide contents as well as to the temperature and pH of the environment.
- Different test techniques and different test environments can give quite different ranking between the alloys tested.

In the following, these two important subjects are discussed further;

6.1 SCC in chloride environments

When testing stainless steels in chloride environments, the following environments and test techniques are used:

Examples of test environments	**Test technique**
30-54% $MgCl_2$, boiling, pH ~1-2	Constant strain
40-60% $CaCl_2$, 100-160°C, pH = 6-7	• U-bend • Reversed u-bent tubes • Bent beam • C-ring
25% NaCl, pH = 6, 100°C	Constant load
Aerated 1-1000 ppm Cl^- solutions, 100-300%	Slow strain rate
Deaerated aqueous solutions, 100-350°C, with and without chlorides	Fracture mechanics

At this conference, Jargelius will show that by combining certain test techniques and environments, she can get any kind of ranking of the material she is testing (53). Schoefield will discuss this subject as well (54). I will therefore limit myself to the following comments:

- Tests in 45-54% $MgCl_2$ at about 150°C cannot be used to determine the SCC resistance of any stainless steel in any environment except for the testing environment itself (55).
- Concentrated $CaCl_2$/NaCl/LiCl-solutions may be used to group stainless steels into more and less resistant ones, but cannot always be used to rank more resistant steels or to determine the applicability of a given stainless steel.
- Slow strain rate (SSR) testing gives invariable very conservative results, especially for DSS. The stress situation that a material experiences in an SSR-test will never occur in practice, i.e. in a SSR test the stress level is monotonically raised far above the yield point of the material. In fact, even a constant load test is rather conservative. In a professionally designed stainless steel equipment, the stress that the

material is exposed to is probably close to constant strain, i.e. stress relaxation can most often occur.

For 3RE60, which then had been used in industry for some 15 years, we compiled, in 1982, the service experience in refineries, petrochemical plants and other types of industries and compared that with experimental data obtained by using a constant strain test technique in continuously refreshed solutions containing about 8 ppm O_2 with a room temperature pH of about 6. The testing time was 1000 hours. The result of the comparison is shown in Figure 19 (55).

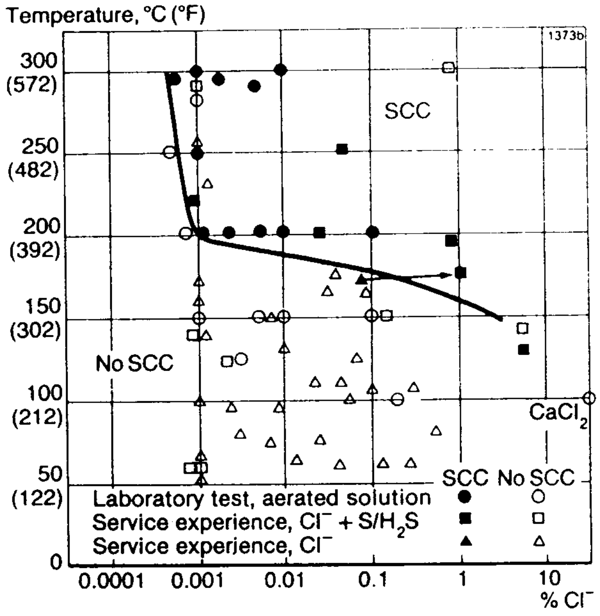

Figure 19. A compilation of practical experience and laboratory SCC test data of 3RE60 (55).

The agreement between laboratory test results and service experience is such that the applied test technique must be considered to describe in a satisfactory way the practical performance of this stainless steel. Comparing service experience for 904L and SAF 2205 with test results obtained in the same way gave the same conclusion. In Figure 20, SCC test results, using this test technique, for a number of DSS are shown.

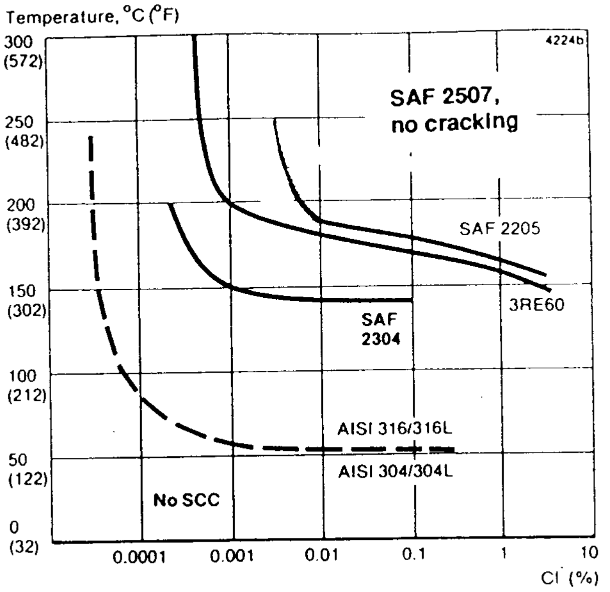

Figure 20. A compilation of practical experience and laboratory test data of different stainless steels in neutral aerated aqueous chloride environments.

A lowered oxygen content increases the chloride content which can be tolerated without SCC to occur. In the compilation made by Speidel (56), it is indicated that for Tp 304 at 200 to 300°C and 0.1 to 10 ppm O_2, the critical product of $[Cl^-]$ and $[O_2]$ is;

$$[Cl^-] \times [O_2] < 1\ ppm_2$$

This type of relationship can also be applied to DSS to estimate critical chloride concentrations at low oxygen contents.

It is indicated by Münster that the SCC resistance of type 2205 materials is lowered by a lowered pH (52). Tests in 40% $CaCl_2$ does show that there is no drastic effect of a pH decrease to 3.5, but that between pH = 3.5 and pH = 1.5 the effect is fairly strong, see Figure 21. This effect may not be the same in a diluted chloride solution.

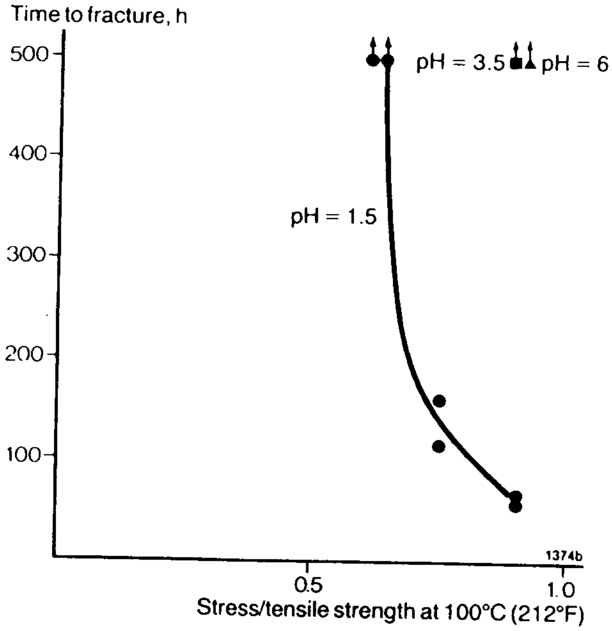

Figure 21. Constant-load SCC tests of SAF 2205 in aerated 40% $CaCl_2$, 100°C (212°F), with 0.008 M PO_4^{-3} added as H_3PO_4 + NaH_2PO_4.

6.2 SCC in hydrogen sulphide/chloride environments

The last two decades, DSS have been to an increasing extent as production tubing liners, piping systems on- and offshore, heat exchangers etc in sour gas and oil production. This means exposure of the DSS material, in the quench-annealed or coldworked condition, to large amounts of chlorides in combination with high amounts of CO_2 and some H_2S in the natural gas produced.

A lot of work has been performed the last 15 years to understand the safe limits of applicability of the DSS in such environments (e.g. 57-63). This subject will also be especially discussed by M Schoefield at this conference. I will therefore limit myself to the following:

The causes to the difference in opinion between different researchers are due to the same reasons as in the case of SCC in chloride environments;

- In practice, the formation water contains HCO_3, which to some extent inhibits SCC (62, 64). However, SCC tests are often performed in solutions acidified with acetic acid, which gives a much lower pH than what the material of the production tubing is exposed to in practice.
- Different test techniques are used, the most conservative one being the SSR test technique. Also in this case, the constant strain test method should be the one most representative for the practical case. Different test methods give, however, quite different results, see Figure 22 (65).

- Duplex stainless steels have not, relative to other materials, as high resistance to SCC in H_2S-/Cl^--environments as in aerated Cl^--containing solutions. One example of this is:
    - In aerated Cl^--containing solutions, different alloys are ranked according to

      SAF 2507 > Sanicro 28 > 904L > SAF 2205 >> 316
    - However, in a H_2S-/Cl^--containing solution:

      Sanicro 28 >> SAF 2507 ~SAF 2205 > 316

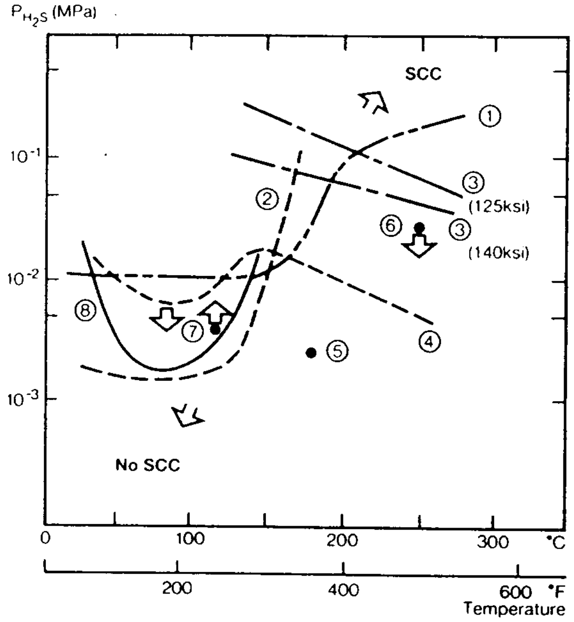

Figure 22. Effect of P_{H2S}, temperature and test method on susceptibility to SCC of duplex stainless steels

The reason for the lowered resistance in H_2S/Cl^- environments of the DSS is probably the presence of the ferritic phase in combination with the ability of H_2S to increase the hydrogen absorption of a steel.

Not much service experience with duplex stainless steels in sour environments has been presented in a systematic way. Some data has, however, been compiled and reported in (62), see Figures 23 and 24.

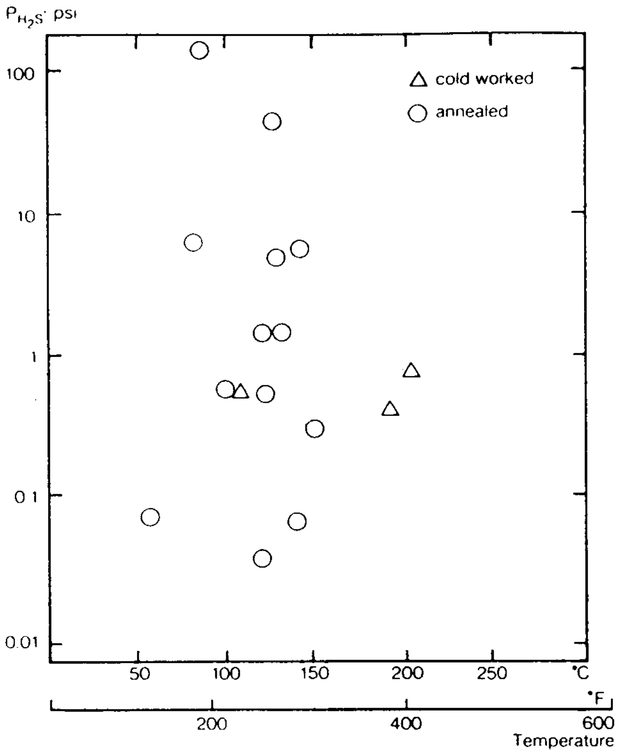

Figure 23. Service experience of duplex stainless steels, 22Cr (UNS S31803) and 18Cr (UNS S31500) in H_2S-Cl^- environments. Oil wells excluded.

In this context, it is interesting to note the guidelines for the use of the type 2205 alloy developed by Shell, USA (63):

"A. This alloy can be used at any temperature up to 232°C in sour environments if the partial pressure of H_2S is ≤ 0.3 psi, the yield strength is ≤ 145 ksi and its hardness is ≤ HRC 34. (These guidelines were incorporated into MRO175 in 1990.)

B. For temperatures between 177 and 232°C, it is also considered acceptable for use as long as the H_2S is ≤ 0.9 psi. (This would permit use for downhole liners.)

C. Avoid the use of HCl acidizing fluids when duplex is present.

D. Clear brine completion fluids should be deaerated to prevent localized corrosion and SCC."

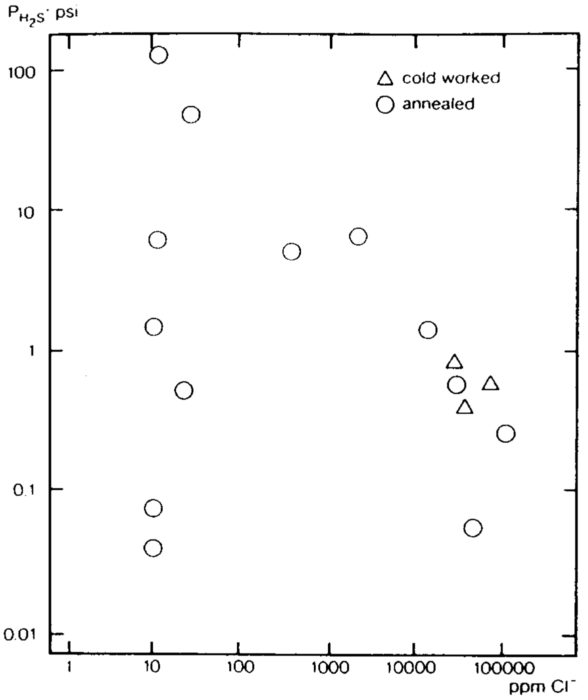

Figure 24. Service experience of duplex stainless steels, 22Cr (UNS S31803) and 18Cr (UNS 31500) in H_2S-Cl^- environments at 80 to 190°C. Oil wells excluded.

7. Corrosion fatigue

Duplex stainless steels have in general a very high resistance to fatigue and corrosion fatigue (e.g. 19, 20, 66, 67). This fact is also utilized in various applications, e.g. as suction rolls in pulp & paper plants (66). The fatigue and corrosion fatigue strength of DSS will be reviewed by Johansson at this conference (68).

8. Intergranular corrosion in welded joints

Intergranular corrosion of Tp 329 has not been uncommon. The reason is that the base metal of this alloy has a microstructure of only about 25% austenite. Furthermore, the nitrogen content is only about 0.05% and the carbon content up to 0.08%.

During welding of a DSS, the material in the high-temperature heat affected zone (HT-HAZ) becomes completely ferritic for a short while. If the driving force (= approx. proportional to the austenite content in the base metal) is high and if the alloy contains a high amount of nitrogen (which is a very strong austenite former and has a high diffusion rate), then fairly large amounts of austenite will reform in the HT-HAZ. The austenite reforms in the ferrite-ferrite grain boundaries and also as Widmanstätten platelets.

Reformation of austenite in the ferrite-ferrite grain boundaries eliminates the risk for intergranular corrosion.

All modern duplex stainless steels are designed to form austenite in ferrite-ferrite grain boundaries provided the cooling rate at welding is not too fast.

Thus, there is no risk for intergranular corrosion in duplex stainless steels if

- A modern duplex stainless steel is used.
- The cooling rate after welding is not too fast. (Follow the recommendation of the alloy manufacturer.)

This subject will be discussed at length at the welding session at this conference.

9. Conclusions

Duplex stainless steels have excellent resistance to various types of corrosion, i.e:

- General corrosion in acids and caustics
- Pitting and crevice corrosion
- SCC in chloride environments
- Intergranular corrosion
- Corrosion fatigue

The SCC resistance in hydrogen sulphide-chloride environments is superior to that of the standard austenitic stainless steels.

There is a huge amount of corrosion test data for DSS in various environments. However, there is a need for compilation of service experience, especially with regard to SCC in hydrogen sulphide-chloride environments.

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Claims

1. Chemical composition (in percent by weight) :

C	0.025 max
Mn	0.80 max
Si	0.80 max
Cr	24 - 26
Ni	6.5 - 8.0
Mo	3.0 - 4.0
S	0.002 max
P	0.025 max
Cu	1.2 - 2.0
W	0.8 - 1.2
N	0.23 - 0.33
Fe	balance

Pitting Index = Cr + 3.3 Mo + 16 N > 42

Balanced chemical composition to obtain after solution heat treatment at 1070-1100 °C an alfa Ferrite of 40 - 60%.

2. Alloy according to claim 1, characterized in that the content of C is 0.01 - 0.02%.

3. Alloy according to claim 1, characterized in that the content of Si is 0.35 - 0.60%.

4. Alloy according to claim 1, characterized in that the content of Ni is 7.0 - 7.5%.

5. Alloy according to claim 1, characterized in that the content of Mo is 3.7 - 4.0%

6. Alloy according to claim 1, characterized in that the content of Cu is 1.6- 1.9%.

7. Alloy according to claim 1, characterized in that the content of W is 0.9- 1.1%.

8. Alloy accorgind to claim 1, characterized in that the content of N is 0.25- 0.30%.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 83 0586

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 360 143 (CARONDELET FOUNDRY COMPANY) *Claims 1-8*	1-8	C22C38/42 C22C38/44
A	US-A-4 816 085 (FLASCHE ET AL.) *Claims 1-5*	1-8	
A	GB-A-2 203 680 (NIPPON YAKIN KOGYO) *Claims 1-3, 9, 13, 17, 18*	1-8	
A	GB-A-2 160 221 (NIPPON KOKAN K.K.) *Claims 1-4*	1-8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 JULY 1993	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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