

A new corrosion-resistant stainless steel on the South African scene

by J.P. HOFFMAN*

SYNOPSIS

This paper describes the metallurgical aspects and properties of a duplex austenitic-ferritic steel SAF 2205. As well as having high yield strength and hardness, SAF 2205 combines the high resistance of ferritic stainless steels to chloride-induced stress-corrosion cracking and the excellent resistance of austenitic stainless steels to hydrogen-induced stress-corrosion cracking. Its alloying elements contribute to its mechanical and corrosion properties as follows: nitrogen increases its pitting potential and improves its strength, nickel increases its resistance to pitting and its toughness, chromium and molybdenum give improved resistance to pitting and crevice corrosion. SAF 2205 has better resistance than steel types 316 L and 317 L both to pitting corrosion and to stress-corrosion. This makes it a very good material for pipes, tanks, and pumps in harsh environments such as those in petrochemical and desalination plants.

SAMEVATTING

Hierdie referaat beskryf die metallurgiese aspekte en eienskappe van 'n oustenitiese ferritiese dupleksstaal SAF 2205.

Benewens sy hoë meegeesterke en hardheid, kombineer SAF 2205 die hoë bestandheid van ferritiese vlekvrystaal teen chloriedgeïnduseerde spanningskorrosiekraakvorming en die uitstekende bestandheid van oustenitiese vlekvrystaal teen waterstofgeïnduseerde spanningskorrosiekraakvorming. Sy legeeëlemente dra soos volg tot sy meganiese en korrosie-eienskappe by: stikstof verhoog sy putjiespotensiaal en verbeter sy strkte, nikkel verhoog sy bestandheid teen putjieskorrosie en taaiheid, chroom en molibdeen verleen beter bestandheid teen putjies- en spleetkorrosie.

SAF 2205 is beter as die staalsoorte 316 L en 317 L bestand teen sowel putjieskorrosie as spanningskorrosie. Dit maak dit 'n baie aantreklike materiaal vir pype, tenks en pompe in strawwe omgewingstoestande soos dié in petrochemiese en ontsoutingsaanlegte.

Introduction

Stainless steels contribute characteristics and properties of ferrous-alloy groups that are otherwise not obtainable, although carbon and low-alloy steels are far more important on a tonnage basis. In view of the corrosion and oxidation-resisting qualities of stainless steels, their functions cannot readily be duplicated by other alloy systems.

Austenitic stainless steels represent the largest group of stainless steels in use. Their dominant position is due to a general high level of formability, fabricability, and corrosion resistance, and also because of the varied specific combinations of properties that can be obtained by different compositions within the group, which provides useful material choices for a vast number of applications.

Southern Cross Steel, the stainless-steel producing division of Middelburg Steel & Alloys (Pty) Ltd, produces sheet and plate of austenitic steel, of which the 304 and 316 types are the most common, as well as sheet and plate of the locally developed 3CR12 (a corrosion-resisting steel). In addition, sheet of types 430 and 409 is produced. The deep-drawing qualities of both 304 and 430 add to their usefulness.

Stainless and corrosion-resisting steels find wide application in the chemical, petrochemical, metallurgical,

mining, and food and beverage fields. Recently, attention was given to stainless and corrosion-resisting steels for the fast-developing container industry and for transport facilities, e.g. bus and rail-coach bodies.

Austenitic stainless steels in the annealed or solution heat-treated condition are not very strong, and high mechanical properties can usually be obtained only by cold-working.

Under certain conditions, austenitic stainless steels may fail in service. The most common single factor is failure due to stress-corrosion cracking (SCC), followed by pitting and crevice corrosion. Collectively, these three corrosion modes contribute approximately 60 per cent to all failures.

Environmental conditions in refineries and in chemical and petrochemical plants vary enormously. There is a constant demand for steels that are more reliable, that give improved safety performance, and that are cost-effective.

In the transport sector, there is a growing demand for stronger, lighter, and corrosion-resisting steels. The emphasis is on energy-saving and maintenance-free units.

At Southern Cross Steel, there is the progressive viewpoint to develop new steels in line with the rest of the stainless-steel industry in order to maintain a competitive edge. The prime objective is to produce steels of higher value for better returns. It must be appreciated, however, that it can take years to develop a new steel (or to improve on existing ones).

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During the past number of years, Southern Cross Steel has progressed, with the development of new corrosion-resisting steels based on the philosophy of 3CR12, a dual-phase duplex ferritic–martensitic steel. Full descriptions of 3CR12 have been given in the literature^{1–5} and will not be repeated here. A new 14 per cent chromium steel was recently patented after initial work by Southern Cross Steel and Nagy⁶. In addition, development work on a duplex austenitic–ferritic steel has progressed to an advanced stage. A high-strength nitrogen-bearing chromium–nickel austenitic steel for the transport industry can now be produced locally.

This paper describes the metallurgical aspects and properties of a duplex austenitic–ferritic steel SAF 2205.

Duplex Austenitic–Ferritic Stainless Steel

Duplex austenitic–ferritic stainless steels are used to an increasing extent in the petrochemical industry, in oil- and gas-winning, and in marine environments. The main reason for this is the excellent resistance to SCC, particularly to hydrogen SCC.

Duplex steel SAF 2205 consists of 22 per cent chromium and 5 per cent nickel, with molybdenum and nitrogen as added elements. It has an austenitic and ferritic microstructure, and provides combinations of properties not readily attainable by conventional single-phase austenitic or ferritic stainless steels. Compared with conventional austenitic stainless steels, 2205 has higher strength, better corrosion resistance, and excellent resistance to pitting and SCC; and compared with ferritic stainless steels, 2205 has better weldability, formability, and toughness.

Duplex stainless steels have been commercially available for many years, mainly in the form of sheets and tubing, but have not found widespread application until fairly recently.

With the development of the AOD (argon–oxygen decarburization) process, it is now practical and economical for close control to be kept on the chemical composition of these steels so that their carbon contents are low enough to prevent sensitization in heavier welded sections. The incorporation of nitrogen has further improved the strength and corrosion resistance, and makes it possible to retard some of the metallurgical reactions responsible for loss in weld toughness.

The chemical composition of 2205 is shown in Table I compared with some conventional austenitic stainless steels. Its composition is covered in the DIN standards (DIN X2CrNiMoN 22 5), and the ‘Werkstoff’ number is 1.4462. It is listed in ASTM standards ASTM A789 and A790 as UNS 31800.

TABLE I
NOMINAL CHEMICAL ANALYSES OF DIFFERENT STEELS
(IN MASS %)

Grade	C (max)	Si (max)	Mn (max)	Cr	Ni	Mo	N
SAF 2205	0,03	1,0	2,0	22,0	5,5	3,0	0,14
UNS 30400	0,08	1,0	2,0	19,0	9,0	–	–
UNS 31600	0,08	1,0	2,0	17,0	12,0	2,5	–
UNS 31703	0,03	0,5	1,75	18,5	13,5	3,25	–

Like all austenitic–ferritic stainless steels, 2205 has about twice the yield strength (0,2 per cent proof stress) of austenitic steels; 20 per cent cold-working of 2205 may increase the yield strength to 1000 MPa. The tensile properties of 2205 at room temperature are shown in Table II.

TABLE II
MECHANICAL PROPERTIES OF SAF 2205 AND CONVENTIONAL
AUSTENITIC STAINLESS STEELS

Grade	$R_{p0,2}$ min MPa	R_m MPa	A_L min %
SAF 2205 ⁷	450	680 to 880	25 (A_2)
UNS 30400	205	515 min	40
UNS 31600	205	515 min	40
UNS 31603	170	485 min	40
UNS 31703	205	515 min	40

A_5 gauge length = $5,65 \sqrt{S_0}$, where S_0 is the cross-sectional area
 A_L gauge length = 50 mm

The hardness of 2205 is relatively high: approximately 260 Vickers, compared with 160 Vickers for austenitic stainless steels.

The ductile-to-brittle transition temperature (DBTT) of 2205 is approximately -55°C but, even at lower temperatures, the impact strength remains higher than 27 J (CVN)⁷.

The yield strength, σ_y (and the fatigue strength), of a duplex steel follows Petch’s Law:

$$\sigma_y = \sigma_0 + K_y d^{-1/2}, \dots\dots\dots (1)$$

where σ_0 and K_y are constants, and d is grain diameter.

The σ_y of a duplex steel is between that of $\sigma_y(\gamma)$ and $\sigma_y(\alpha)$, but closer to the ferrite yield strength than a single rule of mixtures would predict. The extra strengthening is due to the finer grain size of the duplex structure compared with single-phase structures, which are normally coarser.

Many other factors help to determine the mechanical properties of a duplex steel. The volume fractions of γ and α ($V_f\gamma$ and $V_f\alpha$), the morphology of the α and γ , the orientation of the $\alpha + \gamma$ with respect to applied stress and fracture paths, and the exact compositions of both α and γ affect the mechanical properties. The solid-solution hardening effect of nitrogen has an additional effect on the overall mechanical properties of SAF 2205.

The upper temperature limit for long-time service is 300°C . Exposure of the sheet for extended periods between 300 and 950°C embrittles the steel⁸ (Fig. 1). At the lower temperature range, the embrittlement is due to the precipitation of α' (also known as 475°C embrittlement) and nitrides or carbides. In the high temperature range, χ and σ phases precipitate. Fig. 2 shows a time–temperature–precipitation diagram for a 2205 type steel⁹. However, during normal production and fabrication procedures, the times at these critical temperatures are such that the risk of embrittlement and/or a decrease in corrosion resistance is small.

The microstructure of 2205 consists of about 55 per

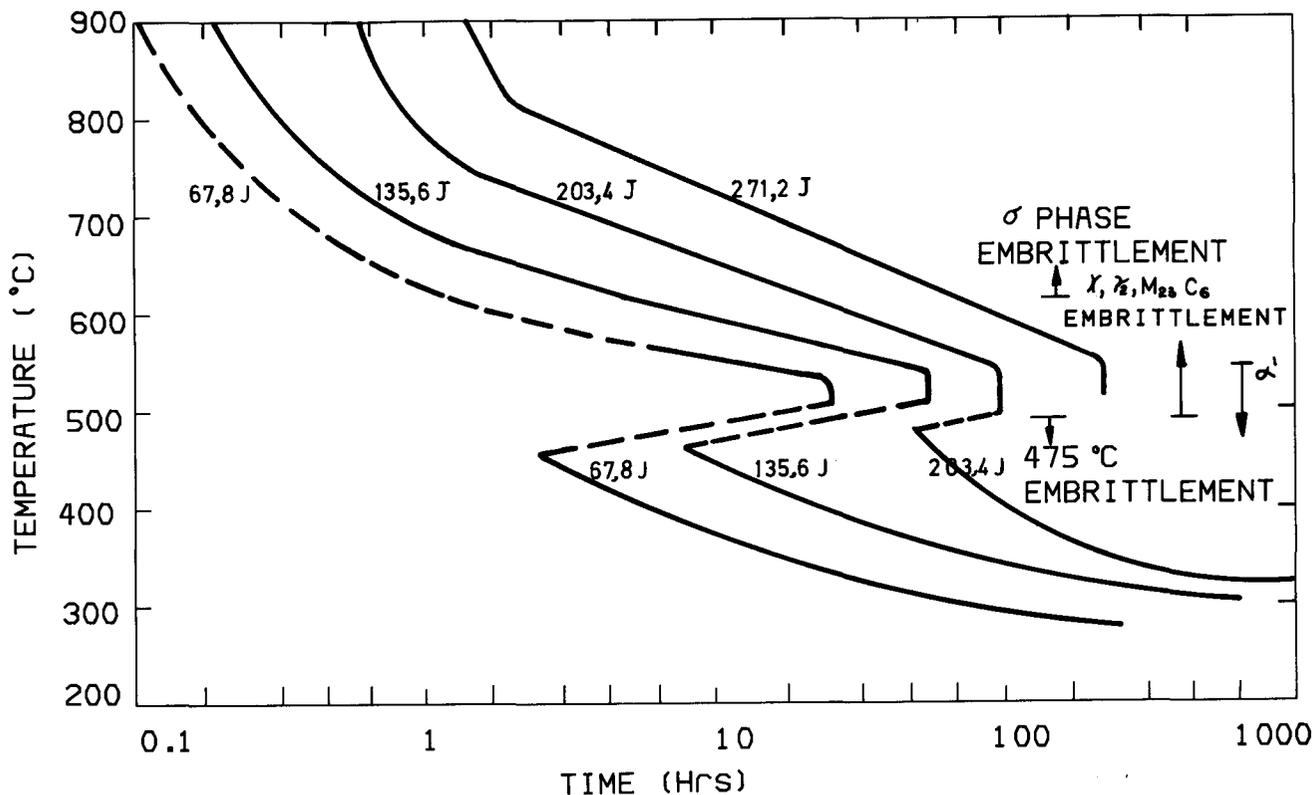


Fig. 1—Time-temperature curves for various decreases in Charpy impact energy at room temperature (after Solomon and Devine⁹)

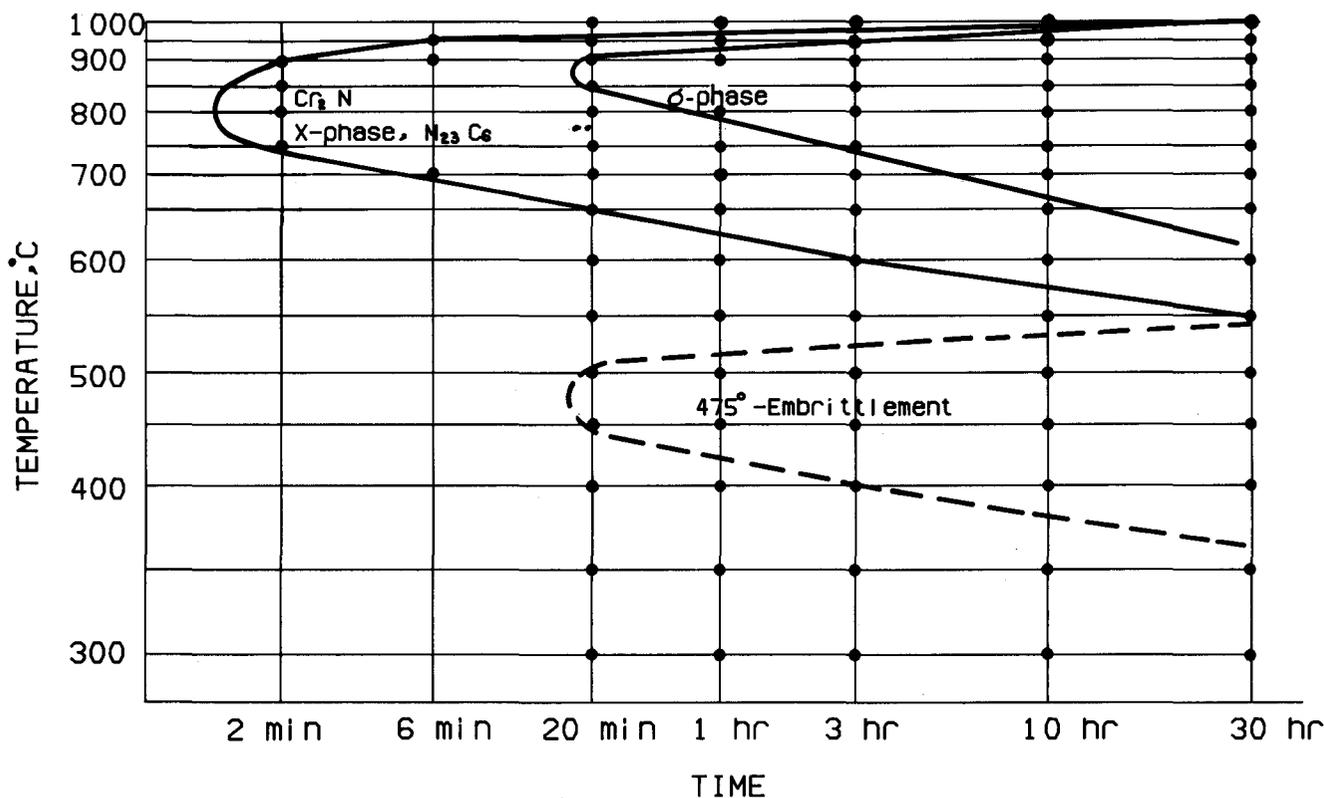


Fig. 2—Time-temperature-precipitation diagram of AF22 solution-annealed for 30 minutes at 1050°C (water-quenched) and heated as shown

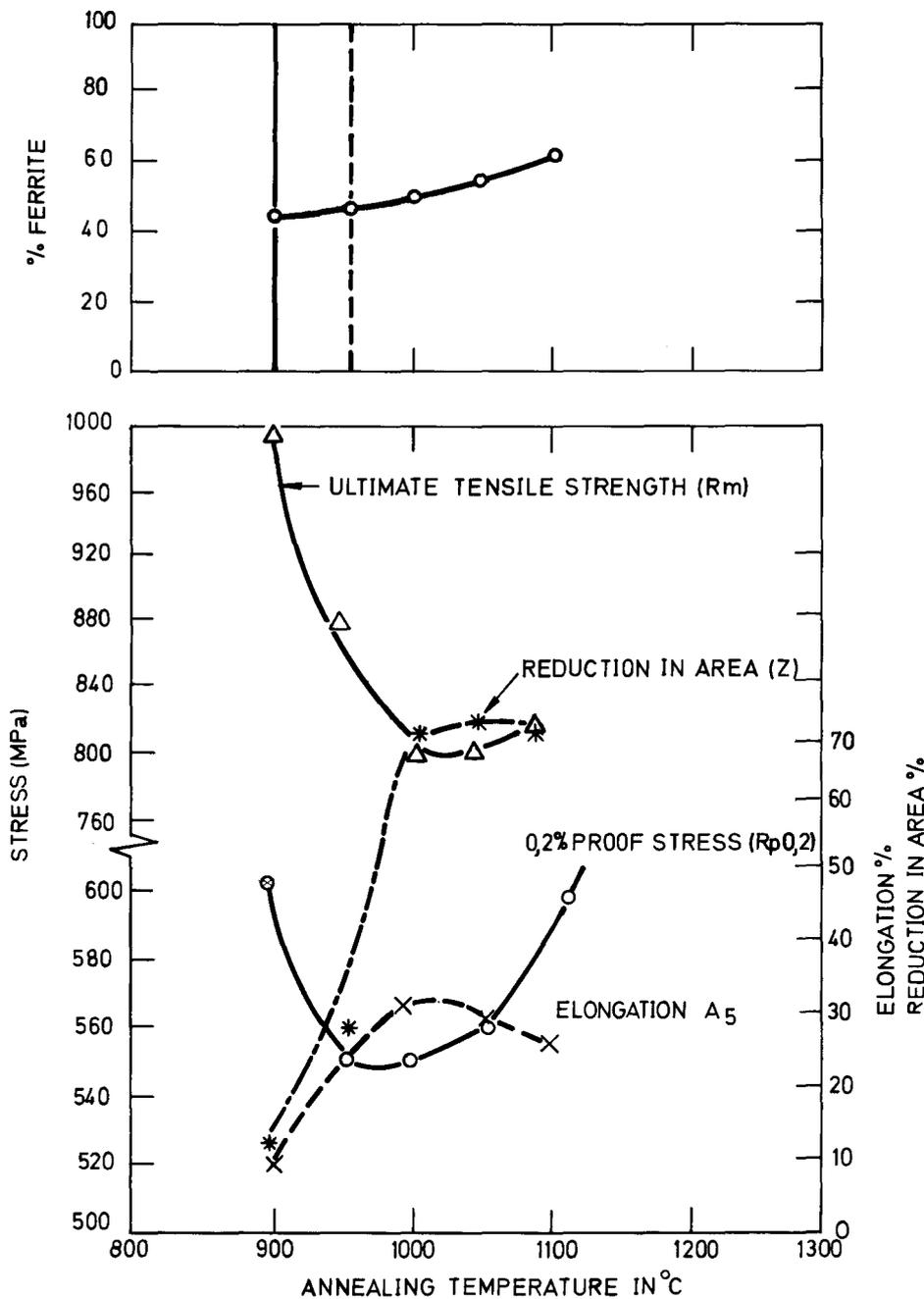


Fig. 3—Ferrite content as a function of annealing temperature (time at temperature 30 minutes and water-quenched)

TABLE III
ANALYSES OF VARIOUS PHASES OF ANNEALED AND QUENCHED 2205

Conditions
Temp. 1030°C
Time 20 min.

Element	Composition, % by mass		
	Nominal (steel)	Ferritic phase	Austenitic phase
Cr	21,9	23,6	21,0
Mo	3,0	3,3	2,1
Ni	5,7	4,8	6,9
N	0,14	—	0,25

cent austenite and 45 per cent ferrite. Normally, 2205 is annealed at between 1020 and 1100°C, and is quenched to give a γ -phase of 50 to 60 per cent. Heat treatment at higher temperatures and quenching result in a higher proportion of α -phase^{7,10,11} (Fig. 3).

The various phases contain less or more of the alloying elements^{7,9}, as is evident from Table III.

In a multicomponent system consisting of iron, chromium, nickel, molybdenum, carbon, and nitrogen, the primary solidification mode has been predicted for different Creq/Nieq ratios^{12,13}, where (in mass percentages)

$$\text{Creq} = \text{Cr} + 1,4 \text{ Mo} + 1,5 \text{ Si} + 3 \text{ Ti} \dots\dots (2)$$

$$\text{Nieq} = \text{Ni} + 0,3 \text{ Mn} + \text{Cu} + 22 \text{ C} + 14 \text{ N}. (3)$$

Optimum hot ductility occurs at a Creq/Nieq ratio of

1,5. At Creq/Nieq values of less than 1,5, the solidification is primary austenite, which may cause problems with the hot-working of the steel, e.g. during rolling. Primary ferrite solidification takes place if the Creq/Nieq ratio is equal to or greater than 1,5, with improved hot-workability. However, an increase in the ratio increases the ferrite content, which in turn reduces the hot-workability. Care must be taken when 2205 steel is hot-worked.

In the presence of an aqueous phase, gases containing hydrogen sulphide and/or carbon dioxide are corrosive to low-alloy steels. Natural gas contains significant amounts of these two gases and, in oil or gas fields in the sea, these gases in solution in sea water form what is known as 'sour brines'.

Hydrogen sulphide deserves special mention since it has a strong tendency to generate hydrogen-induced cracking (HIC) and hydrogen-induced stress-corrosion cracking (HSCC) at temperatures below 60°C. As with SCC, HSCC is encountered only in the presence of an externally applied stress (which could be below the proof stress of the steel) or high residual stresses. HIC is produced in the absence of external stresses.

Ferritic and martensitic stainless steels are prone to HSCC and, although austenitic stainless steels are resistant to HSCC because of their face-centred cubic structure, they are prone to intergranular corrosion (IGC) if the steel is sensitized and, more important, they are also susceptible to pitting and SCC in the presence of chloride ions.

Duplex steel 2205 combines the high resistance of ferritic stainless steels to chloride-induced SCC and the excellent resistance of austenitic stainless steels to HSCC.

The mechanism of the influence of ferrite (α) on the resistance to SCC is explained by Edeleau¹⁴ as follows. When a ferrite phase is formed, the nickel and nitrogen contents of the austenite phase are increased because of the distribution effect, thereby increasing the stability of the γ -phase. α is anodic to γ in duplex stainless steels, and the γ -phase can thus be cathodically protected against SCC by the coupling of the γ to the α .

Ferralium Alloy 225

Clark and Guha¹⁵ describe the effect of each element in Ferralium Alloy 225 on its mechanical and corrosion properties. (This is a 25Cr, 5Ni, Mo, Cu, N duplex steel.)

The addition of *nitrogen* increases the pitting potential in 3 per cent sodium chloride at 30°C from 0,45V standard hydrogen electrode (SHE) to 1,15V (SHE). When little or no nitrogen is added, the carbon has to be controlled to a maximum of 0,04 per cent if IGC and weld decay in nitric acid are to be avoided. Nitrogen is also an austenite stabilizer and appears to modify the γ/α ratio at which maximum pitting resistance is achieved. Nitrogen also improves the strength of the steel.

Optimum *nickel* content for maximum resistance to pitting combined with good toughness is about 5 per cent. If the nickel content is significantly more than the optimum, the γ -content increases to above 50 per cent and the residual ferrite becomes increasingly enriched in chromium, a ferrite stabilizer. The higher-chromium α -phase transforms more readily to the brittle σ -phase (in the temperature range 700 to 790°C), with adverse effects

on hot-workability, weldability, and toughness. If the nickel content is reduced to below the optimum, the ferrite content is higher, again resulting in low toughness since the σ -ferrite formed on solidification also tends to have low ductility and toughness.

Both *chromium* and *molybdenum* lead to improved resistance to pitting and crevice corrosion. The molybdenum content is limited owing to the tendency to form σ and other embrittling compounds.

Copper can be added to about the 1 per cent level to increase the pitting potential in marine environments (3 to 3,5 per cent sodium chloride). Copper is also beneficial at higher levels in lower pH environments such as those experienced in sour oil and gas wells, polluted sea water, and chemical process plant, particularly under conditions of high flow velocities that lead to erosion and cavitation. However, high copper contents tend to reduce the hot-workability and weldability of the steel so that, for duplex steels of the wrought 22CrNi type, the copper is usually limited to about 2 per cent.

Weldability of Duplex 2205 Steel

As mentioned earlier, if the steel is heated to temperatures above about 1040°C, the volume of ferrite increases and the steel becomes fully ferritic just below the solidus temperature. Hence, many aspects of the weld corrosion of duplex stainless steels are similar to those normally encountered in traditional ferritic stainless steels. Although the solubility of nitrogen is high in ferrite at high temperatures, the solubility at room temperature is low, and the precipitation of Cr₂N can occur even on quenching. The ferrite transforms to a Widmanstätten-type austenite (Fig. 4) to which nitrogen can partition. Because of the high diffusivities of chromium, molybdenum, and nitrogen in ferrite, the formation, and (more important) healing, of depletion zones can be affected by the rapid cooling rates found in welds¹⁶.

The work by Honeycombe and Gooch¹⁷ on plates with section thicknesses up to 13 mm has shown that the fusion and penetration characteristics of various commercial duplex stainless steels are comparable with those of types 316L and 317L. No post-weld heat treatment or preheating of the workpiece is required. Conventional welding techniques are appropriate—manual metal arc (MMA), tungsten-inert gas (TIG), and metal-inert gas (MIG). The heat input should be minimized (1,5 kJ/mm) in order to keep the heat-affected zone (HAZ) narrow, and the interpass temperature should not exceed 150°C.

The amount of austenite was reduced in the HAZ and weld metal with some loss of toughness. Sections of Ferralium Alloy 225 at sections up to 25 mm under severe restraint conditions and up to 50 mm thick have been welded in relatively unrestrained conditions (MMA using matching filler rods)¹⁷. The resistance to SCC was not affected by the welding operation.

Although the HAZ shows larger ferrite grains and Widmanstätten austenite, the minimum impact-energy requirement of 27J, which is considered to be the lower limit for ductile behaviour, is easily met. In welding with a matching electrode such as Arosta 4462 (9,0 per cent nickel), the weld metal has an impact toughness of 50 J at 20°C.

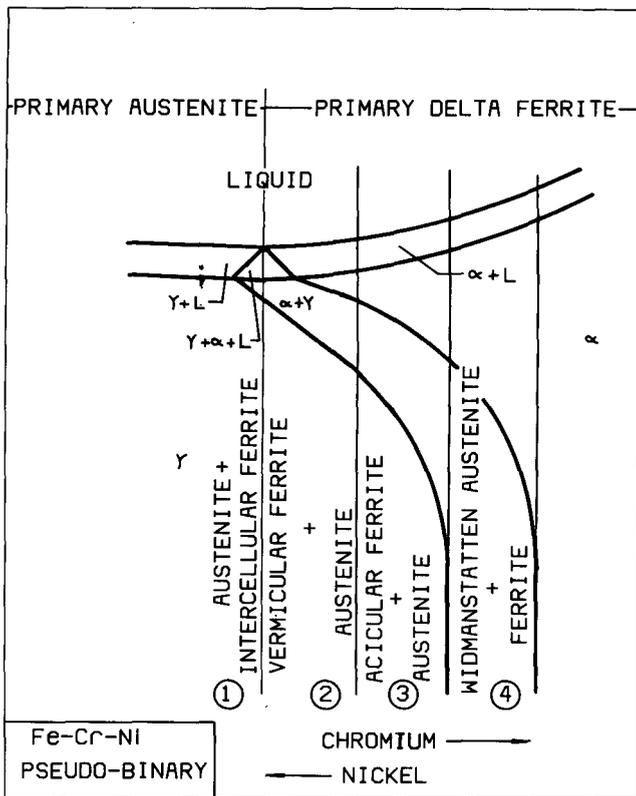


Fig. 4—Schematic pseudobinary diagram for 70 per cent iron, showing the structures developed in iron-chromium-nickel alloys (after Lippold and Savage⁸)

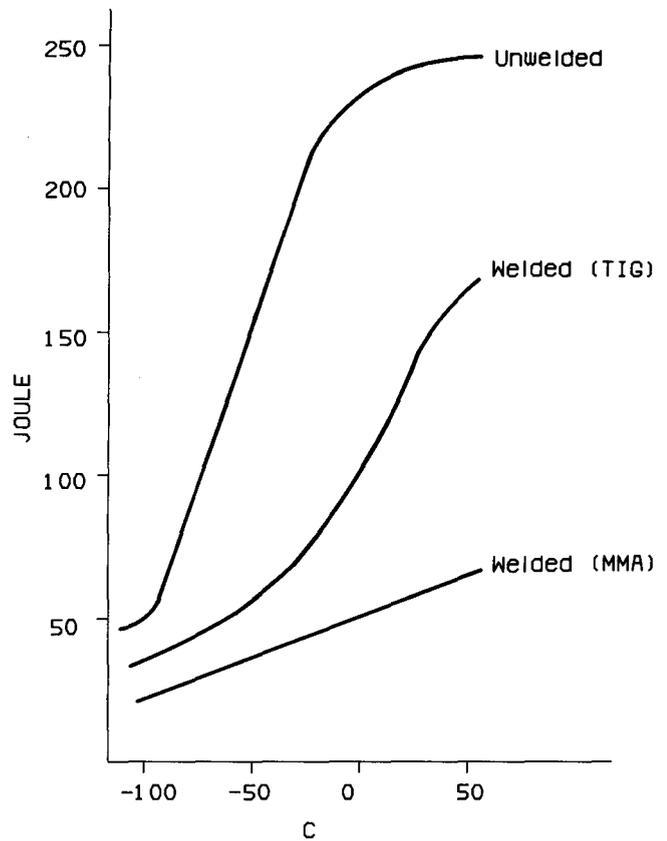


Fig. 5—Impact energy, Charpy V, of SAF 2205 parent metal and welded joint, the latter with a notch across the fusion line¹⁸ TIG = Tungsten-inert gas MMA = Manual metal arc

Fig. 5 shows the impact properties of TIG and MMA welded fabrications¹⁸. Impact energy above 27 J is obtained at temperatures as low as -50°C , which also applies to welded steels.

The duplex 2205 has additions of nitrogen, which are essential for the rapid reformation of austenite. This is decisive for the resistance to the IGC of welded duplex austenitic-ferritic stainless steels.

Corrosion Resistance

Detailed discussions of the corrosion-resisting properties of SAF 2205 (as produced by Sandvik) are given in the literature¹⁹⁻²². SAF 2205 has better corrosion resistance in most media than steel types 316L and 317L.

Table IV shows the relative corrosion rates of SAF 2205, AISI 316L, and AISI 317L in both oxidizing and reducing acids. Fig. 6 is an iso-corrosion diagram showing the relative corrosion rates of these three types of steel.

In oil and gas fields, corrosion results from salt water containing dissolved carbon dioxide and hydrogen sulphide (sour brines). Carbon dioxide dissolved in water lowers the pH. This type of corrosion appears in both oil and gas lines, primarily in the form of pitting. The concentration, partial pressure of carbon dioxide, temperature, and water composition all play a part in the corrosion of plants:

- If $P_{\text{CO}_2} > 2$ bar → Severe corrosion.
- $< 2 > 0,5$ bar → Possible corrosion.
- $< 0,5$ bar → Non-corrosive²³.

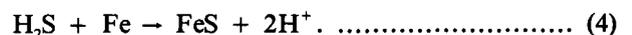
TABLE IV
CORROSION DATA OBTAINED FROM LABORATORY TESTS IN PHOSPHORIC, NITRIC, AND HYDROCHLORIC ACIDS⁷

Mass %	Temperature °C	Corrosion rate*, mm/year		
		SAF 2205	AISI 316L	AISI 317L
<i>Phosphoric acid, H₃PO₄</i>				
70	110	0,22	3,9	2,4
80	100	0,35	1,3	—
<i>Nitric acid, HNO₃</i>				
65,3 (conc.)	B†	0,13	0,25	0,21
<i>Hydrochloric acid, HCl</i>				
0,5	90	0,00	>2,4	—
1,0	60	0,00	—	0,00
2,0	20	0,29	0,26	—

*0,1 mm/year = 4 m/year

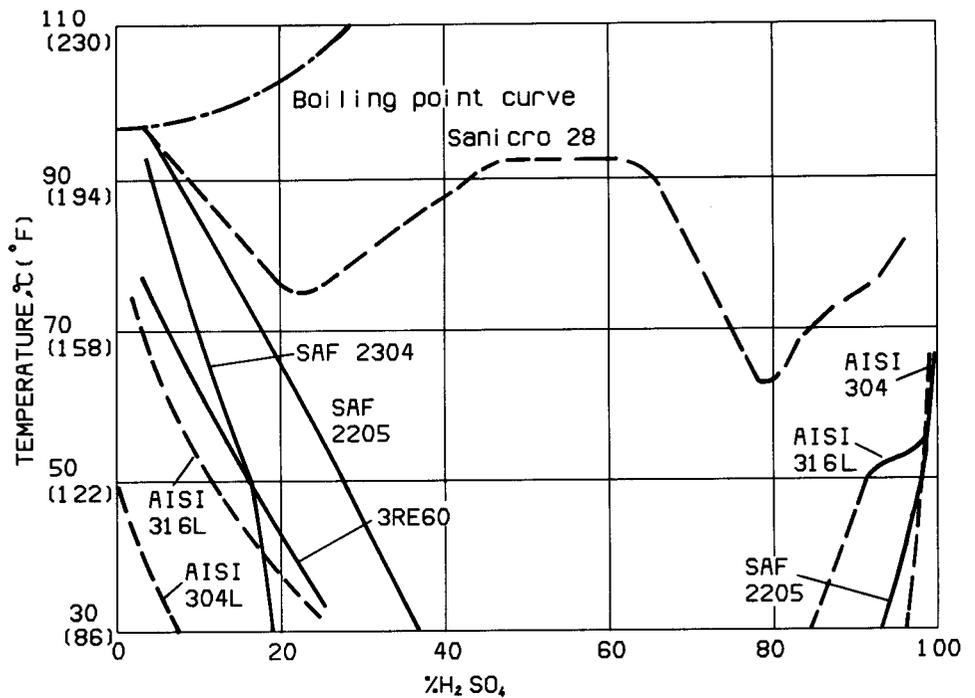
† = Boiling solution

'Sour corrosion' takes place if hydrogen sulphide is also present:



The hydrogen ions diffuse into the crystal lattice, causing localized stresses, which in turn lead to cracking (HISCC). The HISCC mechanism is active if $p_{\text{H}_2\text{S}}$ is greater than 0,0035 bar. HISCC occurs in susceptible steels if the hardness is greater than 237 HB or if $Rp_{0,2}$ is greater than 550 MPa²⁴. Blisters may also form on the steel surface

Fig. 6—Iso-corrosion diagram in stagnant sulphuric acid in contact with air⁷ (at the curves, the annual corrosion rate is 0,3 mm)



due to the recombination of hydrogen atoms into molecular hydrogen gas within the steel.

Resistance to Pitting Corrosion

Resistance to pitting corrosion (as well as to crevice corrosion) is improved mainly by higher chromium and molybdenum contents, as well as by the addition of nitrogen. Fig. 7 shows the pitting potentials of SAF 2205 compared with those of AISI 316L and AISI 317L. It can be seen from this diagram and from Fig. 8 that SAF 2205 is more useful in chloride-containing media than are the standard grades.

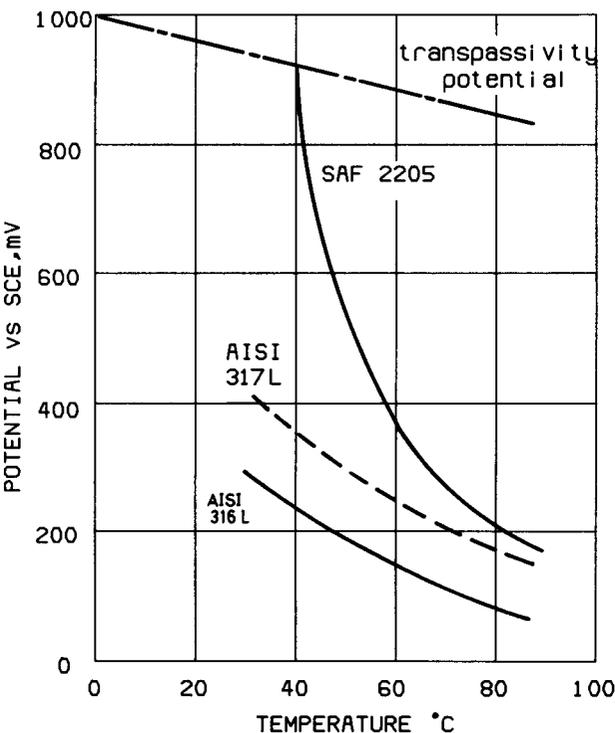


Fig. 7—Pitting potentials for steels in 3 per cent sodium chloride solution⁷ (scanning rate = 20 mV/min)

The pitting resistance equivalent (PRE) can be calculated from different regression formulae²⁴:

$$PRE_1 = \text{mass per cent Cr} + 3 \times \text{mass per cent Mo} \dots\dots\dots (5)$$

or

$$PRE_2 = \text{mass per cent Cr} + 3,3 \times \text{mass per cent Mo} + 16 \times \text{mass per cent N} \dots\dots\dots (6)$$

Generally PRE values of 20 and above indicate an alloy with good pitting resistance.

Fig. 9 shows the critical pitting temperatures (CPT) of SAF 2205 and 316 at 400 mV versus a standard calomel electrode (SCE) or pH 6 (15 minutes at each temperature). Fig. 10 shows the ranking of various alloys according to their PRE values considering the Cr and Mo content. The alloys are ranked as follows: Sanicro 28 > 2RK65 > SAF 2205 > 3RE60 > AISI 316.

Fig. 11 shows good agreement between CPT and PRE₁ in 3 per cent sodium chloride aqueous solutions.

Resistance to Stress Corrosion Cracking

Duplex stainless steels have a very high ratio of property to cost. Where SCC is a problem, duplex stainless steels offer better property-to-cost advantages than the conventional grades, especially in refineries and petrochemical plants.

Figs. 12 and 13 show the huge improvement of SAF 2205 over AISI 316L in calcium chloride and magnesium chloride solutions at 100 and 150°C respectively. It should be noted that the threshold stress at a maximum testing time of 500 hours is far greater for SAF 2205 than for the other austenite grades.

Applications

Some of the applications of SAF 2205 are summarized below.

- (1) Heat-exchangers, tubes, and pipes for the winning, handling, and production of oil and gas.
- (2) Heat-exchangers and pipes in desalination plants.

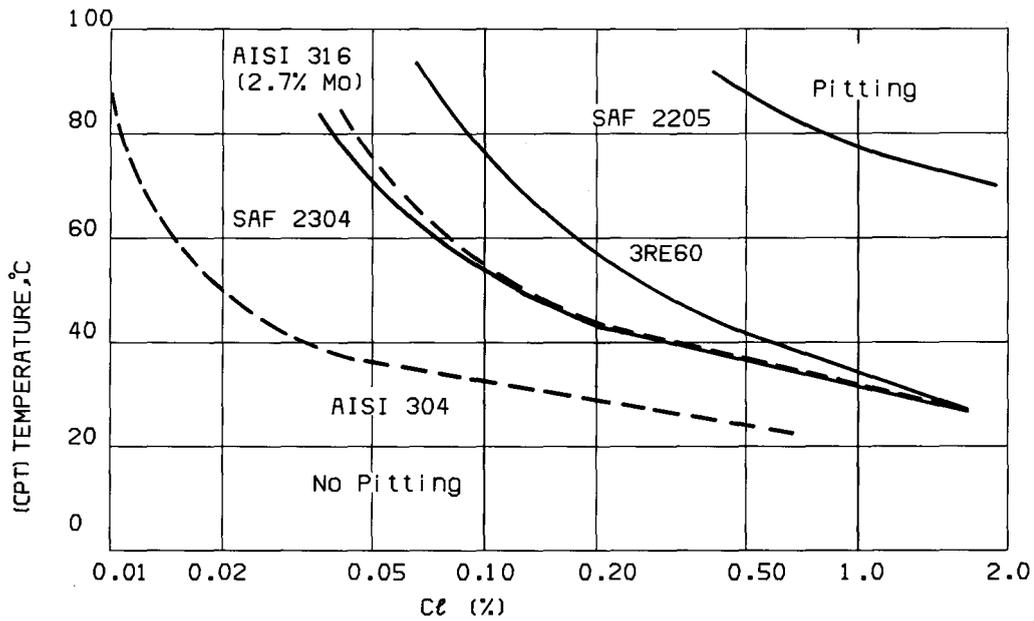
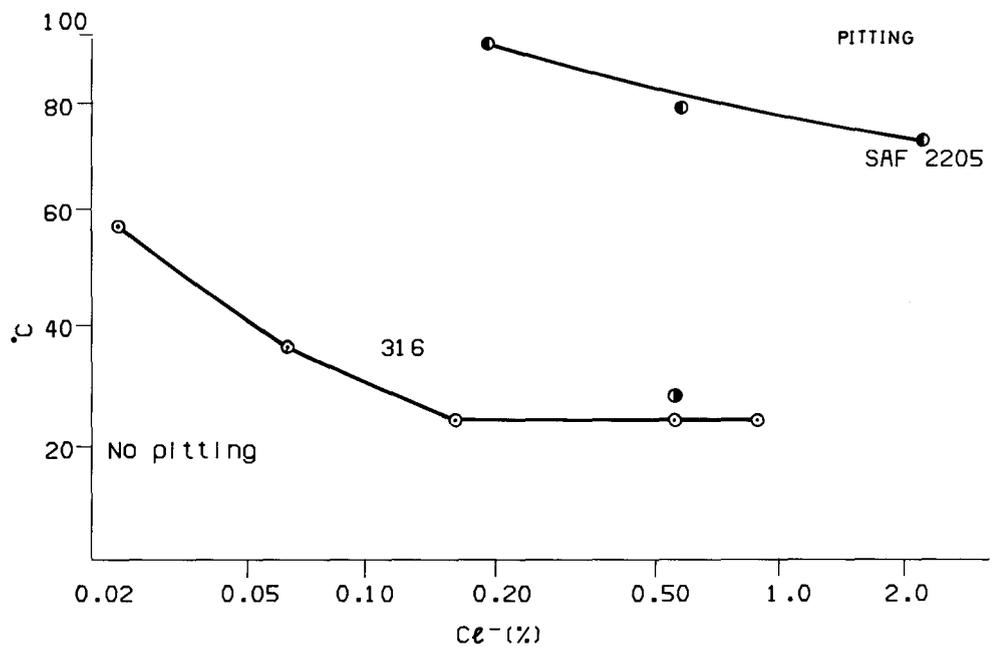


Fig. 8—Critical pitting temperatures (CPT) of different grades of steel in neutral aqueous chloride solutions⁷ (SCE potential + 300 mV)

Fig. 9—Critical pitting temperatures at 400 mV SCE for pH about 6, ground surfaces, and 15 minutes at each temperature¹⁹



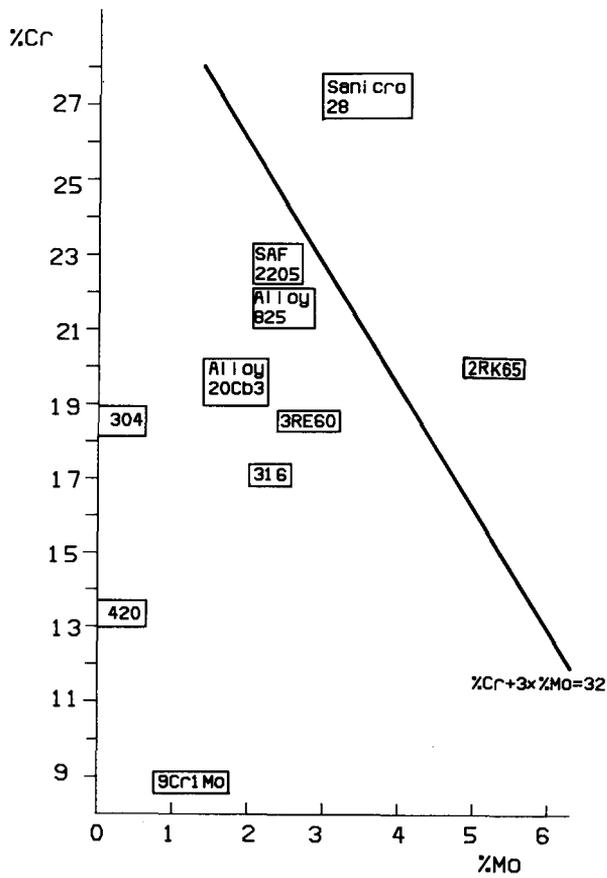


Fig. 10—Ranking of stainless steels and nickel alloys in regard to their chromium and molybdenum contents

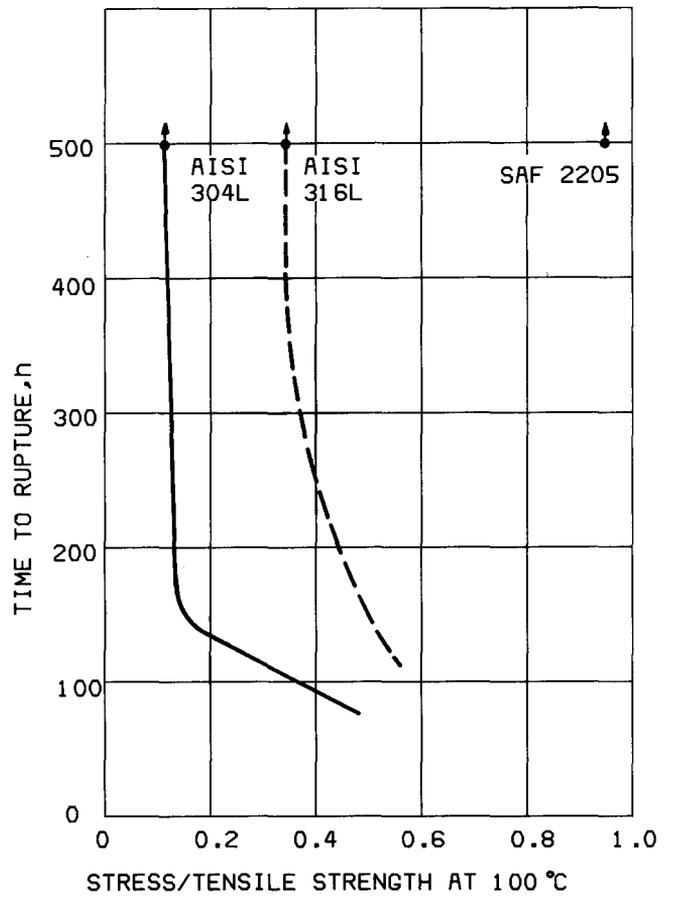


Fig. 12—Stress-corrosion cracking of steels⁷ in aerated 40 per cent calcium chloride at 100°C

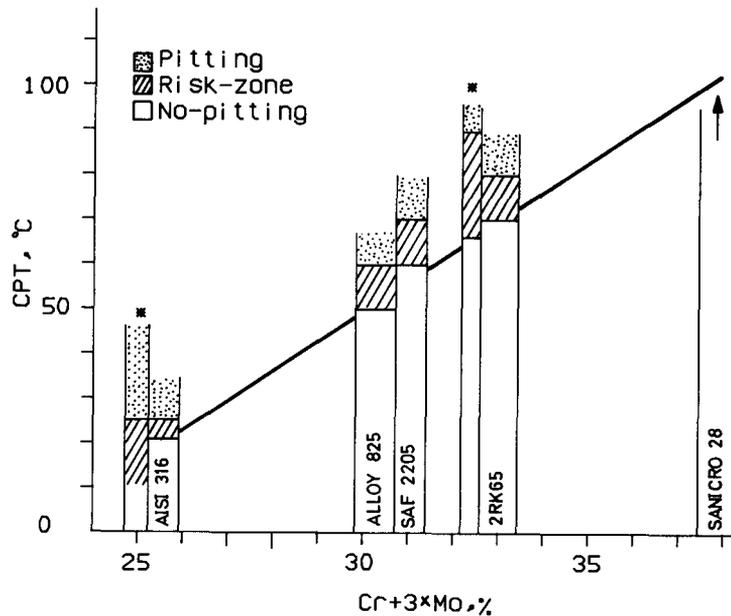


Fig. 11—Critical pitting temperature at 400 mV SCE in a 3 per cent aqueous solution
*From practical experience

Time to fracture (h)

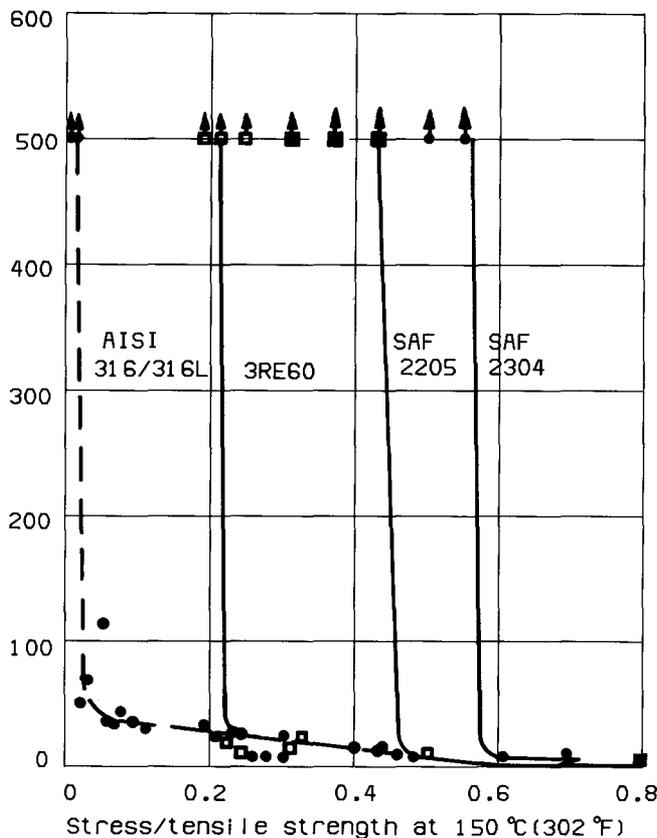


Fig. 13—Stress-corrosion cracking of steels⁷ at constant load in aerated 45 per cent magnesium chloride at 150°C (302°F)

- (3) Flare booms on offshore platforms for oil production.
- (4) Telescopic legs for drilling equipment in coal mines.
- (5) Pumps, fans, and centrifuges for the chemical, fertilizer, and metallurgical industries.
- (6) Pressure vessels, pipes, tanks, and heat-exchangers for the processing and transportation of various acids.
- (7) Sulphur-melting coils in sulphur plants and heating coils in pickling baths.
- (8) Heating coils for chemical tankers.
- (9) Desalting, desulphurization, and distillation units in oil refineries, and in the production of ethylene dichloride, vinyl chloride, and polyethylene.
- (10) In digesters and digester preheaters in the pulp-and-paper industry in both sulphate and sulphite plants.
- (11) Hot-liquor tanks in breweries, abattoirs, and milk and other food-processing industries.
- (12) Cooling tubes for blast furnaces.

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