DEVELOPMENTS IN THE USE OF STAINLESS STEELS FOR OFFSHORE PIPEWORK SYSTEMS

"In a Class of Its Own"

C. V. ROSCOE+, K. J. GRADWELL+, M. R. WATTS+
AND W. J. NISBET*

+ Weir Material Services Ltd, Manchester

*Department of Metallurgy and Materials Science,
University of Manchester/UMIST

ABSTRACT

Conventional duplex stainless steels have been used extensively for process pipework systems in view of their excellent combination of mechanical properties and resistance to stress corrosion cracking. However, field service experience has shown that these low alloy duplex stainless steels have only a limited resistance to pitting and crevice corrosion in sea water. In contrast, the 6Mo super-austenitic grades of stainless steel have excellent resistance to localised corrosion in sea water, but their use in process pipework systems is restricted by their relatively poor mechanical properties and high cost.

The new generation of super duplex stainless steels combine in one alloy the sea water corrosion resistance of the 6Mo super austenitic stainless steels and mechanical properties which are superior to conventional duplex stainless steels. Super duplex stainless steels are distinguishable from earlier duplex stainless steels primarily by the addition of higher levels of nitrogen, chromium, molybdenum, tungsten and nickel. These and other alloying elements must be closely controlled to achieve the correct ferritic/austenitic microstructural phase balance in order to optimise the mechanical and corrosion resistance properties. Furthermore, super duplex stainless steels incorporate a minimum Pitting Resistance Equivalent value of 40 as part of their specifications to guarantee consistent localised corrosion performance.

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Potentiodynamic studies have been undertaken to compare the pitting and crevice corrosion resistance of the various categories of stainless steels in sea water. A number of accelerated corrosion tests have been carried out on weldments in $FeCl_3$ solutions to assess the localised corrosion performance of the heat affected zones and the weld metal.

In this paper the performance of specific categories of stainless steels are compared and their suitability for use in topside and subsea pipework systems assessed. The relative mechanical properties and corrosion resistance of these stainless steels are discussed and examples given to show the advantages of designing systems in super duplex stainless steels to reduce wall thickness and overall system weight.

INTRODUCTION

In offshore pipework systems there is an increasing demand for higher strength and more corrosion resistant materials. Until recently the more conventional duplex stainless steels had been considered to have adequate localised corrosion and stress corrosion cracking resistance when used in subsea process pipelines. However, the more sour nature of the later oil and gas fields in the North Sea has led to the introduction of the more corrosion resistance super duplex stainless steels. In topside sea water pipework systems and fire water systems it is now also economic to use high alloy stainless steels in preference to 90/10 cupro-nickel alloys. Some commercial examples of high alloy stainless steels used for these applications are shown in Table 1.

The development of the highly alloyed and super stainless steels required an understanding of the effect of alloying elements on the corrosion performance and mechanical properties of the steels. A summary of the effect of certain alloying elements on the anodic polarisation curve of stainless steels is shown in Figure 1[1]. The elements that have the most beneficial effect on the resistance to localised corrosion are chromium, molybdenum, nitrogen and tungsten.

The addition of chromium (13wt%) to iron results in the formation of a protective chromium oxide film which isolates the steel from the environment. In chloride solutions, the formation of the protective film expands the passive potential range by increasing the pitting potential and reducing the passive current density (Figure 1). In duplex stainless steels, the ferrite stabilising influence of chromium must be balanced by additions of nickel to preserve the phase balance between austenite and ferrite.

For a given chromium content, molybdenum has a strong beneficial effect on a steel's passivity, primarily by increasing the pitting potential and lowering i_{max} (Figure 1). The mechanism by which molybdenum exerts its influence is not fully understood[2,3], but may be associated with its inhibition of the active dissolution rate in incipient pits[4]. From a practical point of view, it is necessary to have a high chromium and molybdenum content in the stainless steel to prevent crevice corrosion in hot sea water. This has led to additions of 3 to 4wt%Mo in super duplex and 6wt%Mo in super austenitic stainless steels.

Nitrogen additions improve the localised corrosion resistance of stainless steels by increasing the pitting potential[5]. The beneficial effect of nitrogen appears to be enhanced by the presence of a molybdenum[6]. Nitrogen may improve corrosion resistance by being concentrated at the interface between metal and film[7]. More recent work suggests the beneficial effect of nitrogen on pitting corrosion is associated with the blocking effect of nitrogen on anodic dissolution in the local chemistry of a pit[8]. In duplex stainless steels nitrogen may also improve corrosion resistance by reducing partitioning of the chromium[9].

Tungsten (like Mo) has been shown to extend the passive potential range and increase pitting potential when added to duplex stainless steels[10]. Its effect may enhance corrosion properties by being adsorbed into the passive film as WO_3[11]. WO_3 then interacts with the oxides, resulting in enhanced stability and improved bonding of the film to the base metal.

PITTING RESISTANCE EQUIVALENT

The beneficial effects of alloying elements can be combined to give an indication of a stainless steel's corrosion resistance. Such a compositionally derived empirical relationship for pitting resistance of stainless steels is known as the steels Pitting Resistance Equivalent (PRE_N). For nitrogen containing stainless steels the PRE_N has been derived as;[12]

$$PRE_N = \%Cr + 3.3\% Mo + 16\% N_2$$

Other workers suggest a multiplication factor of 30 should be used for nitrogen in stainless steels [13]. There are reservations about these formula as they do not take into account the beneficial effects of other alloying elements, particularly tungsten. Indeed a more relevant PRE_N formula for tungsten containing stainless steels may be

$$PRE_N = \%Cr + 3.3\%(Mo + W) + 16\%N$$

Figure 2 shows that the introduction of tungsten into this formula decreases the amount of scatter when PRE_N is plotted against critical pitting temperature for specific stainless steels.

It is generally considered that PRE_N values of greater than 40 are necessary to guarantee the localised corrosion resistance of a stainless steel in oxygenated sea water and both the super duplex and super austenitic (6Mo) stainless steels satisfy this criterion (Table 1). However further work is required to refine the PRE_N formula so that the beneficial/detrimental effects of all alloying elements and the microstructural factors associated with the breakdown of passivity are considered. In duplex stainless steels, it may be more relevant to use two PRE_N numbers, one for ferrite phase and one for austenite. Table 2[14] shows the compositions and the PRE_N numbers of the bulk metal and individual phases of two super duplex stainless steels. Depending on the element partitioning, one phase may be more susceptible to pitting (lower PRE_N) than the other. It is known that ferrite undergoes preferential dissolution in reducing environments whereas austenite undergoes preferential dissolution in more oxidising environments[15]. Thus depending on which phase is likely to be attacked the PRE_N value of the individual phases may be optimised.

PITTING AND CREVICE CORROSION OF WELDMENTS

It is more relevant to consider the combined influence of the PRE_N value and the microstructure to determine the localised corrosion performance of stainless steels. To demonstrate this fact a series of weldments have been produced in conventional duplex, super duplex and 6Mo austenitic stainless steels.

In respect of the super duplex stainless steel (ZERON 100) a number of production weldments have been studied to examine the effect of heat input, welding position and the addition or deletion of filler metal for both manual TIG and automatic welding techniques. These investigations are discussed in an internal publication [16].

Accelerated localised corrosion assessments have been carried out on all the weldments in 10%$FeCl_3$ solution in accordance with ASTM G48. The results of these investigations are summarised in Table 3. From the results obtained, it can be deduced that the weldments in both the as-welded and solution annealed conditions can be ranked in terms of their critical pitting and critical crevice temperature in the ferric chloride solution as follows:

ZERON 100 (most resistance) > 6Mo austenitic stainless steels > 22% Cr duplex.

The solution heat treated weldments generally give critical pitting and critical crevice temperatures which are similar to those observed for the parent materials. The beneficial influence of higher PRE_N values can readily be seen by comparing the CPT values obtained on the ZERON 100 weldments (65-70°C) and the 22% Cr duplex weldments (20-25°C) in the solution heat treated condition. However, some of the as-welded plates on the 6Mo weldments displayed very severe pitting in the weld metal on the unmachined test specimens when tested at 40°C. Also the machined 6Mo weldments showed extensive crevice corrosion at 35°C in the region of the unmixed zone, heat affected zones and weld metal. These results are generally in agreement with the findings of other workers[17].

The reduction in the corrosion performance of the weld metal is attributed to the precipitation of phases such as Laves, niobium and chromium rich nitrides and M_6C. These phases can contain up to 50wt% of molybdenum (Laves) and up to 70wt% of chromium (nitride) and therefore denude the matrix of these elements in the surrounding areas. This in turn lowers the pitting and crevice corrosion resistance of the weld metal. Similarly both Chi and Laves phases have been reported to precipitate in the heat affected zones of 6Mo weldments[17]. Consequently it is not surprising that the HAZ regions of the 6Mo weldments show severe crevice corrosion attack in the machined specimens.

In respect of the as-welded super duplex stainless steel weldments, these also exhibited a lowering of the localised corrosion resistance. When welded in the optimum heaat input range with metal cased wire hacing a PRE_N value of 41.6 [Table 3] the ZERON 100 weldments in the as-welded condition gave CPT values of 55-65°C. When the heat input levels were purposely varied on weldments in an effort to determine the permissible variation from the optimim welding parameters, only isolated pitting is observed in the unmachined as-welded specimens when tested at 45°C and crevice corrosion is only just discernable on the machined specimens at 45°C.

A typical microstructure of the weld metal, heat affected zone and parent metal of the ZERON 100 weldment which has been welded in the optimum heat input range of 1.00-2.75kJ/mm is shown in Figure 3a. The proportion of austenite varies from 36-44% across the weldment and there is no evidence of deleterious second phase particles.

On these specimens only slight evidence of pitting and crevice corrosion has been observed in the weld metal even though the PRE_N value of the weld (40.1) in these instances is less than that recorded for the parent plate (41.2)

In the specimens welded with heat inputs levels outside the optimum range there is some evidence of M_2X precipitation in isolated areas of the ferrite matrix (Figure 3b) in the heat affected zone.

Lower heat inputs will tend to give insufficient time at temperature for austenite to re-precipitate in the ferrite matrix during cooling which in turn leads to supersaturation of nitrogen in the ferrite resulting in the precipitation of M_2X particles. The M_2X nitride precipitates typically contain high levels of chromium, molybdenum and nitrogen i.e. $(CrMo)^2N$ and are finely dispersed in regions of the microstructure where the proportion austenite is locally less than the average value across the weldment. (i.e. in particular areas of the HAZ). Consequently the matrix is locally deficient in these elements which lowers the pitting resistance of the weldments.

Heat input levels higher than 2.75kJ/mm can also result in the precipitation of M_2X, since the HAZ is effectively being aged in the temperature region where M_2X precipitation will occur virtually independently of area fraction of austenite present in the microstructure. Higher heat inputs can also lead to elemental loss of Cr and N_2 from the weld metal which also leads to a lowering in the pitting resistance of the weldment

Irrespective of the precipitation of these M_2X particles the localised corrosion performance of all the ZERON 100 weldments is better than that observed for the 6Mo austenitic stainless steel weldments. It should also be noted that the solid wire utilised on the ZERON 100 weldments had a PRE_N value of 40.1. Therefore the corrosion results obtained probably reflect the lowest every values likely to be achieved in the TIG welding of ZERON 100 since the PRE_N minimum in the material specification is 40. Of interest is that the P12 filler utilised on the 6Mo weldments had a PRE_N value of 50.0. However, the high molybdenum containing phases and microsegregation present in the weld metal markedly reduces the corrosion performance of the 6Mo weldments. Despite the obvious limitations of the minimum PRE_N value it does allow a more consistent measure of the corrosion performance to be predicted particularly when second phase particles are avoided.

CASE STUDIES

The beneficial effects of using super duplex stainless steels in preference to other materials can be shown by considering typical offshore pipework systems, and these are shown in Table 4[18].

Fire Water Systems - Deluge and Sprinkler Systems

In order to evaluate the potential benefits of using pipework in stainless steels in preference to 90/10 cupro-nickel, a typical deluge system has been designed using a computer hydraulic programme. The system had to meet the minimum nozzle pressure and flow required, and had 10 bar inlet pressure available from the ring main

The design programme utilised 6m/s velocity limit in cupro-nickel and 10m/s in super duplex stainless steel. In fact the super duplex stainless steel is capable of much greater velocities, but the Renolds number of water changes at these higher velocities and a revised calculation procedure is required. The results are shown in Table 5a.

From this study it is possible to deduce the following.

- Due to velocity limitations with cupro-nickel, the system is unable to utilise the available inlet pressure. As a result it would be necessary to install an orifice plate to create a 4.72 bar pressure drop at the deluge valve set.

- The super duplex stainless steel system has smaller pipes and as a consequence a smaller deluge value set would be required.

- As a result of the smaller bore stainless steel system, the dry weight is reduced by 15% compared to cupro-nickel and the wet weight by 33%.

- The increased strength of stainless steel enables 38% few pipe supports to be used and eliminates the need for the comprehensive insulation kits.

Typical costs of a stainless steel pipe and fittings package relative to those in a cupro-nickel deluge system are presented in Table 5b. The overall cost of the system is greatly reduced using super duplex stainless steel in place of 90/10 cupro-nickel.

Support and prefabrication costs are much lower for the super duplex stainless steel. Other savings would also arise from the use of smaller deluge valve sets and skids. The super duplex stainless steel is also easier to handle, whereas the cupro-nickel is prone to damage.

Extending this analysis to include all the fire water deluge and sprinkler systems (excluding the ring main) for a medium sized platform reveals the information presented in Table 5c. The reduced pipe sizes gave a 10 tonne (20%) reduction in the wet (operating) weight for which the platform must be designed.

Table 6 shows a similar case study for a typical firewater ring main. The study has compared pipe call-off quantities using velocity limitations of 3.5m/sec for cupro-nickel and 7m/sec for super duplex stainless steel. A velocity of 10-12m/sec could have been used for the super-duplex stainless steel system to parallel the assumptions used in the deluge system example yielding still greater savings in cost and weight. The study reveals the following information:

- Super duplex stainless steel pipe is lighter than 90/10 cupro-nickel pipe at the larger diameters due to the reduced wall thickness.

- Reduced diameter fire water mains can be utilised with super duplex stainless steel due to their tolerance to higher water velocities. In view of the necessity to supply the helideck on the top of the platform with sea water, there is excess pressure in the ring main for the other duties. Therefore, it is not necessary to specify larger fire pumps when using the additional velocities allowed by stainless steels.

- Both the dry weight and the wet weight is significantly less when using super duplex stainless steel (Table 6b).

Table 6c gives the cost comparisons between 90/10 cupro-nickel and super duplex stainless steel. These figures show cost savings when using super duplex stainless steel for:

- Pipe materials

- Supports

- Prefabrication

The benefits and savings from the easier handling of the stronger super duplex stainless steel have not been reflected; nor have the benefits from smaller pump delivery and ring main valves.

Process Pipework

There is an increasing tendency, particularly in Norway, to specify 6%Mo austenitics stainless steels in preference to standard 22%Cr duplex stainless steels. The rationale supporting this departure from past practice has little to do with Cl^- or H_2S stress corrosion cracking but is concerned principally with localised corrosion performance.

Process fluids in the latest generation of oil and gas fields have higher water cuts than previously encountered. The aqueous phase is frequently at elevated temperatures and often contains high proportions of chlorides and H_2S. Consequently the 22Cr duplex stainless steels do not give adequate resistance to pitting and crevice corrosion, particularly in the root and heat affected zone areas of weldments.

The super duplex stainless steels give a localised corrosion performance equivalent to 6%Mo austenitic stainless steels, but have strength properties even greater than conventional 22%Cr duplex stainless steels.

Therefore process pipework systems in super duplex stainless steels give considerable cost savings in comparison to systems in 6%Mo austenitic stainless steels.

Table 7 shows comparative costs for a simple model of a process manifold system constructed in a 6%Mo austenitic and a super duplex stainless steel (ZERON 100). Assumptions for the model are:

- Temperature 100°C
- Pressure 150 bar
- Simple cylinder - no branches
- Norwegian general rules for piping systems (TBK6 1983)
- No corrosion allowance

As can be seen from Table 7 the significant increase in allowable stress afforded by the super duplex alloy combined with equivalent or superior localised corrosion performance will produce significantly lower system build costs when these alloys are specified in preference to 6%Mo alloys for process pipework.

A natural extension of the proposed move towards alloys with superior localised corrosion performance in process applications will be to specify the alloys for submarine pipelines. A very significant cost in this context is lay barge hire costs. These hire costs are dictated by girth joint welding speeds. Clearly the reduction in wall thickness allowed by the super duplex alloys will reduce the welding costs substantially.

Since the barges typically lay 0.5-1 kilometre of 6" pipe a day, at a cost of approximately £250,000 per day the potential savings are enormous.

CONCLUSIONS

- The use of a Pitting Resistance Equivalence (PRE_N) formula incorporating tungsten, provides a simple method of predicting the localised corrosion performance of stainless steels. However, microstructural factors that affect corrosion performance must also be considered.

- The critical pitting and critical crevice resistance in ferric chloride of the weldments tested can be ranked as follows:

- ZERON 100 (most resistant) > 6Mo austenitic stainless steels > 22% Cr duplexes.
- The use of super duplex stainless steels affords considerable scope for cost reduction when specified for offshore pipework systems. In respect of fire water systems, displacement of cupro-nickel alloys leads to significant direct and indirect cost savings through reductions in material usage (dry weight) and an mpressive associated savings in wet weight. In respect of process pipework, the savings that accrue from the specification of super duplex steels in preference to the 6%Mo grades cannot be overstated.

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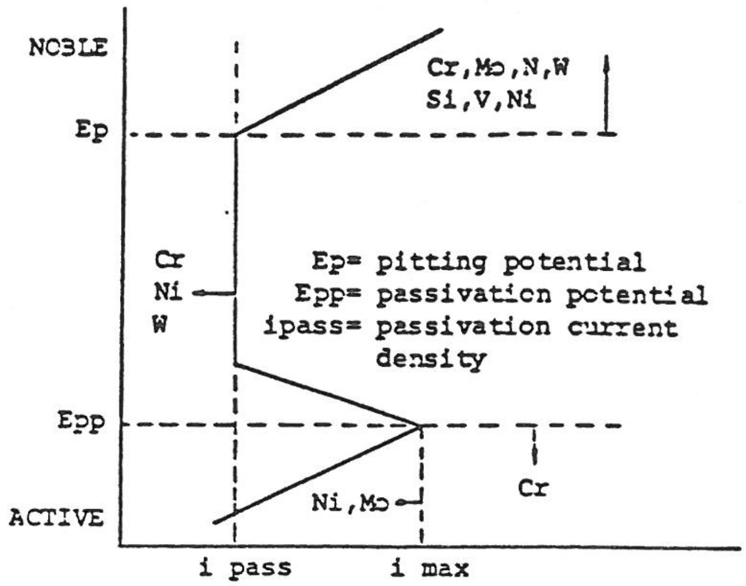


Figure 1 Schematic representation of the effects of certain alloying elements on the polarisation curve of stainless steels[1].

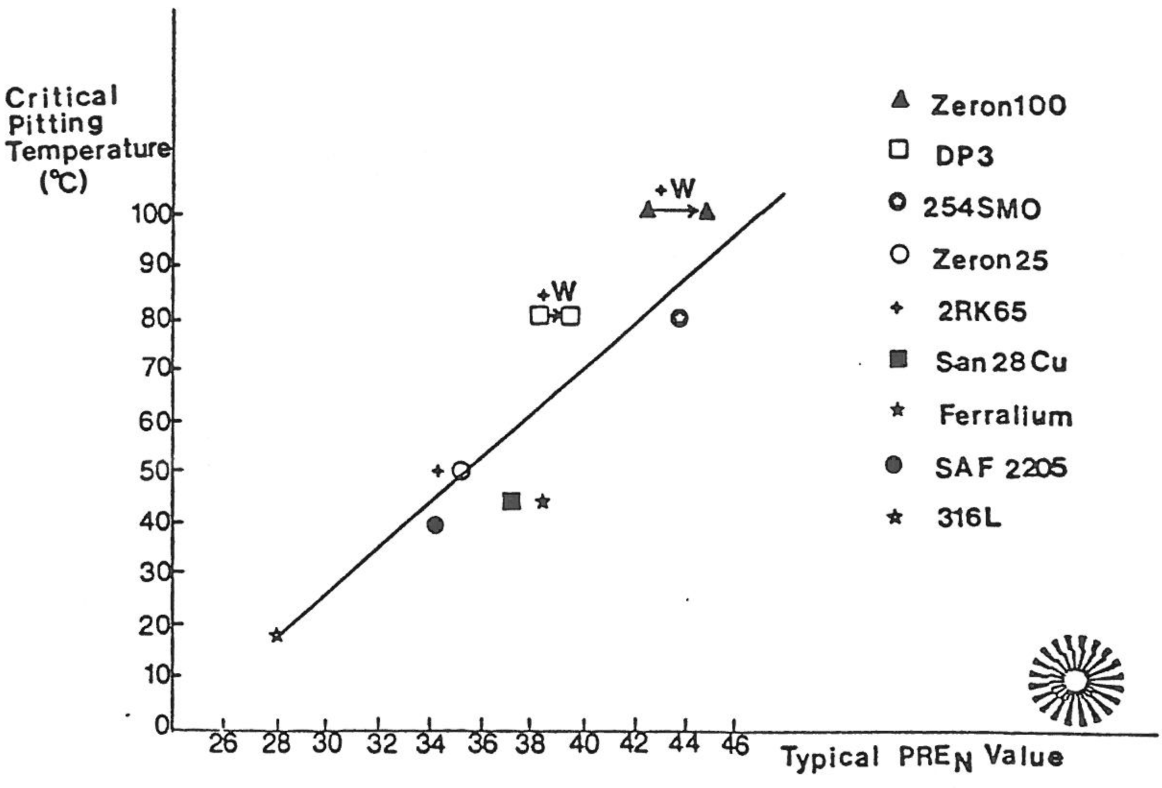
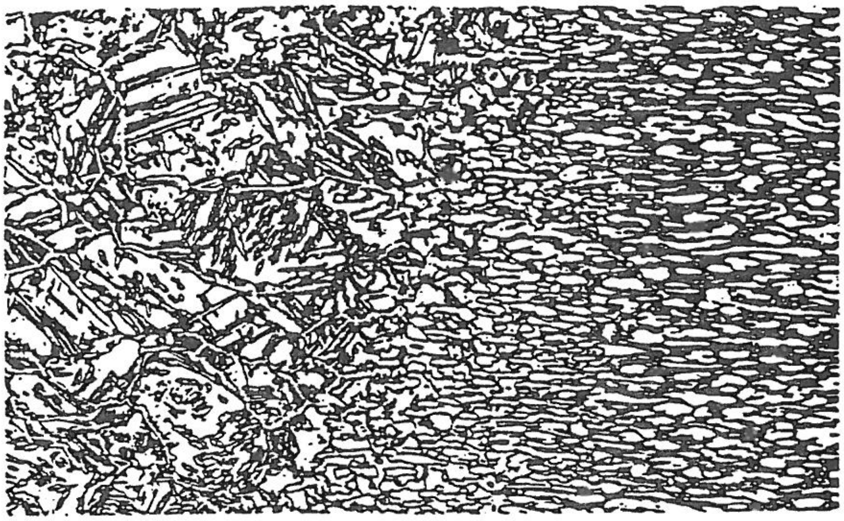


Figure 2 PRE_N (%Cr + 33%Mo + 16%N) and tungsten adjusted PRE_N (%Cr + 3.3(%Mo + %W) + 16%N) versus critical pitting temperature for a selection of stainless steels.

a)



b)

Figure 3 a) Typical microstructure of weld metal + HAZ + parent metal of Zeron 100 welded in the heat input range of 1.25-2.75kJ/mol in b) M_2X precipitates in the ferrite of the HAZ of Zeron 100 welded outside the heat input range of 1.25-2.75kJ/mol.

Table 1

Nominal Compositions of some Commercially Available High Alloyed Stainless Steels

Steel	Cr	Ni	Mo	Cu	W	N_2	PRE_N
Zeron 100*	25	8.0	3.8	0.7	0.7	0.25	41.5 43.8w
SAF 2205ˣ	22	5.0	3.0			0.14	34.1
Sanicro 28⁺	27	31	3.5	1.0			38.9
AL6XN#	20.8	25	6.5			0.20	45.4
254 SMO#	20	18	6.1	0.7		0.20	43.3

* Super duplex
ˣ Duplex
\+ High alloyed austenitic
\# 6Mo super austenitic

w - Tungsten adjusted PRE_N

Table 2

PRE_N values for two duplex stainless steels. Partitioning coefficients determined from Termocalc Version C, iron data base at 1100°C[14].

wt%	Cr	Ni	Mo	W	N	PRE_N
Bulk	24.2	7.37	4.0	0.63	0.25	43.5
K_γ/K_α	0.93	1.4	0.83	0.5	8.8	
α(56%)	24.97	6.27	4.32	0.81	0.06	42.8
γ(44%)	23.22	8.77	3.59	0.40	0.49	44.2
Bulk	24.2	8.0	4.0	0.63	0.25	43.5
K_γ/K_α	0.91	1.41	0.79	0.49	8.35	
α(50%)	25.34	6.64	4.46	0.85	0.05	43.7
γ(50%)	23.06	9.36	3.53	0.41	0.43	42.9

$PRE_N = \%Cr + 3.3\ (\%Mo+\%W) + 16\%N$

Table 3

Summary of Welding Trials Conducted on Zeron 100, 6%Mo Austenitics and SAF 2205 Stainless Steels

Material	PRE_N (base metal)	PRE_N (filler metal)	Condition of material	Heat Input (kJ/mm)	CPT (°C)	CCT (°C)
Zeron 100 base metal	41.7 (43.7)	-	Mill finished plate	-	65-75	60-65
Zeron 100 GTAW with Zeron 100 SW	41.2 (43.1) 41.3 (43.2)	40.1 (42.0) 41.6 (44.0)	As welded plate As welded plate	0.97-3.12 1.95	45-55*,** 55-65**(1)	45-50*,** 50-60**
Zeron 100 GTAW with Zeron 100 MMCW	41.5 (43.6)	42.5 (44.3)	Solution annealed	0.9-2.1	65-75	55-65
6 Mo Austenitics base metal	43.3/45.4	-	Mill finished plate	-	55-65	45-55
6 Mo Austenitics GTAW with P12 filler	43.3/45.4	49.0/49.8	As welded plate	0.9-1.1	35-45*(1)	35-45*,**
6 Mo Austenitics GTAW with P12 filler	43.3/45.4	49.8	Solution annealed	0.9-1.1	50-55	Not assessed
2205 base metal	33.4/34.2	-	Mill finished plate	-	25-35	15-25
2205 GTAW with 22.8.3 filler	33.4/34.2	34.3	Solution annealed	2.0	20-25	Not assessed

Note: PRE_N figures in brackets are adjusted to include tungsten.
* Localised corrosion in the weld metal.
** Localised corrosion in the HAZ.
(1) Optimum Heat Input.

Table 4

Advantages and Disadvantages of Materials in Ring Main, Deluge and Sprinkler Systems.

Material Options	Ring Main	Deluge System	Sprinkler
Carbon Steel Cement lined	Unacceptable Severe wt. penalities high installation costs not now normally specified.	Unacceptable	Unacceptable
Carbon steel lined/galvanised		Corrosion due to evaporation/concentration in seawater droplets remaining after testing. Corrosion products leads to nozzle blockage.	Risk of nozzle failure failure. Examples of failure have been reported.
Cupro-Nickel	Corrosion performance generally good. Occasional damage behind welds and at bends due to eddying. Velocity limitations/ low strength requires larger pipe sections.	Corrosion performance O.K. Dry systems have high potential for heat damage, in the early stages of a hydrocarbon fire. Velocity limitations requires larger pipe sizes.	Generally satisfactory.
Standard stainless (316)	Unacceptable	High salt concentrations combined with evaporation in small pools and droplets leads to severe pitting and perforation & risk of nozzle blockage by corrosion products.	Risk of pitting and perforation.
Super duplex super austenitic	Optimum solution.	Ideal solution.	Ideal solution.
Note	Perhaps surprisingly more problems and failures are reported in notionally dry deluge systems than in ring main or sprinkler systems illustrating the unexpectedly harsh environment that exists.		

Table 5
Case study of a typical 40 nozzle deluge system

5a Alternative designs

Pipe dia. (inches)	lengths of pipe required (metres)	
	90/10 Cupro-Nickel	Super Duplex
1	36.65	52.4
1.5	23.85	33.5
2	25.4	5.9
3	11.5	28.5
4	22.85	25.0
6	25.03	-
Valve Set (mm)	150	100
No of Supports	55	34
Inlet Press Reqd.(bar)	5.28	10
Flow (litres/min)	4368	4880
Pipe Volume (litres)	809	472
Dry Wt. (Kgs)	634	542
Wet Wt. (Kgs)	1442	960

5b Costs

	90/10 Cupro-Nickel (£)	Zeron 100 (£)	Change (%)
Piping Material	6500	6400	-2
Supports	1100	680	-38
Prefab Labour	7000	4000	-43
Total	14600	11080	-24

5c Weights

	90/10 Cupro-Nickel	Super Duplex
Dry Wt. (tonnes)	28.5	24.3
Wet Wt. (tonnes)	46.3	36.8

Table 6

Case Study of a Typical Firewater Ring Main

6a Lengths of Materials Reqired (metres)

Pipe Dia. (inches)	18	12	8	6	4	3	2
Cupro-Nickel (3.5m/sec)	170	-	5	30	40	-	-
Zeron 100 (7m/sec)		170	-	5	30	40	-
Zeron 100 (12m/sec)			170	-	5	30	40

6b Weights

	90/10 Cu-Ni 3.5m/sec	Zeron 100 (7m/sec)
Dry Wt. (tonnes)	17.4	6.7
Wet Wt. (tonnes	46	19
Pipe Supports (No.)	123	82

6c Costs

	90/10 Cu-Ni (£)	Super Duplex (£)	Change (%)
Piping Material	96000	60000	-38
Supports	3700	1650	-55
Prefab Labour	32010	9500	-70
Total	131700	71150	-46

Table 7

Comparative Costs for 6Mo Austenitic and Super-Duplex Stainless Steels for a High Pressure Process System

	6%Mo Austenitic	Super-Duplex (Zeron-100)
Design Stress 100°C MPa	174	291
20" O.D. Pipe Wall Thickness (mm)	21.5	13
Cost ratio	2.4	1