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THICK SECTION CASTINGS FOR THE PUMP INDUSTRY IN 25 CHROMIUM 5 NICKEL DUPLEX STAINLESS STEELS

ABSTRACT

The cast duplex structured stainless steels containing 25% Cr and 5% Ni have come a long way since their original development in the early 60's. This paper summarises some of the experience gained at Mather & Platt Limited during the production of large complex castings in a particular duplex steel — Zeron 25.

The advantages of the duplex steels from the points of view of localised corrosion resistance, cavitation and erosion corrosion resistance, stress corrosion and mechanical properties are discussed relative to seawater pumping applications. The effects of microstructure and composition on thick section properties are considered. In particular, the roles of chromium nickel and nitrogen in relation to their effect on the process route are discussed. Practical problems associated with the production of large complex castings are considered. Attention is given to the solution of foundry, heat treatment and welding problems.

INTRODUCTION

The 25Cr-5Ni duplex stainless steels have been available for a period of five or ten years in both wrought and cast form. There were two major driving forces behind their development. The first was a need to develop stainless steels with equivalent corrosion resistance to the well known AISI Grade 316 but with better mechanical properties. The second was a requirement to conserve nickel which was in short supply, particularly in Japan, after the Korean War.

Historically the steels available to date were developed from the ACI alloy Cd4MCu which was itself pioneered by Fontana et al at Ohio State University in the late 50's. The modern grades of duplex steel differ from the original alloy in so far as a better understanding of the relationship between the austenite/ferrite phase balance and toughness has allowed materials to be produced which do not suffer from the disadvantages shown by their ancestor, particularly, unpredictable elongation and toughness values and quench cracking.

Although it would be proper, in any general review of the corrosion properties of stainless steels, to place the duplex alloys in the same category as CF3M (316L) the duplex alloys offer the pump designer specific advantages when the fluid under consideration is seawater. It is the object of this paper to point out some of the advantages of this type of alloy in respect of localised seawater corrosion, cavitation, corrosion erosion, and stress corrosion resistance. In addition some of the lessons learned over the last few years with respect to the foundry properties, heat treatment practice and weldability of the cast duplex stainless steels will be presented.

COMPOSITION

The compositions of the duplex stainless steels vary widely in terms of both major and minor elements. The core composition of most of the alloys available today is covered by the following (Wt%).

C	0.02	-	0.1
Cr	19	-	30
Ni	3	-	8
Mo	1.5	-	3
Si	1.0	-	max
Mn	2.0	-	max

The ratios of chromium and nickel are adjusted to give a two phase microstructure. Generally speaking chromium levels below 23% give poorer corrosion resistant properties, and in particular poorer pitting and crevice corrosion resistance in seawater. Chromium levels in excess of 28% are undesirable in casting alloys because of problems associated with sigma formation from the ferrite phase in thick section during cooling in the mould, or in extreme cases, during cooling from heat treatment.

Additions of copper, nitrogen and niobium are also made in some cases. Copper is added to improve corrosion performance in sulphuric acid service although at the expense of casting and welding properties. Nitrogen is an important alloy addition since it affects the phase balance, crevice and pitting performance in

seawater and mechanical strength. Niobium is added to stabilise the microstructure against chromium carbide precipitation and this, in turn, ensures freedom of weld decay. It remains questionable whether this addition is necessary since the higher chromium content of the duplex alloys relative to the 316 types renders them inherently less susceptible to sensitisation. Whilst copper and nitrogen may be added either separately or together care must be taken not to add niobium and nitrogen to the same melt since this leads to a problem in the cast duplex alloys analogous to 'rock candy' fracture in thick section carbon steel melts.

The composition favoured by the authors together with minimum mechanical properties are given in Table 1. A typical microstructure is shown in Figure 1.

TABLE 1

Typical Analysis for the Mather & Platt Duplex Stainless Steel Zeron 25

Element		C	Cr	Ni	Mo	Si	Mo	N_2
Typical Analysis	Wt%	0.04	24.5	6.50	0.95	0.61	2.05	0.16
Specification Range		0.06 max	24-26	5-8.5	1.5 max	1.0 max	2-3	0.12-0.20

	0.2% Proof Stress (M.Pa)	U.T.S. (M.Pa)	% El $5.65\sqrt{A}$
Minimum Room Temperature Mechanical Properties	400	630	18

The microstructure consists of a ferrite matrix within which are dispersed laths of austenite which have formed on grain boundaries and on particular close-packed planes in the ferrite during cooling from casting. The structure as presented, contains 65-70% austenite.

TENSILE PROPERTIES

With the exception of carbon and nitrogen the solid solution strengthening effect of the alloy elements added to the duplex steels over the extremes of the specification range are small. At constant carbon and nitrogen levels, the tensile properties of the duplex alloys depend largely on the austenite/ferrite ratio. Figure 2 shows the effects of the austenite ferrite phase balance on mechanical properties for alloys containing 0,04%C and 0,1% N_2. The specimens were cut from the centre of 150mm diameter cast and heat-treated billets. The rate of increase in yield strength and UTS value with ferrite content is similar to that obtained by Floreen and Hayden (1). The precise values differ slightly because the work of Floreen was carried out on wrought material containing very low nitrogen concentrations.

Whilst it is important to keep carbon levels down to eliminate hot tearing, forging and welding problems, nitrogen can be added in amounts up to the limit of solubility. The effect of nitrogen on mechanical properties is shown in Table 2. The effect of nitrogen on localised corrosion resistance and corrosion erosion will be discussed under the relevant headings.

TABLE 2

Effect of Nitrogen Content on the Mechanical Properties of Duplex Stainless Steels. Stress Values in MPa (1MPa = 145 psi). Both Alloys Solution Heat Treated at 1120°C Furnace Cooled to 1040°C and Water Quenched.

Element		C	Cr	Ni	Mn	Si	Mo	N_2
Alloy A	(Wt %)	0.03	23.8	9.15	0.56	0.59	2.20	0.08
Alloy B	(Wt %)	0.04	24.6	6.42	0.80	0.41	1.94	0.26

	%γ	0.2% Proof Stress	U.T.S.	Elongation
Alloy A	80	415	645	33
Alloy B	85	498	716	40

FOUNDRY PROPERTIES

In general the foundry properties of the copper free duplex stainless steels are good. The liquidus temperatures of the alloys vary between 1460 and 1480 degrees C and the solidification range is narrow. Risering and gating practices are similar to those employed in the production of CF3M (316L) type alloys. Hot tearing is not a particular problem. However, difficulties can arise resulting from cold cracking in the mould if careful attention to producing the optimum phase balance is not made. Figure 3 shows the variation in thick section impact strength with austenite content for alloys containing nominally 25Cr, 0.04C, 0,1N₂, 2Mo the phase balance was adjusted by varying the nickel content between 3 and 9%.

It is clear from Figure 3 that at high ferrite contents the alloys behave in a brittle manner irrespective of heat treatment condition. This is hardly surprising since large grain size, high interstitial content high alloy ferrite is known to fail by a brittle cleavage fracture mechanism. It is worth pointing out at this stage that the microstructure of the alloy Cd4MCu contains between 60 and 80% ferrite depending on the particular combination of alloy elements present. The high ferrite content of this alloy is most certainly responsible for reported instances of both quench cracking (2) and cold cracking occurring before 'knockout' at severe changes in section thickness.
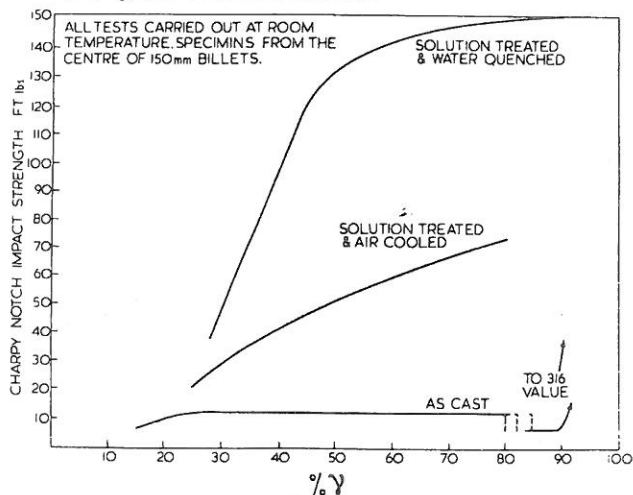

FIG. 3 - The effect of α / γ phase balance on the room temperature, thick section, toughness of duplex stainless steels in various heat treatment conditions. Charpy notch to ASTM A370 - 1977. Type A.

Toughness in the air-cooled and water quenched condition increases continuously with austenite content. The toughness in the water quenched condition peaks and levels out at about 45% γ. The effect of α / γ phase balance on air cooled, thick section toughness is further illustrated in Table 3. Also illustrated is the effect of α / γ phase balance on air-cooled localised corrosion resistance. The increased austenite content results in a generally "cleaner" microstructure containing fewer carbide and

carbonitride precipitates. This in turn renders the localised corrosion resistance of the alloy less sensitive to quenching rate. In the as-cast condition in thick section, the toughness remains low whilst there is any ferrite in the microstructure. A further dip, from an already low value occurs when the austenite content exceeds approx 85%. The poor as cast properties in alloys containing higher proportions of ferrite are due to a precipitation phenomenon occurring in the ferrite known as 475°C enbrittlement. The mechanism of this process is discussed briefly in the section on heat treatment. Air-cooling from solution heat treatment is sufficiently rapid to avoid precipitation at 475°C in sections with an effective diameter up to 200mm. However, slow cooling in the mould will nucleate precipitate particles.

The additional ductility dip at higher austenite contents results from sigma phase formation in the ferrite. Figure 4(a) shows the 1000°C isotherm through the system Fe Cr Ni. The position of the tie lines has been estimated. Knowledge of their exact positions is not essential since the diagram is used here only to illustrate a trend. It can be seen that in general as the ferrite content of the microstructure decreases with increasing nickel, chromium segregates more and more strongly to the ferrite. Figure 4(b) taken from the work of Shortsleeve and Nicholson[3] illustrate the effect of chromium content on the kinetics of sigma formation in ferrite. The results in this case were obtained for straight chromium steels and the temperatures and times may not be directly transferable to a 25Cr-5Ni duplex steel but nevertheless, it remains clear than an increase in chromium content from 24 to 33% produces roughly two orders of magnitude acceleration in sigma formation. Figure (c) shows the as-cast microstructure of an alloy containing approximately 85% austenite sectioned from the centre of a 150mm diameter cast billet. The interphase network of ferrite has transformed to a lamellar structure of sigma and austenite.

TABLE 3

Effect of α/γ Phase Balance on Air Cooled Toughness and Localised Seawater Corrosion Performance. Charpy Impact Tests (Standard Size) From Centre of 150mm diameter Cast Billet. Corrosion Specimens from 25mm Section Cast Bar (Tests to ASTM G48-76)

Element	C	Cr	Ni	Si	Mn	Mo	N_2
Alloy C	0.04	24.2	4.46	0.69	0.67	2.42	0.12
Alloy A	0.03	23.8	9.15	0.59	0.56	2.31	0.11

	% γ	AC Toughness (Ft. lbs)	Critical Crevice Temp. Air Cooled	Critical Crevice Temp. Water Qnch.	Critical Pitting Temperature Air Cooled	Critical Pitting Temperature Water Qnch.
Alloy C	35	30	18°C	30°C	39°C	49°C
Alloy A	80	90	28°C	32°C	52°C	52°C

The loss of toughness in as-cast thick section components due to 475°C embrittlement does not in itself result in embarrassment in the foundry. Experience has shown that arc-air gouging of defects or removal of risers can be carried out with the casting in the unheat-treated condition. However, sigma precipitation when present, occurs along the original ferrite boundaries and it can result in cracking at positions adjacent to welds and flame or plasma cut surfaces in large section castings if they are not firstly heat treated.

HEAT TREATMENT

The heat treatment cycle generally applied to the duplex stainless steels was developed originally for the alloy Cd4MCu(2). It consists of a solution treatment at 1120°C, furnace cooling to 1040°C followed by a water quench. Air cooling was generally thought unsuitable because of the risk of sigma formation. Experience with Zeron 25 duplex alloy has shown this fear to be groundless in cast sections at least up to 250mm diameter providing that the austenite content does not exceed 85%. Both 475°C embrittlement and sigma phase formation are considerably slower in coarse grained cast materials than they are in wrought products.

When reading proprietary literature dealing with the heat treatment of stainless alloys one often comes across the statement "thinner sections may be air-cooled, thicker sections should be water quenched". When considering large section complex geometry castings this general approach represents an over simplification of the position. The ability of a component to relieve elastic stress generated as a result of quenching by plastic deformation depends critically on the stress system generated during the cooling cycle. The stress system in turn is a strong function of casting geometry. Thus irrespective of the ductility shown by a material measured in a uniaxial tensile test, hydrostatic tensile stresses generated in susceptible geometry thick section castings can exceed the ultimate tensile strength of the material and lead to quench cracking. Generally speaking in the case of the duplex alloys it is necessary to air cool castings with sections thicker than 100mm unless they contain no severe changes in section and have a large measure of bi-axial symmetry.

In order to maintain toughness and localised seawater corrosion resistance in the air-cooled condition a minimum of 55% austenite should be present in the microstructure. High austenite contents allow 'cleaner' microstructures to be obtained after air cooling i.e. there is less tendency for precipitate particles such as CrN_2, $Cr_{23}C_6$ to nucleate from solution during air cooling. Table 3 illustrates the general effect of austenite/ferrite volume fraction ratio on toughness and corrosion performance.

Dimensional Stability

Dimensional instability in castings and forgings arises from two main sources;

(i) inappropriate design;

(ii) residual stresses.

Inappropriate Design. Pump designers have long had difficulties in working with 'soft' alloys such as CF3M, CF8M (316 types). These problems result from movement during machining, on and after hydrotest and in service. All materials are dimensionally unstable to some degree or other. The extent to which they are depends upon the shape of the stress strain curve, the thermomechanical history of the alloy and in extreme cases long term stability can be affected by solid state phase changes occurring at room temperature.

ASTM A744 gives the yield and ultimate tensile stresses for CF3M (316L) as 205 and 485 MPa respectively. The ASME Boiler and Pressure Vessel Code (Div VIII) allows for nominal working stresses equal to UTS/4 or 0.67 yield whichever is lower. Thus the nominal working stress for a component in this type of alloy is approximately 60% of the yield stress. Localised stresses around bolt holes or severe changes in section in a complicated casting are computed by multiplying the nominal stress by an appropriate stress concentration factor. It is clear from this simple model that only moderate stress concentration factors are required to produce yielding, and hence deformation in 316 type alloys. The foregoing discussion has of course neglected the effect of residual stresses which can be algebraically added to service stresses. These when present will clearly exacerbate design errors and can lead to movement in their own right.

Problems have been reported in the North Sea with shaft instabilities in multistage injection pumps. These problems arose because the duplex steel used in shaft manufacture was utilised in the 'as quenched' condition or at best, the shafts were heated to a temperature of approximately 300°C which will hardly produce any significant stress relief. High levels of residual stresses can lead to deformation in service when centrifugal stresses are added to residual stresses and yielding occurs.

Residual Stresses. The duplex stainless steels are one of only a few groups of materials 'called up' in the as 'water quenched' condition. Carbon maganese, low alloy constructional steels and martensitic stainless steels are used in the normalized or quenched and tempered condition. The tempering process, providing that it is followed by a slow cool, affords considerable stress relief. In thick section all materials used in the 'as quenched' condition will support residual stresses with values up to the yield stress.

In the general literature stress relief of the duplex stainless steels is often said to be impossible without risk of embrittlement. This statement has been justified on the basis that 475°C embrittlement of ferrite restricts the maximum temperature for stress relieval to 350°C. Figure 5 from the work of Solomon and Devine[4] shows the types of precipitates that can be produced in duplex stainless steels as a function of time and temperature. Embrittlement at 475°C occurs very much as it does in binary iron-chromium alloys [5,6,7,8]. It has been shown that the precipitates that result in 475°C embrittlement in binary alloys will dissolve if the alloy is heated to 520/545°C, the precise solvus temperature dependent on the chromium content. Solomon[4] considers that the behaviour of the duplex alloys is broadly similar to the binaries with the exception that the precipitates do not dissolve entirely, hence the dotted line marked ⟵ in Figure 5. Consideration of Figure 5 shows that if a duplex steel were heated to a temperature of 560 ± 30°C for a period of up to ten hours and subsequently air cooled through the 425/500°C region, stress relief should be achieved without significant loss of impact strength. Experience has shown this to be the case, the duplex alloy Zeron 25 shows impact values of 60 and 85ft/lbs after heat treatment for 6 hours at 560°C in the forged and cast conditions respectively. Solomon and Devine[4] carried out exhaustive tests to check the effect of aging at temperatures of 600°C on localised corrosion properties. No deleterious effects were reported. Direct measurements of internal stresses using the strain gauge stress relaxation technique has shown surface internal stresses to have been reduced from the yield stress (compressive) after quenching to less than 5% of this value after heat treatment at 560°C.

It is clear from this discussion that dimensional stability after machining or the application of service stresses will result from;

(i) Full stress relieval prior to final machining;

(ii) Good design avoiding the generation of localised stresses exceeding the yield.

Instability resulting from localised yielding will of course be reduced by utilising alloys with lower UTS/yield ratios of CF8M 2.36, Zeron 25 1.57, CA6NM (13% Cr martensitic steel) 1.37. The increasing use of finite element programs to more accurately determine stress levels in pump casings is certainly making design with the softer 316 type alloys more precise. The not uncommon sight of a 316 pump casing being alternately pressure cycled and machined in order to redistribute stresses and to strain harden regions of high stress concentration should become progressively more rare.

SEAWATER CORROSION PROPERTIES

General or Uniform Corrosion

The general corrosion rate of most of the stainless steels is perfectly adequate in seawater. Type 316 (18Cr-10Ni) austenitic stainless steel shows a corrosion rate of 0,0025mm per year at ambient temperature in quietly flowing seawater. However, with the less alloyed stainless steels i.e. 13Cr martensitics special measures, e.g. cathodic protection, are required if the alloys are to be used without failure in submerged conditions. In any general review of corrosion resistance the duplex stainless steels should be grouped with the 316 type alloys. However, the 25Cr-5Ni-N_2 alloys have far superior crevice and pitting properties.

Localised Corrosion

All alloys which rely on passivity for their corrosion resistance are susceptible to localised corrosion of one type or another. It is the invasion of the protective passive film by aggressive ions such as Cl or Br that results in pitting and the general breakdown of the film due to lack of oxygen that results in crevice corrosion. It is likely that once initiated both processes proceed by the same mechanism. The susceptibility of a stainless alloy to localised corrosion is a function of seawater flow rate, depth, alloy composition, surface condition and temperature. A high flow rate of seawater brings passivating oxygen to the surface rapidly and promotes the repair of breaks in the film. High velocities also keep the surface free of biofouling, the presence of which produces quiet backwaters where oxygen diffusion is limited. Increasing temperature seriously lowers the resistance of alloys to both pitting and crevice corrosion. The effect is very marked and is used to rank materials as far as localised corrosion performance is concerned.

Figure 6 shows the effect of alloy composition on the critical crevicing temperature for both austenitic and ferritic stainless steels. The results were obtained using the standard ASTM G48-76 10% ferric chloride test. This solution is used as an accelerated test for seawater crevice corrosion resistance, artificial crevices are used to simulate surface conditions. Typical configurations include sand or debris piled on sheet metal, rubber bands wrapped around cylinders, partially immersed specimen threaded bolts etc.. Generally it can be seen that crevicing behaviour is controlled by chromium and molybdenum. In this respect the 29Cr-4Mo extra low interstitial ferritic steels have the advantage over the highly alloy austenitics since these rarely contain more than 20% chromium. It can be seen from Figure 6 that on the basis of this model the duplex 25Cr steels behave as if they were fully ferritic. The position of the duplex alloys on a plot of this type depends to a large extent on the nitrogen content of the alloy. The effect is further illustrated in Table 4. The effect of nitrogen on critical crevicing temperature is marked and presumably results from the interstitial substitution of nitrogen atoms in the corrosion product film which in turn results in a decrease in ionic and electronic conductivity.

TABLE 4

Effect of N_2 Content on the Critical Crevicing and Pitting Temperature of a Duplex 25Cr-5Ni Alloy. Ferric Chloride (ASTM) (G48-76) Test.

Element	C	Cr	Ni	Si	Mn	Mo	N_2
Alloy D	0.04	25.4	5.65	0.92	0.81	2.05	0.26
Alloy E	0.04	25.1	5.23	1.02	0.79	2.20	0.08

	Critical Pitting Temperature °	Critical Crevicing Temperature °
Alloy D	61	51
Alloy E	52	32

Waterflood Enhancement

It is now common practice to use seawater injection to prolong the productive life of oil wells. Water is pumped into the reservoir at a controlled rate towards producing wells. A good waterflood technique can provide enough energy to produce roughly twice the volume of oil recovered by natural processes. The selection of stainless steels for water injection must take account of various water treatment processes which may consist of dosing with;

(i) Oxygen scavengers e.g. sodium bisulphite, ammonium bisulphite;

(ii) Corrosion inhibitors e.g. chromates nitrites;

(iii) Biocides e.g. chlorine injection or the addition of chlorine bearing chemicals such as hypochlorites.

In addition there is an increasing tendency for oil companies to re-inject formation water with a minimum amount of treatment. This means that as the life of the well increases the corrosivity of the injected water increases as a result of;

(i) Increasing temperature;

(ii) Salt concentration up to 30%;

(iii) H_2S concentration up to 500 ppm;

(iv) CO^2 concentrations up to 2000 ppm.

There has been little systematic work carried out with respect to the effect of water treatment agents on corrosion resistance of stainless steels. However, in experiments in which chlorine gas was bubbled through a seawater solution for one hour in every twenty-four alloys such as 316, Incoloy 600 and 825, Carpenter 20 etc., pitted at room temperature. The duplex 25Cr-5Ni alloys were resistant up to 35°C (the nitrogen content of the duplex alloy was not reported). Nickel alloys, unable to resist oxidising environments, such as Monel suffered uniform general corrosion. The same authors examined the effect of a 0.2% NH_4^+ addition (as NH_4Cl) the effect was similar although less dramatic than chlorine injection.

Hydrogen sulphide generally accelerates pitting attack particularly at elevated temperatures and in the presence of oxygen. It has a particularly severe effect on the pitting potential of 316 type alloys (10) reducing it from -100mV SCE at zero concentration to -400mV (SEC) at a concentration of 300 ppm at 200°C. It has been shown that H_2S concentrations of up to 300 ppm in brine solutions containing up to 30% NaCl have little effect on the pitting potential of the nitrogen bearing 25Cr-5Ni duplex alloys.

Stress Corrosion

The duplex steels occupy a unique position within the stainless group of alloys in respect of their excellent resistance to both chloride and hydrogen corrosion. The austenitic alloys suffer from chloride stress corrosion at temperatures above 70°C. The ferritic stainless steels are susceptible to hydrogen sulphide stress corrosion. The martensitic alloys unless specially heat treated are susceptible to both types of stress corrosion. Two representative alloys from the duplex stainless steel group have been proved to be acceptable for sour service at hardness values less than 28Rc (11). Middle East Offshore and shoreline injection installations provide very difficult environments from the point of view of stress corrosion. Chloride cracking of 316 type alloys occurs from the outside as a result of the salt laden atmosphere whilst hydrogen cracking of martensitic alloys occurs as a result of pumping sour oil.

There is an increasing trend in the pump industry towards smaller pumps operating at very high speeds. This, in turn, leads naturally to higher relative fluid velocities. Under these conditions erosion-corrosion of impeller and diffuser tips and volute tongues must be given careful consideration. Corrosion erosion is a vague term and requires some definition before it can be usefully discussed. Among the many mechanisms involved the main velocity related factors resulting in damage can be categorised as follows:

(i) Particle erosion: damage to a metallic surface resulting from absorption of the kinetic energy of particles carried in a moving stream of liquid;

(ii) Cavitation erosion: damage caused by the collapse of cavities in the liquid. Cavities formed in regions of low pressure at areas of flow divergence rotation or vibration, collapse rapidly producing a very high acceleration of the cavity envelope. When the walls of the cavity collide a strong shock wave is generated which damages adjacent materials;

(iii) Liquid Impingement: Erosion damage occurs as a result of;

(a) high pressure generated at the point of impact and;
(b) radial flow along the surface from the point of impact as the initial pulse subsides:

(iv) Accelerated Electrochemical Effects: as velocity and turbulence increase the protective corrosion film is removed, usually at some critical velocity. The exposed area corrodes in the active state and metal loss is accelerated by the unfavourable cathode/anode surface area ratio and the fact that the cathodic reactant, usually dissolved oxygen, is delivered to the active area by mass transport.

Particle erosion, cavitation and impingement erosion mechanisms can proceed without corrosion being pre-requisite. These mechanisms produce mechanical rather than chemical damage. It has been shown (12) in experiments usng jet impingement techniques that materials rank for resistance to impingement in the same order as they do for cavitation resistance using a standard magneto-strictive method. The implication being that damage is produced by the same mechanism in both processes.

Much work has been carried out aimed at the correlation of cavitation performance with material properties. Various parameters such as hardness, true strain at fracture, surface work hardening rates have been used. None has been wholly successful. In some instances work hardening can increase erosion resistance. However, surface work hardening can be a prelude to loss of material by fatigue or fracture. The same comments are true if the bulk hardness of martensitic steels, for example, is increased at the expense of ductility. It would appear therefore, that in the absence of corrosion cavitation erosion resistance is improved with increasing hardness providing there is no accompanying serious loss in ductility.

So far, we have taken no account of corrosion, to take an extreme example electro chemical effects would clearly be of paramount importance in selecting materials for pumping nitric acid. A whole spectrum of conditions exists, at one end of the spectrum where the solution to be pumped is non aggressive to the material under consideration, damage from 'corrosion erosion' is likely to be predominantly mechanical, and factors which improve cavitation and impingement erosion resistance

such as increasing hardness, surface fatigue properites etc., will improve performance. At the opposite end of the spectrum inherent corrosion resistance will be the over-riding consideration for material selection.

High speed seawater pumps will unfortunately 'see' all sub-categories of the erosion corrosion process. The 25Cr-5Ni steels have much improved mechanical properties relative to the 316 type alloys and consequently we would expect to see a substantial improvement in cavitation and, by implication, impingement erosion. Table 5, compares the cavitation erosion resistance, in seawater, of the 25Cr-5Ni duplex steels with the well used stainless steels CF8M (18Cr-10Ni-3Mo) and the martensitic steel CA6NM (13Cr-4Ni). The comparatively poor performance of CA6NM, relative to its strength and hardness reflects the fact that seawater is aggressive to the 13Cr steels.

TABLE 5

A comparison of Cavitation Erosion Performance in Seawater with Mechanical Properties for Three Stainless Steels. Weight loss in Mg/Decimeter^2/day. Stress Values in MPa (1MPa = 145 psi). Cavitation Conditions; Magnetostrictive Test Frequency 20 kHz, Power 350 Watt Amplitude 0.03mm Gap 0.25mm

	0.2% Proof Stress	U.T.S.	Elong %	Cavitation Rate
ASTM A743 CA6NM	550	755	15	8,808
ASTM A744 CF8M	205	485	30	15,400
ZERON 25	400	630	30	2,640

There has been little information published in the literature that considers the effect of seawater flow rate on the corrosion performance of material at velocities above 10 meters per second. The work that has been published (13-16) has been carried out by Marine Engineers interested in materials selection for the construction of hydrofoil craft. Unfortunately little or no attempt has been made when carrying out this work to seperate the effects of cavitation and liquid impingement erosion from the purely electro chemical effects and hence any ranking produced may be misleading.

In order to provide reliable data for pump designers a test rig has been designed and commissioned which allows metallic specimens, in the form of impellers, to be rotated at speeds sufficient to generate relative fluid velocities of 100m sec⁻¹. Suction pressures can be varied from a few kPa up to 5000 kPa. Preliminary results comparing the various grades of stainless steels in sweet seawater indicate a strong correlation between localised corrosion resistance and the critical velocity for passive film detachment. Trials are in hand aimed at a comparison in performance of the nitrogen containing and nitrogen free duplex stainless steels. In view of the marked influence of nitrogen on crevice and pitting performance we should expect better results from the higher nitrogen alloys. Initial results suggest that this is the case. Table 6 gives some typical results for a series of steels tested at a relative velocity of 85m sec⁻¹.

TABLE 6

Relative Corrosion Rates of Some Representative Alloys, in Seawater, at Relative Fluid Velocities of 85m sec⁻¹. Temperature (65°C). All Materials in Standard Heat Treatment Condition. Specimens in the Form of Pump Impellers, with Velocity Gradient from Tip to Hub. Tip Velocity Quoted, All Impellers Identical.

Material	Weight Loss mg/hr/unit Surface Area
ASTM A216 WCB (Carbon Steel)	45
ASTM A743 CA6NM	0.75
ASTM A744 CF8M	0.15
Zeron 25	No measureable loss

WELDABILITY

Generally speaking the weldability of the copper free duplex steels is very good. Their high chromium content together with low carbon level renders them virtually immune to sensitisation.

Weld repair is an essential tool in any foundry producing large complex castings in any material. Elements that segregate strongly during solidification either in the mould or during welding, such as copper, should be avoided if possible. Matching composition consumables are available for SMAW and GMAW welding of the duplex steels. These consumables when used properly give properties in weldments which compare favourably in terms of mechanical strength and corrosion resistance with the parent materials. Thin section castings can be welded in the 'as cast' condition. Larger section castings should be heat treated to remove any sigma phase that may have formed during cooling from casting. The maintenance of a high austenite/ferrite phase balance is an important factor in avoiding intergranular corrosion and possible HAZ toughness problems in so far as a properly balanced alloy will avoid the formation of fully ferritic areas in the parent metal heat affected zone. This problem is not so important if heat treatment after welding is possible. However, the possible presence of fully ferritic zones in the HAZ of 'as welded' thick section joints in steels with high ferrite/austenite phase ratios should not be ruled out.

Most sources in the literature recommend that no pre-heat be used when welding duplex steels. In addition it is recommended that weld metal should be deposited utilizing the stringer bead technique with small diameter rods. Both these factors seek to keep interpass temperatures low to avoid 475°C embrittlement of ferrite. It is possible to speculate however, that it is unwise to eliminate pre-heat entirely since it has been suggested that very highly alloyed ferrites may be susceptible to hydrogen embrittlement. No unequivical evidence in support of this has been found in the foundry although it is our practice to pre-heat welds to 100°C as a matter of routine. Cracking problems associated with pipework fabrications in duplex steels have been solved by the application of pre-heat (17). The evidence for hydrogen cracking is in a sense circumstantial but, it should not be ignored entirely.

SUMMARY

The duplex stainless steels possess a combination of mechanical and corrosion resistant properties that makes them ideally suited to the production of brine injection pumps.

In order to extract the best performance from the alloys the role and relative importance of the alloy additions must be fully appreciated. In so far as localised seawater corrosion performance is concerned, chromium, molybdenum and nitrogen have the most significant effect. Copper plays a neutral role and can be eliminated from the composition without loss. The importance of the austenite-ferrite phase balance cannot be over-stressed. High ferrite contents should be avoided since they can lead to;

(i) Susceptibility to quench cracking;

(ii) Poor air-cooled thick section toughness;

(iii) Reduced air-cooled localised corrosion resistance;

(iv) Poorer weldability.

Very high austenite contents ($\geqslant$85%) will increase the tendency for sigma formation in the mould in very thick section castings. High austenite contents will ultimately lead to sigma formation during cooling from heat treatment as the section thickness increases to 250mm and beyond. It is clear therefore that the austenite/ferrite ratio should be optimised.

The heat treatment of the duplex alloys is clearly of prime importance. The significance of full stress relief in respect of dimensional stability in service has been pointed out. The use of a 560°C soak followed by a moderate cooling rate to room temperature is not in general use. It will hopefully become more common.

New materials present a challenge to both the designer and the fabricator. The duplex stainless steels present a challenge to the Metallurgist and the Foundryman. The number and variety of phase changes occurring in these materials over the whole temperature range is daunting. It would be inadvisable for a foundry to attempt to produce large section castings in a duplex alloy without an appreciation of the metallurgy of the material. Having said this the rewards for perseverance are great. The duplex alloys have the strength of martensitic steels and a corrosion performance in seawater approaching that of the Hasteloysall for the price of 316.

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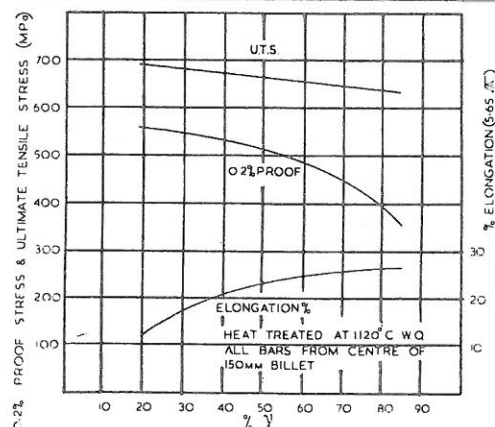FIG. 1 - Microstructure of Cast and Heat Treated Zeron 25. Magnification X80

FIG. 2 - The effect of $\propto$ / γ phase balance on the room temperature thick section tensile, properties of the duplex stainless steels.
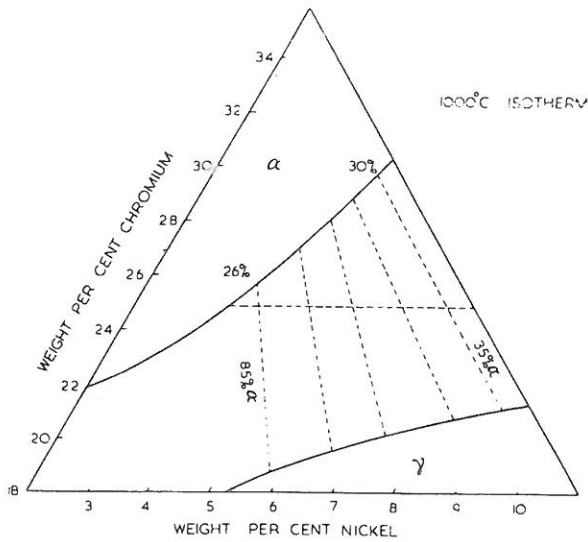
FIG. 4(a) – Isothermal section through the FeCrNi diagram at 1000°C
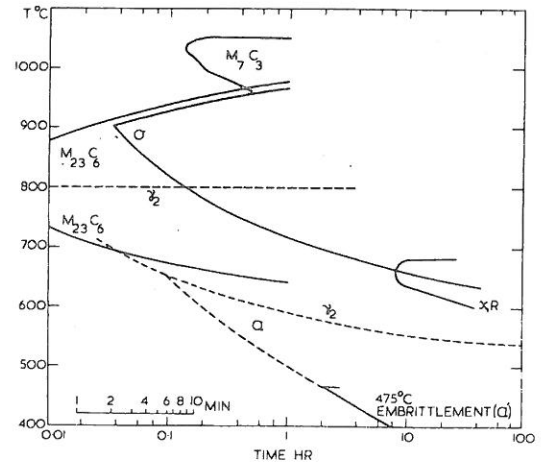

FIG. 5 – Phase transformations in duplex stainless steels. After Solomon and Devine (4).
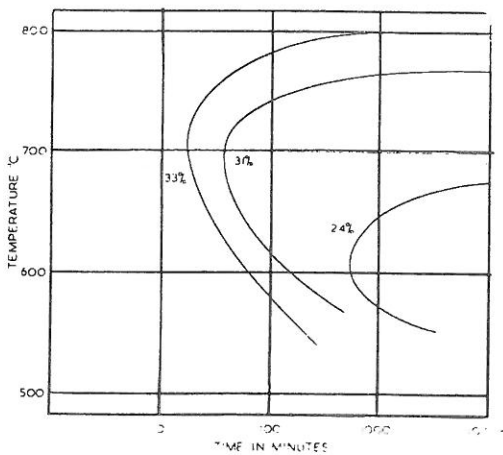

FIG. 4(b) – The effect of chromium content on the kinetics of sigma formation in wholly ferritic steels. After Shortsleeve and Nicholson (3)
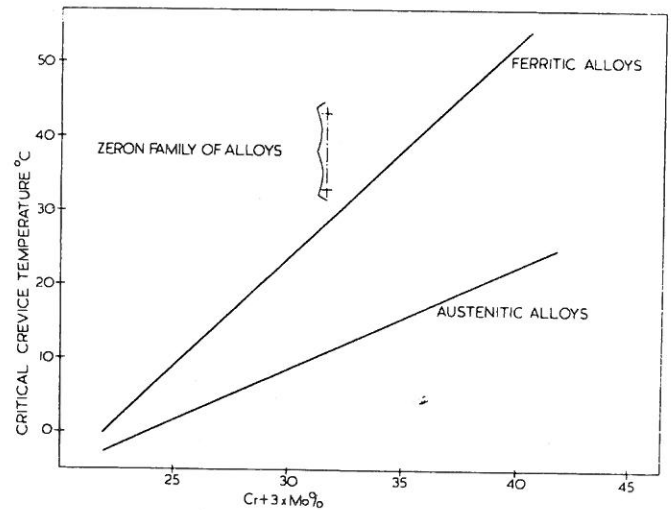

FIG. 6 – Relationship between composition and critical crevicing temperature, in 10% Ferric Chloride, for austenitic, ferritic and duplex steels. The range shown for the 25Cr-5Ni alloys includes the effect of nitrogen.
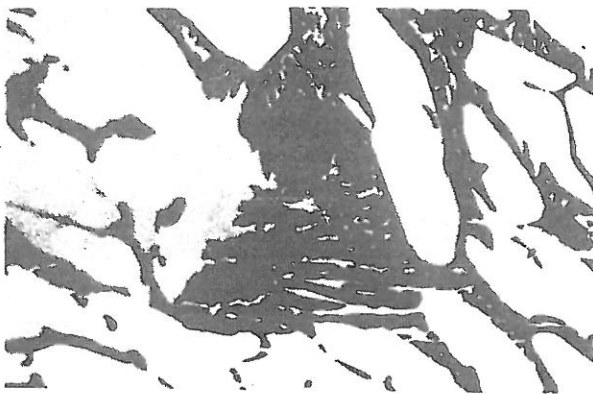

FIG. 4(c) – Sigma formation in thick section high austenitic castng (As cast condition) Magnification X250.