MATERIALS FOR SEAWATER AND

PRODUCED WATER SERVICE ENVIRONMENTS

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A B S T R A C T

In recent years there has been considerable development in stainless steel technology at Mather & Platt Ltd, which has resulted in the introduction of new grades of super-austenitic and super-duplex stainless steels. This paper summarises some of the experience gained at Mather & Platt Ltd, during the production of large complex castings and forgings in the new generation of stainless steels. The advantages of the duplex categories of stainless steels compared to the austenitic stainless steels in respect of their mechanical properties, foundry characteristics, weldability, localised corrosion resistance, stress corrosion cracking resistance and corrosion-erosion/cavitation resistance are discussed relative to injection pump applications. The relationship between microstructure and properties is shown to be paramount. The importance of microstructural control in the avoidance of casting and welding problems is also emphasised.

INTRODUCTION.

Offshore oil production now accounts for a significant share of the current total oil production and the accelerated development in offshore technology is certain to encourage further exploitation. This rapidly expanding market is providing an interesting challenge to pump manufacturers throughout the world, particularly in respect of the materials utilised in the manufacture of the high technology water injection pumps. Indeed Mather and Platt Ltd. have found it necessary to continuously develop new materials which are capable of satisfying the increasingly stringent demands of the oil exploration industry.

The two categories of stainless steels which are most frequently under consideration when the fluid media to be pumped is either sea water or produced water are the highly alloyed austenitic stainless steels" and the duplex ferritic-austenitic stainless steels. Historically the austenitic stainless steels have represented the largest proportion of the worlds consumption, whereas the duplex stainless steels up until fairly recently have been limited to specialist applications. The Standard grades of austenitic stainless steel in common use in the 300 series have been in existence for many years but their usefulness is limited by their relatively low strength properties and poor localised corrosion performance.

Indirect contrast the standard duplex stainless steel offer several advantages when compared to conventional austenitic stainless steels and some of these are listed below: [1-5]

(1) Proof strengths are substantially higher than those of austenitic types while still retaining excellent levels of toughness;

(2) the contents of those elements giving improved resistance to pitting and crevice corrosion may be increased without undue increase in nickel content;

(3) an attractive balance between resistance to pitting in chloride solutions and general corrosion in acids is attainable in one alloy;

(4) resistance to sensitisation during welding is good even without stabilisation;

(5) Resistance to chloride stress corrosion cracking is better than that of the austenitic grades.

Notwithstanding these comments, the exhaustion of existing oil and gas deposits has lead to exploration in increasingly harsh elevated temperature environments containing significant quantities of chlorides, CO_2 and H_2S .

However, important new developments have occurred at Mather and Platt Limited in recent years resulting in the introduction of steels with improved combinations of strength and general corrosion resistance, plus vastly improved localised corrosion resistance in hot sea water and produced water environments. The most important of these has been the use of nitrogen additions of typically 0.2 - 0.3 Wt% and high molybdenum levels to produce super-austenitic and super-duplex stainless steels with combinations of higher proof and tensile strengths without loss of ductility, improved pitting and crevice corrosion resistance, good wear resistance and good toughness at sub zero temperatures.

In selecting suitable materials for the manufacture of water injection pumps it is necessary to take cognisance of the many material characteristics which can ultimately decide the optimum engineering solution. Parameters such as the mechanical properties, foundry characteristics, heat treatment, weldability, general and localised corrosion, stress corrosion cracking resistance, cavitation and corrosion-erosion all figure prominently in the pump technologist's mind when considering the suitability of a material for a particular application. The ensuing discussion will therefore compare the performance of certain austenitic and duplex stainless steel alloys in the context of these parameters.

MECHANICAL PROPERTIES

The chemical compositions of the alloys under consideration are given in Table 1a, along with their respective mechanical properties (Table 1b) in both the wrought and cast conditions. The relationship between the properties of wrought and cast duplex stainless steels and the properties of the individual ferrite and austenite phases has been investigated previously [6-7]. It has been confirmed that the mechanical properties of a ferritic-austenitic duplex stainless steel reflect the properties of the individual phases. Solution annealed austenitic stainless steels generally exhibit lower yield strengths than ferritic stainless steels. Not surprisingly therefore, the presence of ferrite in a duplex stainless steel increases the yield strength of the alloy. The yield strength of the duplex stainless steel is closer to the ferrite yield strength than a simple rule of mixtures would predict in view of the finer grain size of the duplex structure compared to the single phase structure. Other reasons for the proof strength enhancement of duplex steels have been discussed previously [8] and include solution hardening of the austenite phase due to enrichment of carbon and nitrogen arising from elemental partitioning, a fibre strengthening effect and dislocations generated during thermal cycling due to the different coefficients of expansion of the two phases. Furthermore, there is a solid solution hardening effect notably in the ferrite, by substitutional elements due to the composition balancing necessary to give a higher ferrite content. Conversely, the ultimate tensile strength is marginally reduced as the volume fraction of ferrite in a duplex stainless steel is increased. This is in view of the constraint of the ferrite phase which reduces the work hardening rate of the austenite phase. The ductility of duplex steels is generally less than austenitic stainless steels. There is a reduction in ductility with increasing ferrite content and decreasing temperature which prevents the alloy from work hardening to as high an ultimate tensile strength as would have occurred if cleavage fracture had not intervened.

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The development of cleavage fractures in the ferrite phase also marginally reduces the toughness of duplex steels, particularly in the high ferrite containing steels. Nothwithstanding this comment it is observed that the impact strengths of Zeron 25 and Zeron 100 are excellent (Table 1b) primarily due to the crack arresting properties of the austenite although the introduction of nickel into the ferrite also improves toughness [9]. From the foregoing it can be deduced that austenitic stainless steels possess inferior strength properties to the duplex stainless steels even in the case of nitrogen strengthened highly alloyed super-austenitic grades such as Zetium 55. Therefore, since the ASME Boiler and Pressure Vessel Code Div, VIII only allows for nominal working stresses equal to UTS/4 or 0.67 of the yield stress whichever is the lower, significant weight savings can be made by utilising duplex stainless steels in preference to the austenitic grades. This can be demonstrated more clearly by projecting the barrel casing weights of a typical radially split shear ring construction design of injection pump, of the type shown in Figure 1. A comparison of the 'Ekofisk' injection pump barrel casing weights for the alloys being discussed in this paper is shown in Table 2. From these results it is clear that significant reductions in weight can also be gained by utilising forged barrel casings instead of centrifugally cast casings primarily because of the following factors :

(1) In the Pressure Vessel Code the centrifugally cast components have to take account of a design criterion which multiplies the maximum permissible stress by a factor of 0.95.

(2) The minimum mechanical properties of the forged barrel casings are inevitably greater than the respective cast properties and thus the weight savings are even more significant.

FOUNDRY CHARACTERISTICS.

In general, the foundry characteristics of duplex stainless steels are extremely good. The liquidus temperatures of the alloys is approximately 1480°C and the solidification range is narrow. Risering and gating practices are similar to those employed in the production of 316L type alloys although hot tearing is not a problem. In contrast fully austenitic alloys suffer from solidification cracking. The hot cracking results from the rupture of liquid films separating already solidified materials or the rupture of isolated solid bridges [10]. Cracking is promoted when there is a large temperature range over which freezing occurs, since this extends the time over which the liquid films or isolated solid bridges exist. Solutes which are rejected into the liquid during solidification and depress the melting point will act to expand the freezing temperature range and thus promote hot cracking [10-15]. Sulphur, phosphorus, boron, arsenic, antimony and tin can all act to promote hot cracking whereas manganese and oxygen retard hot cracking perhaps through their action in tying up the elements which accentuate the hot cracking phemomenon or in altering the surface tension which influences the nature of any liquid film which is present [16].

It has long been known that the presence of some ferrite at the solidification temperature is required to suppress solidification cracking in austenitic stainless steel [17] and an intimate understanding of the chromium and nickel equivalents is required to ensure that 5-10% of ferrite will be present in the 'as cast' microstructure. The presence of the ferrite inhibits grain growth and increases the amount of grain boundary area, thereby giving more area over which to distribute the harmful impurities. The presence of ferrite also helps to reduce the shrinkage stresses because of its smaller coefficient of thermal expansion greater thermal conductivity and lower high temperature strength and in this way, can also reduce the tendency for hot cracking. It is likely that it is not just the amount of ferrite that suppresses hot cracking but also the nature of the solidification, ie. whether the ferrite or austenite

precipitates firstly from the liquid, especially when one considers that sulphur and phosphorus segregate preferentially to the ferrite rather than the austenite.

In addition to the problems of hot cracking, the highly alloyed super-austenitic stainless steels can suffer from cold cracking in the mould, a phenomenon which is sometimes referred to as "chicken wire cracking" or grain boundary craze cracking.

This can occur in medium and large section thickness castings and is due to the precipitation of chromium and molybdenum rich phases such as the Chi, Laves and sigma phases which can form at the austenite/ferrite and austenite/austenite grain boundaries. These phases tend to grow in various morphologies and form brittle films at the grain boundaries. Consequently, any large stresses which develop during the cooling processes or thermal stresses applied subsequently, for example during the removal of risers from castings, can result in spontaneous craze cracking along the grain boundaries and lead to the scrapping of castings. This phenomenon is analogous to the process that occurs in duplex alloys when under similar circumstances the sigma phase precipitates at the ferrite/austenite phase boundaries. It should be emphasised however, that Mather and Platt Limited have developed foundry expertise to overcome these problems in both the highly alloyed austenitic and duplex stainless steels categories.

SOLUTION HEAT TREATMENT

It is necessary to solution heat treat castings in super-austenitic stainless steels at a minimum of $1150^\circ C$ followed by a rapid water quench. The temperature must be sufficiently high and the heat treatment time long enough to minimise the chromium and molybdenum micro-segregation that is prevalent in the microstructure of these steels owing to the generally slower diffusion which occurs in fully austenitic alloys. Furthermore, care should be exercised to ensure that the intermetallic and carbide/nitride phases which precipitate in the microstructure during cooling in the mould are taken into solution and prevented from being re-precipitated.

Alternatively if the solution heat treatment temperature is too high, excessive scaling can result and this can lead to problems in respect of the water passage ways of impellers and of horizontally split casing pumps which cannot be subsequently dressed or machined. This statement can only be fully appreciated if one considers the intricacy of a typical multi stage horizontally split casing pump as shown in figure 2.

Regarding the duplex alloys, a considerable amount of fine tuning of the solution treatment temperature has been achieved over the many years of producing these alloys. The practice of solution heat treating at $1120^{\circ}C$ furnace cooling to $1040^{\circ}C$ followed by a water quench, which was originally suggested by Fontana and Beck [18,19] to supersede the air cooling techniques originally employed for duplex stainless, is not undertaken these days. This is in view of the possibility of precipitating M_7C_3 or the sigma phase in the region of $1000-1050^{\circ}C$ which will adversely affect the localised corrosion performance and mechanical properties of the duplex alloys. Nowadays the solution heat treatment temperatures adopted in respect of Zeron 25 and Zeron 100 are specified to ensure that the correct microstructural phase balance is achieved, which in turn, is predetermined by closely controlling the chromium and nickel equivalents in terms of empirical relationships.

Furthermore, a considerable amount of energy dispersive X-ray microanalyses and physical metallurgical studies [20-23] have focussed on heat treatment temperature regions for these alloys where the partitioning of elements between the austenite and ferrite phases is at a minimum. Therefore the kinetics of phases such as the sigma, $M_{23}C_6$, M_2X and α' phases have been retarded, which is particularly important in thick section castings, and thus the corrosion performance and mechanical properties of these alloys have been optimised. Suffice it to say that all section thicknesses of these duplex alloys are rapidly water quenched to ensure that no deleterious phases precipitate during cooling.

WELDABILITY

The use of welding for fabrication in such instances as welding nozzles onto pump barrel casings (figure 1) can greatly modify the structure and properties of duplex and highly alloyed austenitic stainless steels if the welding parameters are not accurately controlled [24,25].

It is pre-requisite before any decision is made relative to the welding of the alloy for any technologist to thoroughly understand the possible phase transformations which can occur whether related to the minor repairs of castings or the fabrication of nozzles, where weld metal thicknesses can approach 80mm as in the case of the 'Ekofisk' pumps. Indeed the necessity to control phase transformation on welding to obtain good weldability can significantly change the design of commercial alloys. It is well known that single phase ferritic steels are particularly sensitive to hydrogen embrittlement in the heat affected zone (HAZ) of the parent material where lattice imperfections and precipitated carbides/nitrides can form trapping sites for hydrogen [26]. Single phase austenitic steels on the other hand have been shown to be susceptible to hot cracking in the weld and parent metal. Stabilising elements such as titanium or niobium and impurities such as sulphur and phosphorus accentuate this problem. It is also known that small amounts of ferrite can reduce the tendency for hot cracking as reported previously. Furthermore, if the welding parameters such as pre-heat temperature, interpass temperature, rate of cooling, post weld heat treatment, heat input and welding consumable composition are not accurately selected and controlled for super-austenitic alloys like Zetium 55 and duplex alloys such as Zeron 25 and Zeron 100, then it is possible to precipitate intermetallic and carbide/nitride phases in the HAZ with a resultant loss of mechanical and corrosion properties. However, if the welding operation is controlled properly the duplex weldment possesses toughness and corrosion resistance from the presence of the austenite phase, whilst the ferrite will impart good strength and resistance to SCC. Combining the austenite and ferrite phases in a duplex structure improves weldability above that of

single phase stainless steels. The austenite having a higher solubility for hydrogen acts as a 'sink' thus reducing the likelihood of cracking in the heat affected zone at low temperatures and the presence of ferrite reduces any tendancy for hot cracking of weld metal.

Furthermore, duplex stainless steels are more resistant to weld decay than austenitic stainless steels since the chromium depleted zone, which occurs if $M_{23}C_6$ were to precipitate, is extremely narrow. Therefore it is quickly replenished with chromium by diffusion from the interior of the austenite grains. This results in rapid healing of the sensitised microstructure. Indeed since the maximum carbon level permissible in Zeron 100 is 0.03 wt% the resistance to sensitisation is even greater owing to the low propensity of $M_{23}C_6$ precipitation. Notwithstanding these comments a strict control of the microstructure is an absolute necessity to obtaining good weldability in duplex stainless steels and as already indicated there have been several investigations to study the effect of the weld metal and HAZ microstructure on the mechanical and corrosion properties [24, 26, 27-32].

Frequently in welding it is thought desirable to match the composition of the consumables with that of the parent metal in order to maintain the properties of the joint relative to those of the parent material. However it is often found that consumables with higher nickel and or nitrogen levels are recommended for welding duplex stainless steels [6, 27, 28] to ensure that the austenite/ferrite ratio is the same in the weld metal as that found in the parent material, thereby matching the properties of the parent material. Consequently Mather and Platt Ltd. in co-operation with Metrode have developed consumables for their proprietary duplex alloys which give the same volume fractions of austenite in the weld metal as in the parent material and these give virtually the same impact toughness in the weld metal and HAZ as in the parent metal. Furthermore, localised corrosion tests have shown that the HAZ and weld material display the same corrosion resistance as the parent material.

In respect of the highly alloyed austenitic stainless steels, the matching composition consumables utilised for welding alloys such as Zetium 55 can give marginally inferior localised corrosion performances and mechanical properties if retained in the as welded condition owing to the molybdenum microsegregation which results during solidification and the precipitation of intermetallic phases in the HAZ as previously reported. However, provided the welded components are subsequently solution heat treated at a minimum of $1150^{\circ}C$ and then water quenched, the localised corrosion performance and impact properties are restored. If it is not possible to carry out a post weld heat treatment operation then over-alloyed nickel base alloy consumables containing approximately 9 wt% of molybdenum, (ie E Ni Cr Mo-3) have to be utilised to ensure that the localised corrosion performance and mechanical properties of the weld metal and HAZ are not inferior to that of the parent materials. However, it should be highlighted that minor amounts of second phase intermetallics, carbides and nitride phases have been reported to precipitate in the interdendritic regions of highly alloyed austenitic structures [25]. Notwithstanding this comment the localised corrosion and impact toughness results in respect of Zetium 55, using overalloyed rods, are extremely good.

CORROSION PROPERTIES.

General and Localised Corrosion.

The general corrosion rate of the majority of austenitic and duplex stainless steels is extremely good in sea water and in a variety of produced waters. However, since stainless steels rely on passivity for their corrosion resistance they are susceptible to localised corrosion. It is the invasion of the protective passive film by aggressive ions such as Cl^{-} which results in pitting and the general breakdown of the film due to oxygen starvation that results in crevice corrosion. It is likely that once initiated both processes proceed by similar mechanisms. In the case of commercially produced highly alloyed austenitic and duplex stainless steels a large number

of metallurgical factors can have a significant influence on passivity. Alloying elements in the solid solution, various phases which can precipitate if certain parameters are not properly controlled giving rise to chromium and molybdenum depleted zones around the precipitates and manganese sulphide inclusions can all have a profound influence on the maintenance and breakdown of passivity. A detailed examination of how certain alloying elements affect passivity has been discussed elsewhere [33]. However, reference to the anodic polarisation curve shown in figure 3 schematically summarises the effect of certain alloying elements in enhancing the passivity of stainless steels. It is evident from studying figure 3 that a number of elements in stainless steel move the pitting potential in the noble direction, expand the passive potential range and reduce the passive current density. These beneficial effects are complex and interactive and attempts have been made to use compositionally derived empirical relationships for pitting resistance indices. (PRE Pitting Resistance Equivalent). The general formulae for non-nitrogen and nitrogen containing stainless steels respectively are shown below :-

$$PRE = \% \ Cr + 3.3\% \ Mo.$$
$$PRE^N = \% \ Cr + 3.3\% \ Mo + 16\% \ N$$

It is generally regarded that PRE values of ≥ 35 are necessary to determine whether an alloy will display good pitting performance in low-medium temperature sea water whereas PRE values > 40 are necessary in respect of hot sea water. In addition to the factors already discussed, the susceptibility of stainless steels to localised corrosion is a function of, water flow rate, depth, surface condition and temperature. A high flow rate of sea water brings passivating oxygen to the surface rapidly and promotes the healing of the film. High velocities also keep the surface free of biofouling, since these stagnant conditions limit oxygen diffusion and enhance localised corrosion. Increasing temperature seriously lowers the resistance of alloys to both pitting and crevice corrosion, the former of which has been demonstrated in figure 4. The results displayed have been obtained using a potentiostatic

polarisation technique originally devised by Wilde [34] which can be utilised to obtain quantitative results in respect of both pitting and crevice corrosion. Reference to figure 4 shows plots of critical pitting potential versus temperature for the materials under consideration. From these results it can be deduced that the wrought alloys display a better localised corrosion performance than cast alloys. This difference is probably attributable to the improved cleanness of the wrought alloys compared to the cast alloys in addition to the removal of the microsegregational effects generally experienced in cast alloys, particularly in respect of the highly alloyed austenitic stainless steels. Furthermore, it is also observed that the 316L type stainless steels exhibit very poor localised corrosion performance even in sea water at ambient temperatures.

A summary of the critical pitting and critical crevicing results of the alloys referred to in the text have been tabulated and can be seen in Table 3. From these results, the ranking of the alloys in terms of localised corrosion performance in sea water is as follows:

Zeron 100, Zetium 55, Zeron 25 and 316L.

In selecting stainless steels for water injection, it is necessary to take account of various water treatments which may consist of dosing with agents such as:-

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

(2) Corrosion inhibitors e.g. chromates, nitrites;

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

In addition, the chemical analysis and pH of the water to be injected has to be studied very carefully since 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 increasing temperature, salt concentrations up to 30%, H_2S concentrations up to 500ppm and CO_2 concentrations up to 2000ppm. Hydrogen sulphide generally accelerates localised corrosion particularly at

elevated temperature in the presence of oxygen. It has a very severe effect on the pitting potential of 316L type alloys [35] reducing it from -100 mV SCE at zero concentration to -400 mV SCE at a concentration of 300 ppm at $20^{\circ}C$. Alternatively, experience has shown that H_2S concentrations up to 400ppm in brine solutions containing up to 30% of chlorides have little effect on Zeron 25 duplex stainless steel providing the operating temperature is not too high. Indeed Zeron 100 and Zetium 55 have primarily been developed because of the increasingly harsh elevated temperature sweet and sour environments Mather and Platt have to combat when supplying injection pumps.

Typical examples of produced water analyses where the operating temperature is approximately $150^{\circ}F$ to $175^{\circ}F$ are shown in Tables 4a and 4b. The localised corrosion performances of Zetium 55 and Zeron 100 have been monitored in these produced waters and graphs of the critical pitting potentials versus temperature are shown in figures 5a and 5b. From the results obtained, it can be seen that there is only a marginal difference in the critical pitting performance of the two alloys in these environments with Zeron 100 giving the slightly better performance. The critical crevice corrosion temperatures recorded in these types of environment for Zetium 55 and Zeron 100 are $60^{\circ}C$ to $65^{\circ}C$ and $70^{\circ}C$ to $75^{\circ}C$ respectively. These materials have been tested in various media and the general ranking of the alloys is similar irrespective of the test environment utilised albeit that the actual critical pitting and crevice temperatures vary according to the aggressiveness of the environment.

STRESS CORROSION CRACKING (SCC)

Highly alloyed austenitic Stainless Steels exhibit better SCC resistance than conventional 316L type alloys (36). However, these alloys show a susceptibility to stress corrosion cracking in H_2S/brine environments at elevated temperature [37,38]. The action of H_2S and chlorides tends to be synergistic since the combination of H_2S and chlorides

produces cracking in austenitic materials not usually susceptible to cracking in either agent alone. The more susceptible austenitic stainless steels seem to contain in the region of 8-10 wt% Ni, whereas increasing nickel levels to approximately 25 wt% in respect of cold worked materials increases the resistance to SCC [39]. These statements of course, do not take account of the important influence of nitrogen in improving the SCC performance of the new breed of super-austenitic stainless steel. Duplex stainless steels have very good resistance to SCC in aqueous chloride environments. This resistance is inevitably reduced by high temperature, low pH, the presence of H_2S and high applied stress. There have been many studies conducted on the SCC behaviour of duplex stainless steels [40-46] some of which relate the important influence of the austenite-ferrite phase balance and others which suggest that the threshold stress for SCC is mainly dependent on yield strength. However, the performance of a conventional duplex alloy compared to alloys with compositions corresponding to its austenite and ferrite phases is demonstrated clearly by studying figure 6 [40]. It is seen that the ferrite phase cracks very quickly and at very low stresses. The threshold stress for SCC of single phase austenite is higher than that of ferrite and the time to fracture is between that of the ferrite and austenite. This is attributed to the fact that at low stresses, only the austenite is strained, but the ferrite cathodically protects the austenite which therefore does not crack. At high stresses, the ferrite is also strained which makes it susceptible to cracking. It is generally agreed that the presence of ferrite in a duplex stainless steel strongly increases the resistance to SCC due to a combination of a mechanical and a galvanic effect.

The SCC behaviour of cast Zeron 25 in the NACE TM-01-77 test has been established and is shown in figure 7. Assuming the highly alloyed austenitic stainless steels exhibit a similar resistance to SCC in the NACE solution in terms of the threshold cracking stress, i.e. 0.9 - 1.1 of the yield

strength, then the degree of overloading permissible calculated on the basis of the ASME VIII design criterion, is less in the highly alloyed austenitic stainless steels than for the duplex stainless steels. This could be particularly important where stress raising notches might be developed in service. It should be further emphasised that recent SCC tests on wrought Zeron 100 have proved that the alloy is not susceptible to cracking in the NACE solution at ambient temperature.

CORROSION EROSION/CAVITATION

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:

(1) Particle Erosion: damage to a metallic surface resulting from absorption of the kinetic energy of particles carried in a moving stream of liquid.

(2) 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.

(3) Liquid Impingement: erosion damage which occurs as a result of:
   a) high pressure generated at the point of impact;
   b) radial flow along the surface from the point of impact as the initial pulse subsides.

(4) 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 [47] in experiments using 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 stainless steels 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 not taken account of corrosion and to take an extreme example, electrochemical effects would clearly be of paramount importance in selecting materials for pumping nitric acid. Therefore, a whole range of possible conditions can exist. 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 properties etc., will improve performance. At the opposite end of the spectrum inherent corrosion resistance will be in the overriding consideration for material selection.

High speed seawater pumps will unfortunately see all subcategories of the erosion-corrosion process. The duplex stainless steels have much improved mechanical properties relative to the 316 type alloy (Table 1b) and consequently we would expect to see a substantial improvement in cavitation and by implication, impingement erosion. Indeed this has been confirmed and the cavitation rates for 316L and Zeron 25 alloys are 15,400 and 2,640 mg/dm^2/day respectively.

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 metres per second. The work that has been published [48-51] 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 separate 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 speed sufficient to generate relative fluid velocities of 100m sec^{-1}. Suction pressures can be varied from a few kPa up to 5000kPa. 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. These tests have also indicated that regardless of the test environment or conditions, the duplex alloy such as Zeron 25 and Zeron 100 do not exhibit any measurable weight losses whereas the austenitic grades of stainless steel show evidence of loss in weight. However, experience in sour service environments has shown that localised corrosion, particularly when stagnant conditions prevail, should be given far more consideration than attention to the effect of sea water flow rate.

CONCLUSION

Conventional duplex and super-duplex stainless steels possess a combination of mechanical and corrosion resistance properties which make them ideally suited for the production of water injection pumps to be utilised in a wide range of medium and elevated temperature sea water or produced water environments. Alternatively, although the super-austenitic grades of stainless steel have much improved localised corrosion properties compared to the traditional austenitic stainless steels, there usefulness for off-shore applications is restricted by their relatively low strength properties, which inevitably imposes severe weight penalties. In order to extract the best performance from the highly alloyed duplex and austenitic stainless steels, it is necessary to have an intimate knowledge of all the parameters which need to be controlled throughout manufacture if the desired mechanical and corrosion resistance properties are to be attained. Furthermore, the understanding of the physical metallurgy of these materials regarding the role of alloying additions and the control of the microstructure is of paramount importance if the alloys are to be utilised successfully. These statements are particularly important in view of the multitude of phase transformations which can precipitate in these highly alloyed stainless steels, the majority of which can adversely affect mechanical properties and corrosion performance of the alloys. Indeed, it would be inadviseable for a manufacturer with little experience to attempt to produce large section castings and forgings in these materials without a prior knowledge of the physical metallurgy of the alloy systems. However, the rewards for overcoming the difficulties associated with these materials are great.
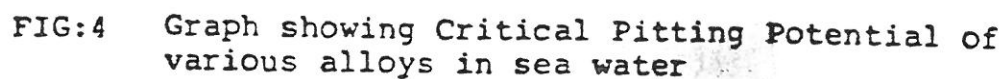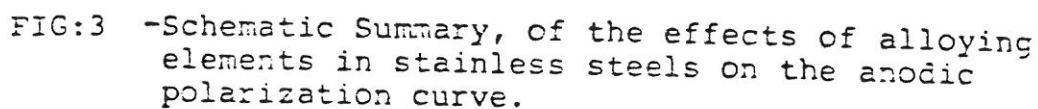
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FIG: 1 - Barrel Casing Shear Ring Construction
Design of Pump

FIG:2 - Multistage Horizontally Split Casing
Design of Pump

NOBLE

Ep — — — — — — — — — — — Cr,Mo,N.W
                         Si,V,Ni

Cr,Ni,W →

Epp — — — — — — — — — — — — — — Cr

                    Cr,Ni,V
                    Mo

ACTIVE   ipass   imax

LOG CURRENT DENSITY —

FIG:3 —Schematic Summary, of the effects of alloying
       elements in stainless steels on the anodic
       polarization curve.

1·5
1·3
1·2
1·1
1·0   ○ CAST ZERON 100
0·9   ● WROUGHT ZERON 100
0·8   ■ WROUGHT ZETIUM 55
0·7   □ CAST ZETIUM 55
0·6   ✳ WROUGHT ZERON 25
0·5   ✿ CAST ZERON 25
0·4   ▲ CAST 316L
0·3   - - - - CAST MATERIAL
0·2   ——— WROUGHT
            MATERIAL
0·1
0
   0 10 20 30 40 50 60 70 80 90 100 110
              TEMPERATURE (°C)

FIG:4   Graph showing Critical Pitting Potential of
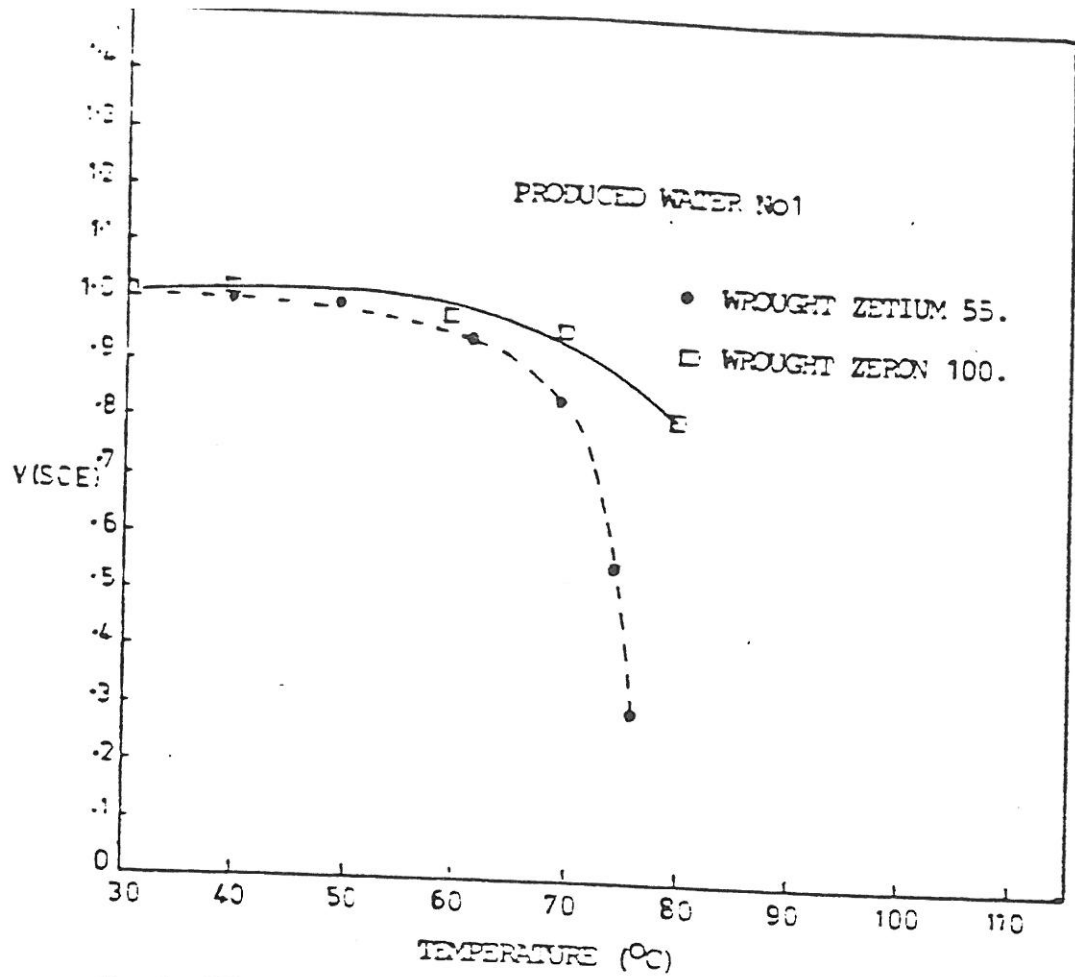   various alloys in sea water

<u>FIG 5a</u>   Graph illustrating Critical Pitting Potential VS Temperature
for wrought Zeron 100, and Zetium 55 in produced water No1.
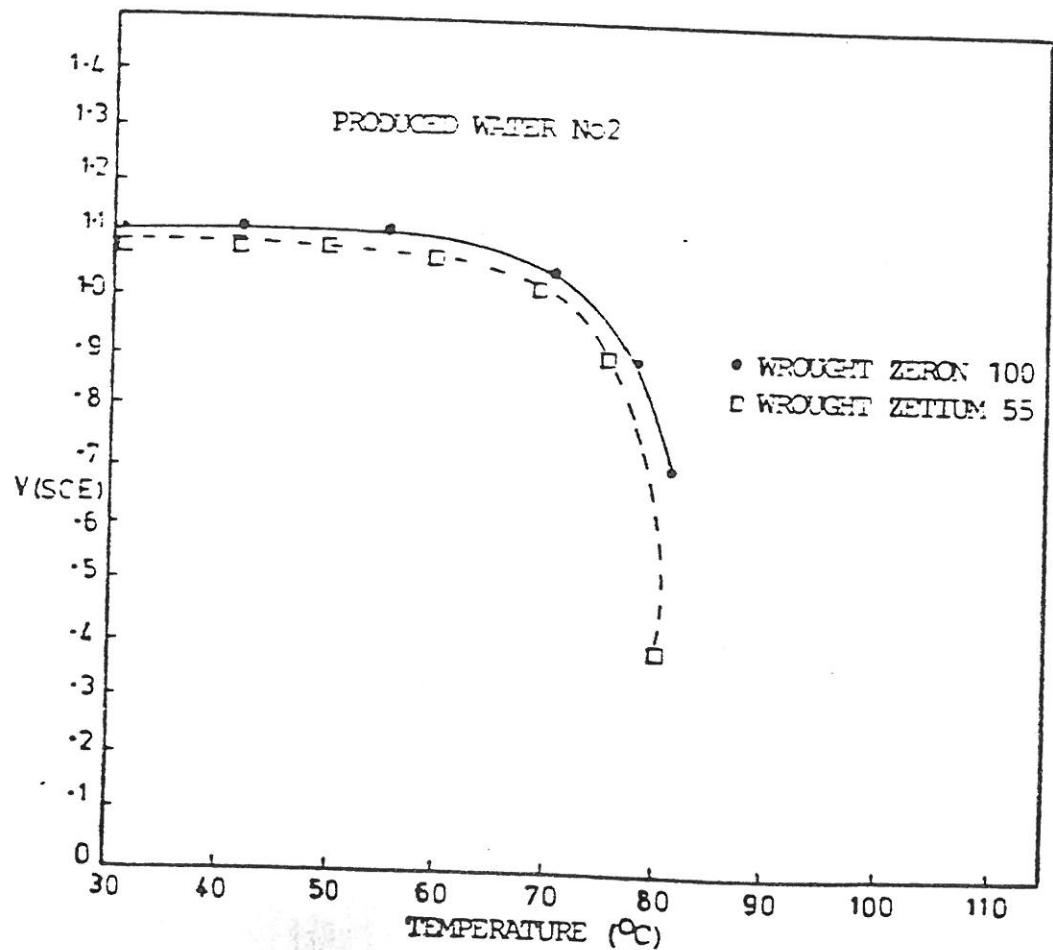

<u>FIG 5b</u>   Graph illustrating Critical Pitting Potential VS Temperature
For wrought Zeron 100 and Zetium 55 in produced water No2.

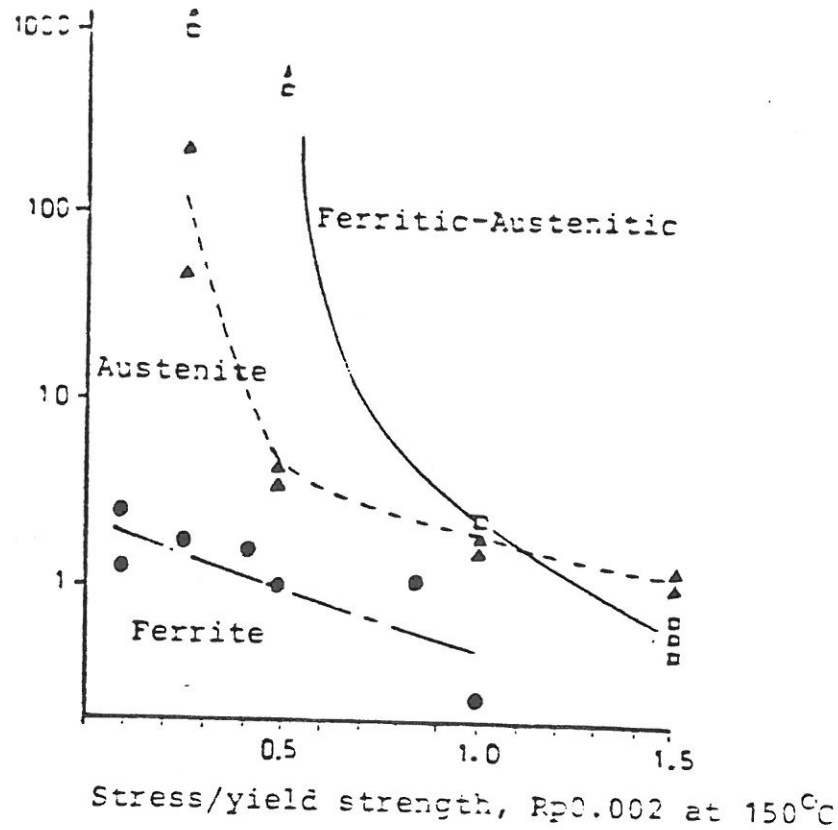FIG 6　　Performance of the duplex alloys and of alloys
with compositions corresponding to its γ and
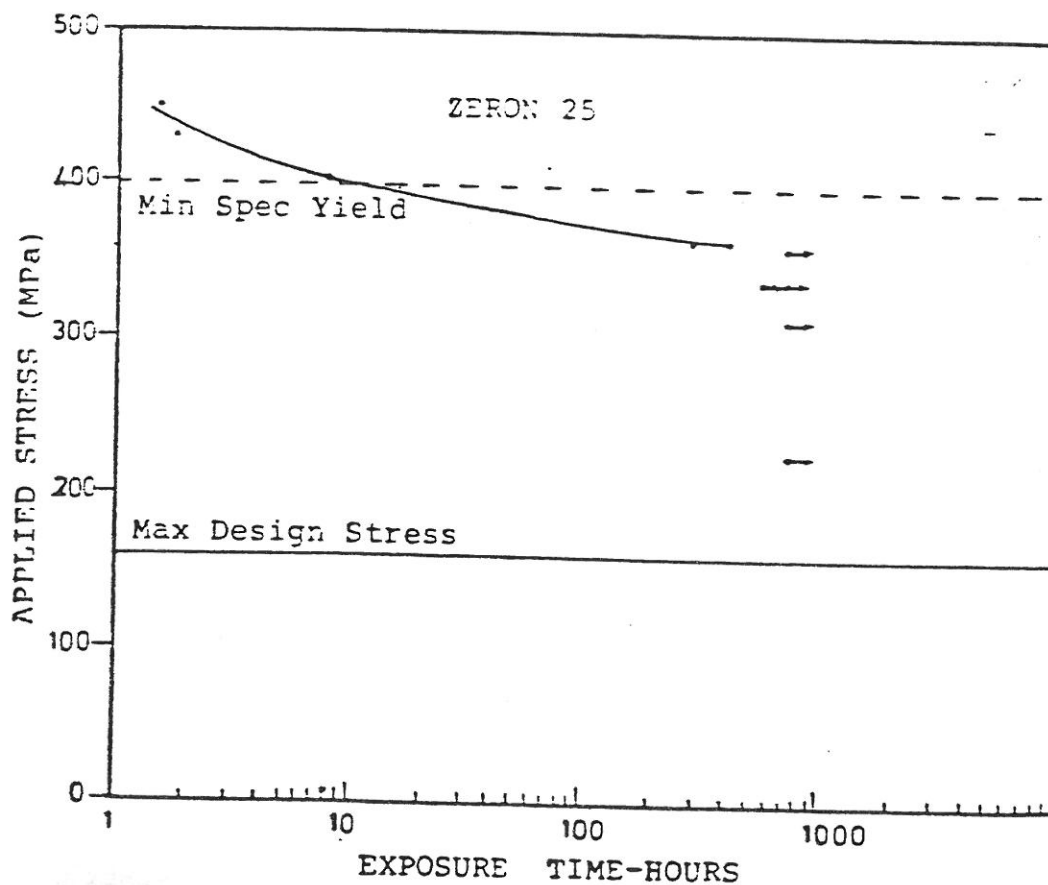α phases.　Constant load tests in 44% $MgCl_2$
at 153°C.

FIG 7　　Stress Corrosion Performance of cast Zeron 25 in
the Nace TM 01.77 Test.

Chemical Composition of Austenitic and Duplex Stainless Steel

MATERIAL	C	Si	Mn	S	P	Cr	Ni	Mo	Cu	N2	W	PRE (Min)
316L	.03 max	1.5 max	1.5 max	.04 max	.04 max	17.0 21.0	9.0 13.0	2.0 3.0				27
Zetium 55	.03 max	0.8 max	1.0 max	.015 max	.03 max	20.5 21.5	17.5 18.5	5.0 5.4	0.5 1.0	0.19 0.22		40
Zeron 25	.05 max	0.2 1.0	0.2 1.5	.04 max	.04 max	23.0 26.0	5.0 8.0	1.75 3.0	0.5 max	0.1 0.2		35
Zeron 100	.03 max	2.0 max	2.0 max	.04 max	.04 max	24.0 26.0	5.0 8.0	3.0 4.0	0.5 1.0	0.2 0.3	0.5 1.0	40

TABLE 1b.
Minimum Mechanical Properties of Austenitic & Duplex Stainless Steel (Solution Annealed Condition

Material		Proof Strength Min (MPa)	T.S. Minimum (MPa)	Elongation Minimum (%)	Impact Toughness -10°C	Hardness Range (HB)
316L	Cast	205	485	30 (4D)	100	140/200
	Wrought	205	515	40 (4D)	100	140/200
Zetium 55	Cast	250	500	35 (4D)	100	150/200
	Wrought	300	600	35 (4D)	120	160/210
Zeron 25	Cast	400	630	20 (5D)	70	200/280
	Wrought	480	650	25 (5D)	100	200 (min)
Zeron 100	Cast	470	680	25 (5D)	100	200/280
	Wrought	550	750	25 (5D)	150	200 (Min)

TABLE 2

COMPARISON OF PUMP CASING WEIGHTS

FOR DIFFERENT MATERIALS OF CONSTRUCTION

	MATERIAL OF CONSTRUCTION	PROJECTED EKOFISK PUMP CASING WEIGHT (TONNES)
316L	CENTRIFUGALLY CAST	9.74
	FORGED	8.86
ZETIUM 55	CENTRIFUGALLY CAST	8.37
	FORGED	7.69
ZERON 25	CENTRIFUGALLY CAST	7.50
	FORGED	6.62
ZERON 100	CENTRIFUGALLY CAST	7.00
	FORGED	6.13

TABLE 3

SUMMARY OF CRITICAL PITTING AND CREVICE TEMPERATURES IN SEA WATER

ALLOY	CPT °C	CCT °C
ZERON 100 (Wrought)	100	75-80
Cast	82	65-70
ZETIUM 55 (Wrought)	80	60-65
Cast	65	50-55
ZERON 25 (Wrought)	55	38
Cast	48	35
316L Cast	20	11

TABLE 4a

Produced Water No. 1

pH	4.5
TDS	207000 mg/l
S.G.	1.23 at 15°C
Resistivity	0.048 ohm-metres at 25°C mg/l
Sodium	60530 mg/l
Calcium	14920 mg/l
Magnesium	2211 mg/l
Iron	470.4 mg/l
Barium	0 mg/l
Chloride	127800 mg/l
Bicarbonate	190 mg/l
Sulphate	540 mg/l
Carbonate	0 mg/l
Hydroxide	0 mg/l

TABLE 4b

Produced Water No. 2

pH	5.8
Calcium	19880 mg/l
Magnesium	3200 mg/l
Barium	12 mg/l
Strontium	952 mg/l
Sodium	69000 mg/l
Iron Total	6 mg/l
Iron Dissolved	55 mg/l
HCO_3	222 mg/l
CO_2	490 mg/l
H_2S	270 mg/l
Chloride	150000 mg/l
Sulphate	455 mg/l

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