Factors Influencing the Microstructure and Corrosion Resistance of Austenitic and Duplex Stainless Steel Castings

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***Abstract*—The demand for Austenitic and Duplex Stainless Steel Castings has increased with investment in the petrochemical industry, transportation infrastructure and electric vehicle production in Thailand. To achieve high quality casting of these two grades, alloying elements melt quality, pre and post-treatment of castings play an important role in quality level determination. These important factors are discussed along with guidelines for good manufacturing practices to achieve the required microstructures and high-quality castings from the domestic foundry sector in Thailand.**

***Index Terms*—Austenitic and Duplex Grades, Corrosion Resistance, Microstructure, Stainless Steels**

I. INTRODUCTION

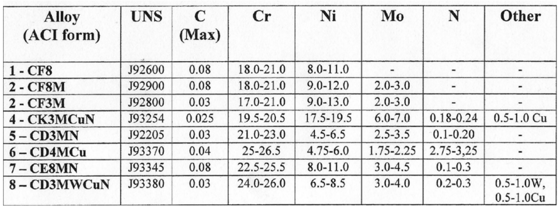
The formation of air formed oxide films on the surface of metallic materials can offer some protection against subsequent attack by corrosive media. This is known as *"passivation"*. In stainless steels passivation is achieved by alloying with chromium which gives rise to a thin, self-repairing, protective layer of chromium-based oxide over the surface of the steel. For stainless behavior a minimum of 12% Cr is required in solid solution in the matrix of the steel. Even though protected by an oxide film stainless steel can still be prone to highly damaging localized forms of corrosion such as pitting, crevice and intergranular attack and not least stress corrosion cracking [1]. Additions of other alloying elements, notably Ni, Mo and N, are therefore also included in stainless steels in order to improve resistance to such local forms of corrosion and to control the matrix structure and mechanical properties. Stainless steels can be supplied in cast, wrought and powder metallurgy product forms. In all of these forms the composition, especially the carbon level, and the processing, welding, and heat treatment variables must be carefully controlled. Correct control ensures that the required distribution of alloying elements is obtained and that the formation of Cr rich carbides and other damaging second phases in the microstructure is minimized. The presence of carbides and second phases can not only cause severe pitting and intergranular attack due to micro-galvanic effects but can also reduce mechanical properties such as toughness.

A number of types of stainless steel have been developed including:

- Ferritic, containing 12 - 30 % Cr and very low C levels
- Martensitic with 12 - 17 % Cr and 0.1 - 1.0%C
- Austenitic containing 17 - 25% Cr with 8 - 12 % Ni + other alloy elements or 20 - 27% Cr with 20 - 35 % Ni
- Duplex alloys with 22 - 30 % Cr, 3 - 7% Ni + other alloy elements
- Precipitation hardening alloys which can have austenitic or martensitic matrices with additions of Cu, Ti, Al, Mo, Nb or N

There are many comprehensive reviews and guides [2]-[6] covering the compositions, physical metallurgy, properties, corrosion behavior and service performance of stainless steels. Much of these literatures focus on wrought grades with relatively little attention being given to casting grades. Compared to wrought grades, the grades for castings have modified compositions to improve fluidity during mould filling and to prevent hot cracking during solidification and cooling. Levels of residual elements may also be more variable due to the relatively smaller melt sizes used for castings production. The presence of typically coarser and less homogeneous microstructures in castings together with such compositional differences will result in some differences in mechanical properties and corrosion resistance between castings and wrought products [7]. Composition and property requirements for stainless steel castings are covered by a number of international, patent licence-holder and individual company standards. Never the less, it is common practice for many foundries and their customers in S.E. Asia to refer and produce to compositions from wrought grades such as AISI 316. To obtain suitable cast ability and to avoid problems with casting quality issues, foundries should produce to recognized casting standards, the most widely accepted of these are those issued by ASTM, e.g. A743/A743M and A744/A744M [8], [9]. The chemical compositions of some austenitic and duplex casting grades are listed in Table 1.

TABLE I
EXAMPLES OF MAIN ALLOY ELEMENTS USED IN CAST STAINLESS STEELS
(VALUES IN WT.%).
[DATA FROM 8.9.19.20,43]



Alloy (ACI form)	UNS	C (Max)	Cr	Ni	Mo	N	Other
1 - CF8	J92600	0.08	18.0-21.0	8.0-11.0	-	-	-
2 - CF8M	J92900	0.08	18.0-21.0	9.0-12.0	2.0-3.0	-	-
2 - CF3M	J92800	0.03	17.0-21.0	9.0-13.0	2.0-3.0	-	-
4 - CK3MCuN	J93254	0.025	19.5-20.5	17.5-19.5	6.0-7.0	0.18-0.24	0.5-1.0 Cu
5 – CD3MN	J92205	0.03	21.0-23.0	4.5-6.5	2.5-3.5	0.1-0.20	-
6 – CD4MCu	J93370	0.04	25-26.5	4.75-6.0	1.75-2.25	2.75-3,25	-
7 – CE8MN	J93345	0.08	22.5-25.5	8.0-11.0	3.0-4.5	0.1-0.3	-
8 – CD3MWCuN	J93380	0.03	24.0-26.0	6.5-8.5	3.0-4.0	0.2-0.3	0.5-1.0W, 0.5-1.0Cu

In Table I Steels 1-4 are austenitic grades, steels 5-8 are duplex grades, The grades are in the ACI form used in ASTM standards. For reference each equivalent UNS number is listed. CF8 and CF8M are the casting alloy equivalents to 304 and 316, CF3M is equivalent to 316L. The Mn level is normally <1.0% with Si<1.5%, S<0.04% and P<0.04%.

To satisfy local market demand for cast components such as valve or pump bodies and impellers Thai foundry companies have shown increasing interest in producing austenitic and duplex grades of stainless steel. This short article provides an outline of the important metallurgical factors that must be controlled when producing corrosion resistant castings in such grades. With reference to some microstructural observations emphasis is given to the relationships between composition, microstructure and corrosion resistance.

II. EFFECTS OF ALLOYING IN AUSTENITIC AND DUPLEX GRADES.

The basic effects of the main alloying elements can be outlined as [2]:

A. *Chromium*

This is the main element to give corrosion resistance by providing a stable, protective, self-healing oxide film on exposure to air or aqueous environments.

B. *Nickel*

This stabilizes austenite and improves general corrosion resistance in most environments which do not contain sulphides.

C. *Molybdenum*

Increases resistance to pitting and crevice corrosion resistance especially in aggressive environments containing chlorides and sulphur.

D. *Nitrogen*

Stabilizes and solid solution strengthens austenite and increases pitting resistance.

E. *Copper*

Improves general corrosion resistance and can act as a substitute austenite former in place of Ni.

As a result of steel making processes the common elements Mn, Si, S and P are all present. The Mn level is normally kept below 1.5% and Si below 1% in wrought grades and below 2% in casting grades. S and P have harmful effects on corrosion resistance and weldability and must be below 0.03 and 0.045% respectively to meet standards. Preferably S and P should be as low as possible. However, in some grades additions of S can be made to improve machinability. Higher additions of Mn in combination with 0.25% N addition have been used to reduce costs by substituting for Ni, for example at 6-7% Mn the Ni content can be reduced from 8-10% to 4-6%. This has resulted in the development of the 200 series wrought austenitic stainless grades as a cheaper alternative to AISI 304 [10].

In Austenitic Grades a stable austenitic matrix is obtained by the addition of at least 8% Ni to 18% Cr steels. Nickel increases the amount of austenite produced during solution heat treatment and also lowers the Ms (martensite start temperature) to sub-zero. The steels often contain additions of Mo, N, Nb, Ti and Cu to improve properties and remain essentially austenitic at all temperatures [2]. Some grades contain up to 20% delta ferrite to improve weldability [2], [11]. The interaction between Cr (which is a ferrite former) and Ni (which is an austenite former) and other alloying elements is most conveniently described by the use of Cr and Ni equivalents based on wt.% amounts of given alloy elements, for example:

$$\text{Chromium equivalent } Cr_e = (Cr) + 2(Si) + 1.5(Mo) + 5.5(Al) + 1.75(Nb) + 1.5(Ti) + 0.75\,(W) \tag{1}$$

$$\text{Nickel equivalent } Ni_e = (Ni) + (Co) + 0.5(Mn) + 0.3(Cu) + 25(N) + 30(C) \tag{2}$$

These equivalents, some based on different formulae, are used in the plotting of Schaeffer type diagrams as illustrated in Fig. 1, such diagrams [11]-[13] are used to predict weld microstructures, especially the proportion of ferrite, but can also provide a guide to expected as-cast structures in small sectioned castings in that they indicate the approximate areas of stability of the various microstructures in stainless steels. The presence of a controlled amount of primary delta ferrite minimizes hot cracking in welds [11].

Due to their FCC crystal structure austenitic grades are non-magnetic, relatively tough at low temperatures, and have useful creep resistance up to about 900°C. Their yield strengths are relatively low. Interstitial solid solution hardening is the most effective means of strengthening but C addition cannot be used since C encourages the precipitation of Cr carbides, which seriously reduce corrosion resistance. N, in additions normally up to 0.2% is therefore the main element used for solid solution strengthening.

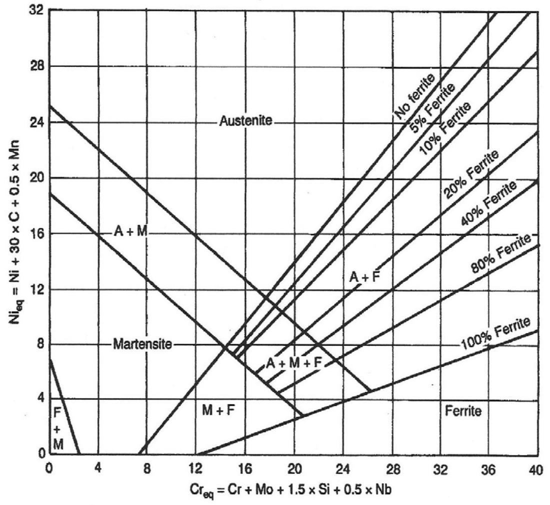


Fig. 1. Example of a Schaeffler-delong diagram using basic formulae for Ni and Cr equivalents [11]-[13]

Austenitic grades are susceptible to Stress Corrosion Cracking (SCC) when exposed to chloride containing environments [5]. SCC tends to occur in stainless steels and other alloys under a particular set of circumstances for a given alloy i.e. *particular alloy and condition, specific corrosive media, sufficient local tensile stress.* SCC is most likely nucleated at pitting damage sites and develops under the action of local tensile stresses as a highly branched network of intergranular or trans granular fine cracks depending on the nature of the alloy. SCC tendency is lower in ferritic and martensitic alloys. The presence of delta ferrite in austenitic steels is known to improve SCC resistance.

If slowly cooled through or held in the temperature range 450-850°C austenitic stainless steels can be sensitized by the formation of grain boundary Cr-rich carbides [14]. This can occur in heat affected zones during welding and in thicker sections of solution treated castings. The presence of such carbides can then lead to intergranular corrosion in service, as indicated schematically in Fig. 2 [15].

For austenitic steels to be welded without the precipitation of Cr carbides and the accompanying danger of subsequent intergranular attack additions of titanium $(\%Ti = 5 \times \%C)$ or niobium $(\%Nb = 10 \times \%C)$ are used. These additions result in precipitation of stable TiC or NbC carbides in heat affected zones. The carbon is therefore not free to form Cr carbides and the steel is said to be "stabilized". Chromium rich carbide precipitation can also be minimized by producing very low carbon steels, ideally containing below 0.02% C [2], [5].

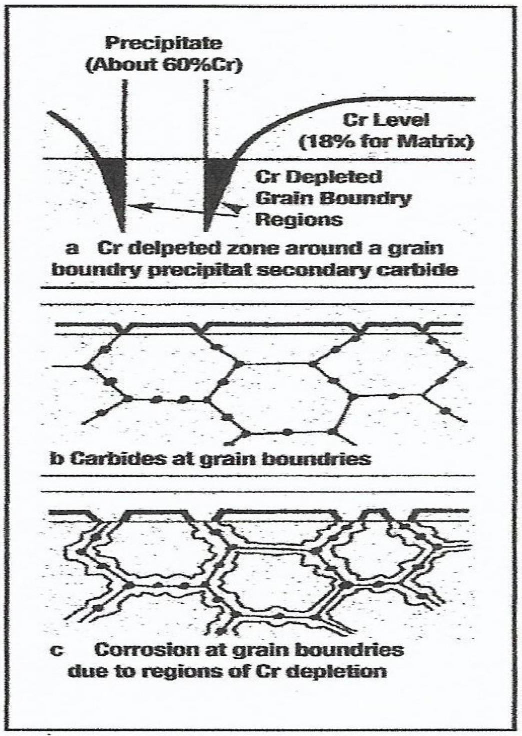


Fig. 2. Schematic view of intergranular attack caused by precipitation of Cr-rich carbides at grain boundaries in an austenitic stainless steel [1], [15].

The **Duplex** grades with mixed austenite and ferrite structures are designed to give greater SCC resistance than austenitic steels [4], [16], [17]. The duplex microstructure helps to inhibit crack growth by arresting or deflecting the cracks at the austenite/ferrite interfaces. Maximum SCC resistance appears to be obtained in 50-50 austenite-ferrite microstructures and ideally the dispersion of the two phases should be as fine as possible. To produce duplex grades the Cr content is raised to 20-25%, and Ni reduced to 4-7% with additional control of the levels of Mo and N. Duplex grades have higher yield (proof) strengths but lower toughness than the austenitic grades. Their 0.2% proof stress values range from 400 to 550 MPa compared to only 200 - 300 MPa for low N austenitic grades. Because austenite work hardens during plastic deformation the UTS values for the duplex and austenite grades are similar. The higher proof stress levels of duplex steels offer savings in material and weight over austenitic grades, and also allow castings to be designed with thinner, easier to feed sections. Although the Ni content of the duplex grades, at 4-8%, is lower than for conventional austenitic steels their pitting resistance, if correctly heat treated, is at least equivalent to that of the austenitic grades due to their higher Cr and Mo levels [2], [18].

Duplex stainless steels can be classified into four groups:

- Lean alloy Mo-free such as 23Cr-4Ni-0.1N.
- Standard 22%Cr SS of the type 22Cr-5Ni-3Mo-0.17N.
- High Alloy 25 Cr with Mo, N and Cu or W.
- Super-duplex e.g. 25 Cr-7Ni -3.5Mo-0.27N.

The use of duplex grades in various wrought product forms such as bar, tube and plate has been well established for a number of years. In recent years interest has grown in their use as castings especially for applications such as pump and valve bodies [18] since they can be used to provide greater resistance to corrosion in seawater and in sour gas applications where there may be contamination from hydrogen sulphide and ammonia. For applications in the oil, gas, and petroleum sector duplex grades are increasingly used in preference to austenitic especially in chloride or sulphide containing environments. The first ASTM standard specific to duplex stainless steel castings was issued in 1988 as ASTM A890 [19]. Later in 1998 to meet the requirements for pressure containment another standard, ASTM A995 [20], was issued setting down tighter requirements for compositional limits, traceability, tensile and pressure testing, weld repair and heat treatment, etc. A casting which satisfies A995 also satisfies A890.

Additions of Mo are made to both austenitic and duplex stainless steels to improve both general corrosion and pitting resistance with Mo contents of 4.5 to 7% giving rise to the so called *"Superstainless"* grades [4], [6], [21]-[24]. These alloys were initially developed to provide greater resistance to resist corrosion in sea water where it has been found that at least 3% Mo is needed in ferritic steels and at least 6% Mo in austenitic steels to avoid crevice corrosion attack. In both austenitic and duplex steels additions of N can give further improvements in pitting resistance [2]-[7].

The combined effects of alloying elements on corrosion resistance can be described by a *Pitting Resistance Equivalent Number PREN* calculated from composition such as:

$$PREN = \%\,Cr + 3.3\,(\%\,Mo) + X\,(\%\,N) \quad (3)$$

X = 16 for duplex and X = 30 for austenitic.

Several different formulae have been proposed for PREN including the contribution by W addition when present [22], [23], [25]-[27]. All are empirical relationships based upon laboratory corrosion tests in chloride containing solutions. Superstainless grades give PREN values of 40-45 compared to 20-25 for normal grades. Pitting resistance is measured in chloride containing environments since it is the chloride ion which is mainly responsible for localized damage to the passive oxide film. Pits tend to develop at microstructural features such as grain boundaries, second phase particles or inclusions (carbides, oxides, sulphides) and at delta ferrite/austenite interfaces in duplex structures. PREN values have become commonly used for general ranking of pitting resistance. For example, a PREN value of >40 is normally specified for seawater service [28].

Calculated PREN values do not always take into account the effect of other alloy additions such as Ni, Cu, Mn, etc., which must also have some influence on pitting behaviour. It must be recognized that using bulk composition as a basis for pitting resistance can be misleading when both austenite and ferrite phases are present in the microstructure as in duplex steels and austenitic grades containing ferrite. Elemental partitioning between austenite and ferrite determines the pitting resistance of each phase, hence the PREN value should relate to that of the phase with the lesser resistance [25]-[27] where possible composition and heat treatment conditions must be controlled to give equal pitting resistance in the austenite and ferrite fractions. Another indicator of pitting is the "Critical Pitting Temperature" which is found by exposing test pieces to 6%Fe (III) Chloride solutions and raising the temperature gradually until onset of pitting [29]-[30].

In developing pitting and crevice corrosion resistance in duplex grades alloy designers must try to obtain equivalent pitting resistance in both the austenite and ferrite (to prevent preferential attack of either phase) and must avoid the use of too high Cr and Mo levels to minimize the risk of precipitation of intermetallic phases.

III. MELT QUALITY

As well as Cr carbides and other precipitated phases, non-metallic inclusions or second phases containing impurities can have deleterious effects on the passive behaviour of stainless steels since these microstructural features not only give rise to discontinuities or defects in the thin passive oxide film but can also cause micro-galvanic corrosion cells. Sulphur will form sulphides which can generate hydrogen sulphide in acidic solutions or form galvanic cells which reduce corrosion resistance in the local areas around each inclusion. In producing ingot material, liquid metal improvements via vacuum and electroslag melting and refining processes have been made to produce the very low carbon and sulphur levels. These processes ensure the reduced levels of other impurities and inclusions that are especially required for the super stainless grades.

In arc melting of stainless-steel scrap for casting production final refining is normally achieved by AOD (Argon Oxygen Decarburization). AOD uses commercial high purity argon and nitrogen as well as oxygen injected through side tuyeres in a small converter type vessel. This allows carbon removal in the presence of high Cr concentrations and controlled introduction of nitrogen into the steel. Most steel foundries in Thailand use induction melting furnaces. For induction melting of stainless grades purer charge materials are required such as controlled quality wrought stainless scrap or special billet or ingot. Foundries that are familiar with producing higher C heat resistant steel castings such as parts for cement clinker and other grate plates cannot base production of corrosion resistant grades on similar types of charge materials. Heat resistant austenitic steel casting are not covered in the present paper and have been outlined elsewhere [31], [32].

In producing stainless steel melts based on scrap charges the nature of the scrap is critical. It must be clean and dry and be completely free from oils and other C bearing contaminants. Shapes such as bar stock, sheet and strip are acceptable if of known composition i.e. supplied with analysis certificate. Tube and pipe shapes must be not be used because of possible contamination from their internal surfaces. Any scrap that has been in service in carburizing conditions must be avoided. It must also be noted that the high Mn 200 series steels have become increasingly used in Asia, especially in India and China. Scrap from such Cr-Mn grades is not easily distinguished from the normal Cr-Ni material. Suppliers of stainless scrap and foundries in Thailand must take extra care to ensure that the 200 series material is effectively separated.

For cleaner lower C stainless grades Vacuum Induction Melting (VIM) and/or Vacuum Oxygen Decarburization (VOD) need to be used. These processes can be used for small tonnages of 1-20 tonnes in foundry applications. For duplex and superaustenitic grades AOD or VOD refining is needed to ensure that precise chemical compositions with the required low C, S, and other impurity levels are achieved.

During melt preparation liquid metal holding times and melt & pouring temperature temperatures must be as low as possible to decrease oxygen pick-up and promote cleanliness. The use of an Argon shield during melting, and if possible, during pouring, is recommended.

Feeding and running systems must be designed to prevent shrinkage defects in castings [33] and to minimize turbulence during filling of the mould cavities [34]. The materials used and production of moulds and cores and application of coatings must be selected not only to provide sufficient refractoriness to meet high pouring temperatures but also prevent the pick-up at cast surfaces of C, S and N from metal-mould interaction. Inorganic binders are preferable since organic binders tend to decompose when moulds are poured.

IV. CONTROL OF MICROSTRUCTURE AND HEAT TREATMENT IN CASTINGS.

The solubility of C in austenite decreases with temperature. Hence, alloy Cr rich carbides can precipitate if austenitic or duplex steels are slowly cooled, such as during cooling of a casting in a mould, or are held in service or otherwise in the temperature range of 350-850°C. Precipitation usually occurs at grain boundaries in the austenite as illustrated earlier in Fig. 2 and in interdendritic zones. Segregation of C and Cr, and other carbide forming elements into the last regions of interdendritic liquid during solidification can give rise to interdendritic eutectic carbides. These are just as if not more damaging in promoting micro-galvanic attack as the carbides precipitated in the solid state. Therefore, castings must be annealed (solution treated) in the range of 1050-1175°C (depending on composition) in order to dissolve any primary non-equilibrium eutectic carbides and any alloy carbide precipitates and then they must be cooled rapidly by water quenching to prevent any re-precipitation of carbides or other second phases.

Fig. 3 to Fig. 5 are used to illustrate that, without correct heat treatment, components used in the as-cast condition, will be prone to corrosive attack. Fig. 3 shows interdendritic eutectic carbide that has formed in the cast structure of a 0.2% C-20% Cr-18% Ni-6% Mo-0.18% N steel. This carbide together with dendritic segregation and possibly finer precipitated carbides has resulted in the corrosion damage seen in Fig. 4 and Fig. 5. The damage, produced during potentiostatic testing in chloride containing sulphuric acid, also illustrates the importance of controlling the % C to the lowest possible level. In this case, even after heat treatment, the large amount of alloying additions, which should give high pitting resistance, is wasted since the % C level is way over specification and should be below 0.03%.

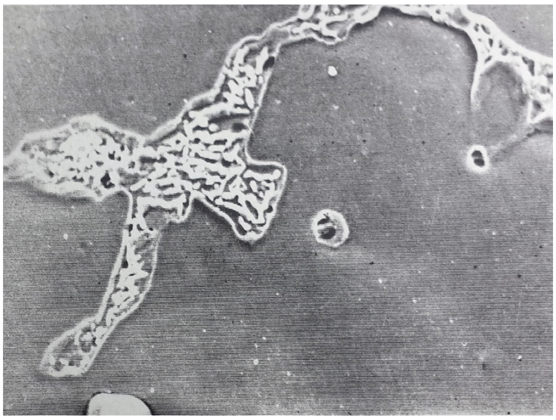


Fig. 3. As-cast microstructure of austenitic stainless steel containing excessive % C content showing the presence of interdendritic eutectic carbides (SEM x2000) [35].

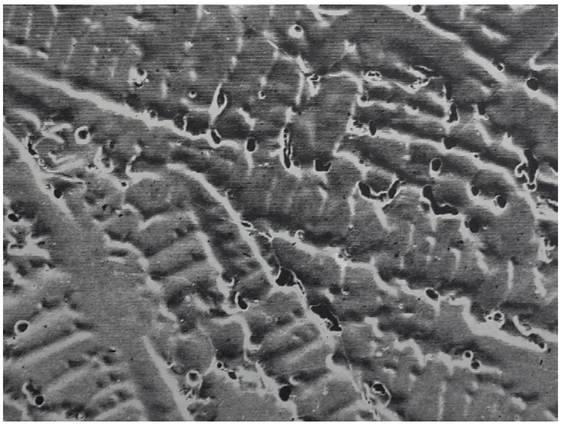


Fig. 4. Dendritic structure revealed by potentiostatic testing of the steel shown in Fig. 4 Pitting occurs at grain boundary and interdendritic regions (SEM x200) [35].

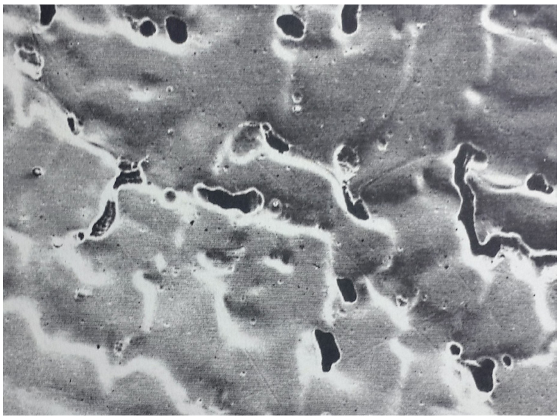


Fig. 5. The extent of interdendritic pitting seen in Fig. 4 (SEM x500) [35].

Duplex Grade castings must also be heat treated to remove segregation and to dissolve as cast carbides and precipitated second phases. The aim is to produce a precipitate free 50% ferrite - 50% austenite structure. Duplex grades present more problems than the austenitic grades since they are prone to the formation of a variety of embrittling precipitates such as sigma, carbides, nitrides, chi phases, etc. during slow cooling of castings after solidification. Secondary phase formation can be related to TTT diagrams for duplex steels as indicated in Fig. 6.

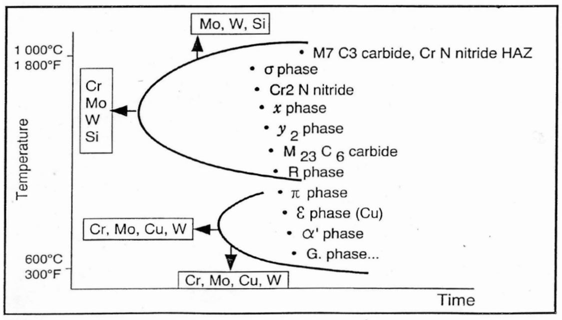


Fig. 6. A schematic Time-Temperature-Transformation diagram (TTT) for duplex stainless steel showing possible precipitating phases and the relative effects of alloying elements [16].

During production the castings must be left to cool to ambient in the mould to avoid cracking due to the presence of these precipitates. In the as cast state, there is a danger of cracking during feeder removal and fettling, especially for heavier sections. Hence before these cleaning operations castings often have to be solution treated to take the unwanted brittle phases into solution. Afterwards larger castings may require repeat heat treatment to remove any precipitation effects from the heat affected zones beneath removed feeders caused by thermal cutting or due to the inadequate cooling rate of the first treatment due to the mass effect of the previously attached feeder head.

For solution treatment castings must be charged into a cool furnace (below 250°C) and heated carefully at a maximum rate of 150°C per hour up to 700°C. They then should be held at 700°C for 1 hour per 25 mm of section to equalize temperatures in different sections and to ensure relief of stress before being raised, as quickly as possible, to 1175°C and held for 1 hr. per 25 mm of section. The heating rate from 700°C up to 1175°C needs to be rapid to minimize any second precipitation. The precipitation nose on TTT curves is around 850°C such that slow heating would allow formation of secondary phase precipitates, which in turn would result in excessive holding times for solution treatment in order to dissolve them.

Austenitic and duplex castings must be quenched from solution treatment temperatures into an agitated water bath where water can be rapidly recirculated by pumping from a second header tank. The transfer time before the quench must be minimal to prevent precipitation. With heavy section castings precipitation cannot always be prevented at the centres of sections such that although surface regions may meet specifications the centre sections may not. Therefore, producing bolt holes with cores rather than by drilling helps to lighten sections as does proof machining before final heat treatment in order to get the maximum depth of effectively heat-treated material.

Duplex grade castings may be tempered at 350°C after quenching to relieve residual stresses. It is not unusual for certain casting defects in larger steel castings to be subjected to weld repair. In these cases, castings must be given a post-weld solution treatment to ensure freedom from the danger of intergranular corrosion. Minor repair may be carried out without post weld treatment but only in very low carbon grades, (< 0.03%C).

The as-cast microstructure of duplex steel with a composition of 0.05%C-23%Cr-6%Ni-3%Mo-0.2%N is shown in Fig. 7. The secondary phases that have formed within the ferrite and at austenite/ferrite interfaces result in the pitting attack and removal of ferrite seen in Fig. 8 to Fig. 11 illustrate the effects of correct and incorrect heat treatment of the as-cast steel shown in Fig. 7 and Fig. 8.

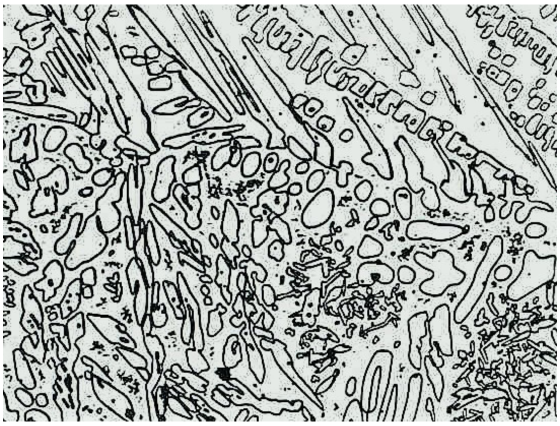


Fig. 7. As cast microstructure of duplex stainless steel showing blocks of austenite in a ferrite matrix which also contains precipitated secondary phases (Optical view x75).

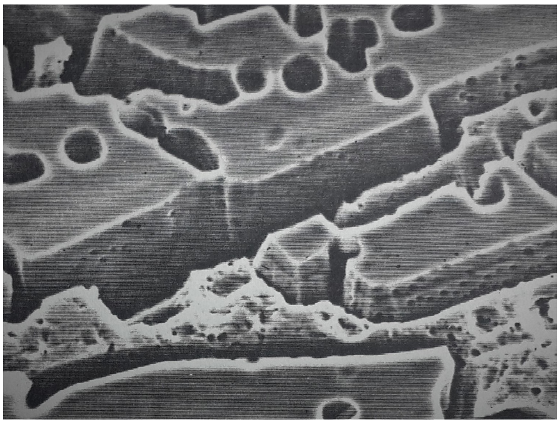


Fig. 8. Corrosion damage produced during potentiostatic testing in 3.5% sodium chloride solution. Ferrite is preferentially removed with pitting damage in the ferrite and at the austenite/ferrite boundaries (SEM x3000) [35].

Quenching should prevent precipitation of carbides and any other secondary phases during cooling. Solution treatment at 1175°C followed by effective water quenching has prevented the formation of secondary phases in the ferrite such that relatively littles corrosion has occurred during potentiostatic testing in 3-5% sodium chloride solution as shown in Fig. 9.

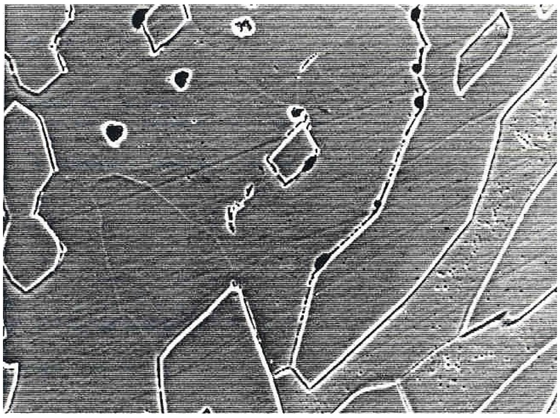


Fig. 9. Correct solution treatment: pitting at isolated non-metallic inclusions with some smaller pits in some ferrite areas (SEM x1000) [35].

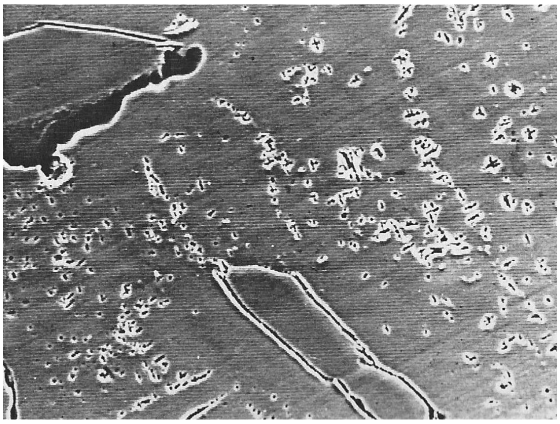


Fig. 10. The effect of a time delay before water quenching after solution treatment. Some precipitation has occurred in the ferrite and at ferrite/austenite interfaces giving pitting damage (SEM x1000).

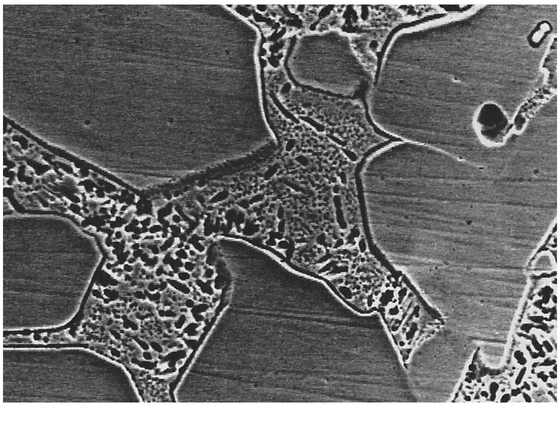


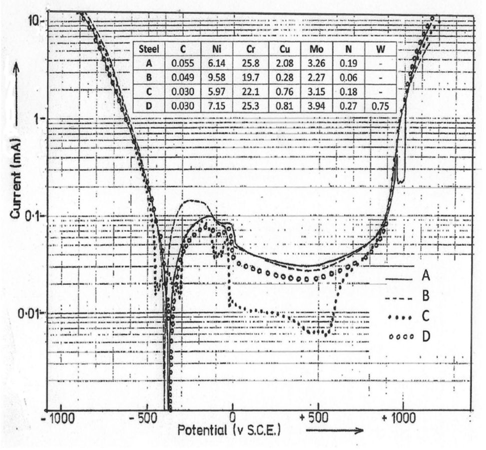
Fig. 11. Incorrect solution treatment. Slow cooling has resulted in extensive secondary phase formation that has caused severe pitting in the ferrite areas. There is no pitting in the austenite except at interphase boundaries. The microstructure and corrosion damage are similar to the as-cast condition in Fig. 8 (SEM x1000).

However, any delay before quenching will allow some precipitation to occur and hence result in pitting damage in ferrite as shown in Fig. 10. Slow cooling from 1175°C is highly damaging since this allows considerable secondary phase formation and results in severe damage in the ferrite as shown in Fig. 11. To obtain comparative corrosion behaviour the damage seen in Figs. 8 to Fig. 11 was produced by holding each specimen in the trans-passive region to give 50mA/cm^2 current density for 1 minute. The small number of relatively large pits seen in Fig. 9 have resulted from the presence of non-metallic inclusions. The avoidance of such pits highlights the importance of producing "clean" steel.

The passivation behaviour of 4 cast stainless steels in the solution heat treated condition is shown in Fig. 12 in the form of potentiostatic scans obtained during testing in de-aerated stirred 0.1M H_2SO_4 using a saturated calomel electrode (SCE) as reference. The steels, whose compositions are also shown, were produced and heat treated in industry. Steels A, D and C are duplex grades while steel B is austenitic containing some 15-20% ferrite. The duplex steels were water quenched from 1175°C and then stress relieved at 350°C. Steel B was water quenched from 1150°C and does not normally require subsequent stress relief. Corrosion data from these curves is given in Table II as values for E_{pp}, i_{crit} and i_{pass} together with the ACI alloy type designation of each steel.

E_{pp} indicates the peak passivation potential at which the maximum rate of anodic dissolution occurs at a critical value of the current density i_{crit}. The smaller the value of i_{crit} the greater is the tendency for the alloy to passivate. Once passivation has occurred the minimum rate of corrosion in this state is indicated by i_{pass} [36], [37]. As the potential becomes more positive there is a rapid rise in the current density and pitting can occur: this is called the transpassive region. For ease of passivation of a steel (i.e. reduced corrosion rate) a combination of a more negative E_{pp} and low values of i_{crit} and i_{pass} and a wide passive range is required.

Also given in Table II are the equivalent data from steel A (CE8Mn) in the as-cast condition. The data shows that solution heat treatment of this steel has reduced the current density i_{crit} for passivation from 125 to 100 µA/cm^2 and i_{pass} from 60 to 30 µA/cm^2.



Steel	C	Ni	Cr	Cu	Mo	N	W
A	0.055	6.14	25.8	2.08	3.26	0.19	-
B	0.049	9.58	19.7	0.28	2.27	0.06	-
C	0.030	5.97	22.1	0.76	3.15	0.18	-
D	0.030	7.15	25.3	0.81	3.94	0.27	0.75

Fig. 12. Potentiostatic scans in 0.1M sulphuric acid

TABLE II
DATA FROM FIGURE 12 WITH EQUIVALENT VALUES FOR STEEL A IN THE AS-CAST CONDITION

Steel	Alloy Type	E_{pp} (mV v SCE)	i_{crit} (µA/cm^2)	i_{pass} (µA/cm^2)
A	CE8MN	-150	100	30
B	CF8M	-250	140	27
C	CD3MN	-200	90	6
D	CD3MWCuN	-150	78	23
A (As-cast)	CE8MN	-160	125	60

As explained earlier solution heat treatment takes any damaging intermetallic phases such as sigma that are formed in the as-cast structure into solution at high temperature with subsequent rapid cooling by water quenching preventing their reformation. It also allows homogenization of the distribution of alloy elements in solid solution in the austenite and ferrite phases. Stress relief treatment at 350°C does not normally result in any subsequent precipitation of carbides or other phases.

The austenite grade (steel B) shows similar passivation behaviour to the duplex grades but, for service applications, it is disadvantaged by low yield strength (0.2% proof stress) of 337 MPa when compared to the duplex grades. Steels A, D and C have yield strengths of 667, 544 and 617 MPa respectively.

The PREN values calculated from composition for the four steels are as follows: for A-40, B-28, C-35 and D-43. For the duplex grades these values suggest that steel D should show better passivation than steels A and C. However, steel C with the lowest alloy content of the duplex grades had the smallest value of i_{pass}. For the solution treated condition, steel

A showed a higher i_{pass} value than the C and D. This was due to its higher %C content of 0.055wt.% and the presence of patches of carbide precipitation in some ferrite regions in the microstructure. Consequently, during testing this steel suffered from pitting damage. The dual-peak nature for passivation potentials seen in the scans is most likely due to the presence of both austenite and ferrite in the microstructures but needs further study together with why the leaner duplex grade steel C showed unusually better passivation than the super-duplex grade steel D.

The tendency for secondary phase formation in duplex grades, as indicated by Fig. 6, provides a complex problem and in practice means that these grades cannot be used at temperatures above 350°C. Secondary phase formation significantly reduces toughness. Work on wrought 22Cr-5Ni-3Mo duplex has shown that the V-notch Charpy toughness falls from 150-175J to 100J when 0.5% volume fraction of secondary phases are present. For 1% of second phases the impact toughness falls sharply to 50J and to below 25J when 2% or more is present [38]. Similar levels of reduction are expected in cast grades.

To characterize the various secondary phases that may form during solidification and heat treatment transmission electron microscopy coupled with advanced micro-analytical procedures are necessary. For example, the transformation sequence and types and compositions of complex carbide and secondary phases formed in a 22Cr-3Mo-6Ni duplex casting grade have been identified [39]-[41]. Figs. 13-Fig. 15 show how atomic number contrast in back scattered electron SEM images can reveal the phases present in a 0.37C-22Cr-6Ni-3Mo-0.2N-0.75Cu duplex steel in the as-cast, solution treated, and after holding post-solution treatment for 16h at 900°C. The phases seen in Fig. 13-Fig. 15 have been identified by TEM electron diffraction as ferrite (δ), primary austenite (Υ_1), secondary austenite (Υ_2), sigma phase (σ) and chi (χ) [40], [41].

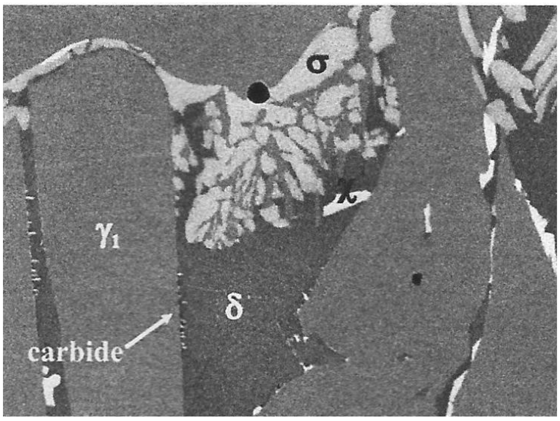


Fig. 13. As-cast microstructure of duplex SS showing various phases identified (SEM BSE x1000) [40].

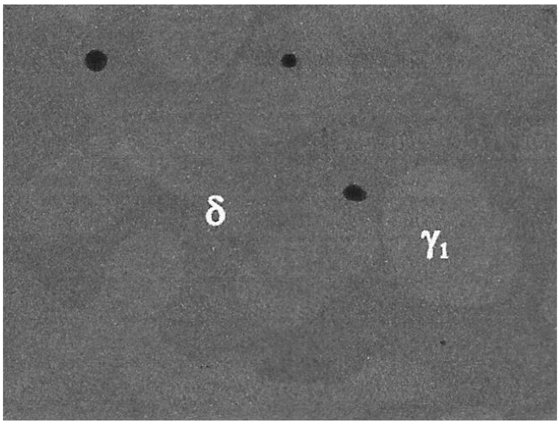


Fig. 14. Correctly solution treated condition (Water quenched from 1175°C. Only ferrite (δ) and austenite (ϒ) are present (BSE SEM view x1000) [40].

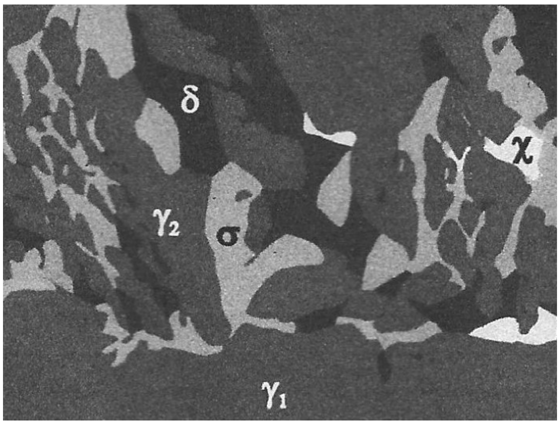


Fig. 15. Phase present after holding at 900°C for 16h (BSE SEM view x1000) [40].

V. CONCLUSION

In producing any stainless steel casting, the surface condition, cleanliness, soundness and freedom from other defects such as laps or tears are significant. Non-metallic inclusions may lead to localized pitting. Micro-porosity reduces pressure tightness and provides pathways for corrosion, and as for rough surface finish, may lead to increased rate of erosion-corrosion in pumps or impellors. Heat treatment, any weld repair and post-weld heat treatment must all be correctly carried out.

In S.E. Asia, some steel jobbing foundries often encounter difficulties when asked to produce corrosion resistant replacement parts for equipment which, having originally been manufactured overseas, now needs repair. In such cases low cost is often the major consideration, and if the relevant metallurgical and corrosion aspects are ignored, then the end result may be early or catastrophic failure in service with serious safety and financial consequences. Foundries must understand any customer requirements for castings that require particular corrosion resisting properties.

In Thailand the domestic demand for steel products (both long and flat) in 2018 was approximately about 17 million tones. For these, the domestic production was only 40% [42]. The demand for stainless steel, especially shaped casting products will increase with the demand for electric vehicles and the promotion of mega infrastructure investments such as the three airports rail links and other smart city transportation projects [43]. Thai stainless steel foundries need to apply good manufacturing practices in order to be able to compete with the imported products from China, Japan, Malaysia, Taiwan, and South Korea. Appropriate pre and post-treatment controls denoted in the paper should be able to provide guidelines on cast stainless steels for operation and quality assurance in the workplace.

Due to the complex nature of observed corrosion damage and electrochemical corrosion data which in turn are influenced by composition, casting section thickness and heat treatment, there is still considerable scope for further research on cast stainless steels. Microstructures in castings are coarser, contain both macro and micro-forms of segregation and can contain a greater variety of intermetallic phases when compared to wrought grades, hence, in addition to more intense corrosion studies, there is a need for improved melt treatments to refine primary grain sizes, detailed microstructural TEM characterization especially of the fine carbide/nitride precipitates and other intermetallics that may form, and optimization of weld repair and heat treatment conditions. For example, probe techniques such as Scanning Kelvin Probe Force Microscopy (SKPFM) which have been successfully used to obtain valuable data in wrought duplex steels need to be applied to study casting grades [44].

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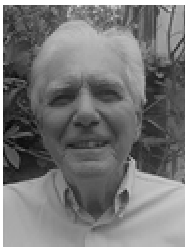

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