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Chapter 5

Duplex Stainless Steels: Effect of Reversion Heat Treatment

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.80007

Abstract

Duplex stainless steels present good corrosion resistant and mechanical properties hence they are being used in various pressure boundary components of nuclear power plants such as primary coolant pipes, valves and pump bodies because of the presence of the dual microstructure which consists of equal amounts of austenite and α-ferrite phases. The ratio of austenite and α-ferrite phases mainly depends on the chemical composition. However, when DSS are subjected to the service temperature range of about 300–500°C they undergo embrittlement due to spinodal decomposition of highly alloyed ferrite matrix into iron rich (α) phase and chromium rich (α') phase. The embrittlement significantly affects impact toughness, tensile strength, ductility, fracture toughness and fatigue behavior limiting the industrial applicability of this steel to temperatures below 280°C. In this chapter, the basic overview of duplex stainless steels and the effect of reversion heat treatment on the thermally embrittled duplex steel is discussed.

Keywords: duplex stainless steels, 475°C embrittlement, reversion heat treatment, alpha and alpha-prime precipitates

1. Introduction

Stainless steels are alloys of iron containing at least 11% chromium by weight. They exhibit superior corrosion resistance compared to other steels mainly due to the passive film of chromium oxide which forms on the surface. However, in order for a stainless steel to retain its "stainless-ness" in aggressive chemical environments, larger amounts of chromium need to be added to the alloy [1]. In addition to chromium, other alloying elements such as nickel, molybdenum, manganese, nitrogen etc. are also added in order to provide better resistance to different

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forms of corrosion. Some alloying elements are also added to enhance mechanical properties and weldability without compromising on the corrosion resistance [2]. Stainless steels can be classified into five groups based on their microstructures: ferritic, austenitic, martensitic, duplex and precipitation hardening stainless steels [3].

Duplex stainless steels (DSS) have a microstructure consisting of ferrite and austenite in nearly equal proportions and exhibit better corrosion resistance and mechanical properties in comparison to single phase stainless steels [4]. They provide excellent resistance to pitting corrosion and stress corrosion cracking even in chloride environments. DSS can be classified into three families based on their pitting resistance equivalent numbers (PREN). They are: "lean duplex" alloys having a PREN slightly higher than that of austenitic stainless steel grades and contain up to 20 wt% Cr and no molybdenum, "standard duplex" alloys with around 22 wt% Cr and 3 wt% Mo, having a PREN lying between 33 and 36, and, "superduplex" alloys with more than 25 wt% Cr, 3.5 wt% Mo and 0.2–0.3 wt% N, with a PREN greater than 40. Recently, special grades called "hyperduplex" stainless steels with much higher chromium and nitrogen levels have also been developed [5].

DSS find applications in various industries which involve hostile environments and such as chemical and petrochemical, oil and gas, pulp and paper, power generation, hydrometallurgy, marine transportation, construction etc. which involve hostile environments. A major limiting factor in the applicability of DSS is their susceptibility to thermal embrittlement when exposed to temperatures in the range of 280–525°C. This form of embrittlement is popularly known as "475°C embrittlement" since the rate of embrittlement within this temperature range is maximum at 475°C [6]. The embrittlement is believed to be because of the formation of Cr-rich precipitates called "α'" in the ferrite phase. The embrittlement is accompanied by a drop-in corrosion resistance because of the depletion of chromium levels within the ferrite phase and around the precipitates [7].

Studies conducted on ferritic and duplex stainless steels have shown that the changes in microstructure and mechanical properties associated with the 475°C embrittlement can be undone by subjecting the material to a short term "reversion" heat treatment within the range of 550–600°C [8]. Although the effect of subjecting a 475°C embrittled DSS to reversion heat treatment has been studied by investigators in the past. In our investigation the focus was mainly on the recovery of microstructure and mechanical properties. However, when cast austenitic stainless steels are exposed to the 550°C or higher for a long time, various types of detrimental intermetallic phases, such as sigma (σ) phase, Chi (χ) phase, R phase, and M23C6 carbides could be formed in the ferrite phase or at ferrite phase boundaries. As a result, the mechanical properties will be significantly degraded. Therefore, to apply the reversion heat treatment to alleviate the thermal aging embrittlement, the possibility of inadvertent embrittlement of DSS by the reversion heat treatment has been carefully investigated. However, it was not completely clear that how these microstructural changes translate on mechanical properties of DSS and vice-versa. In addition, there was a concern that the recovered DSS after the reversion heat treatment could be re-embrittled faster when it is subjected to the service temperature of nuclear power plants [9]. Therefore, understanding the re-aging behaviors of the recovered DSS is also important to determine the applicability of the reversion heat treatment. In this regard, the Scope of present work was aimed to develop an economic approach to extend the service life of long term working duplex stainless steel components which are susceptible for embrittlement.

http://dx.doi.org/10.5772/intechopen.80007

2. Duplex stainless steels: development and applications

The development of stainless steels began in the early twentieth century in the United Kingdom and Germany. The austenitic Fe-Cr-Ni steels became the largest group of stainless steels even though the earliest grades were martensitic and ferritic Fe-Cr steels. The minimum carbon levels in these steels were high (around 0.08%), due to existing furnaces and refining techniques, making them prone to grain boundary carbide precipitation during heat treatment and welding, and sensitive to intergranular corrosion attack.

The first reference to Fe-Cr-Ni duplex stainless steels with between 30 and 70% ferrite was made by Bain and Griffith in 1927. Soon after, several countries explored such steels in cast form. The first commercial duplex stainless steel product, a grade called 453E, was made in 1929 with an approximate composition of 25%Cr–5%Ni followed by a modified grade, 453S, with 25%Cr–5%Ni–1%Mo which was marketed in 1932. Applications in the form of castings involved autoclaves for gunpowder production and valves for sulfide pulping and as coolers of the Brobeck type in the form of plate and forgings. By the late 1940s, duplex stainless steels with high volume fractions of ferrite in an austenitic matrix, which were not sensitive to intergranular corrosion (IGC) even in the most aggressive media were available and marketed simultaneously in France, Sweden and the USA.

Development of low nickel-content duplex alloys was encouraged due to nickel shortage following the Korean War in 1950–1951, and it became apparent that a balance of ferrite and austenite provided better resistance to stress corrosion cracking (SCC) in chloride medium than fully austenitic grades. In France a grade with 20–35% ferrite called UR50 (UNS32404) was marketed in various forms for industries such as oil refining, food processing, pulp and paper, and pharmaceuticals. These steels were produced in high frequency induction furnaces with a partial vacuum that ensured carbon removal, rudimentary de-oxidation and restricted nitrogen ingress.

The understanding of the physical metallurgy of DSS had not progressed sufficiently to offer a material having good ductility and toughness that was easy to manufacture and fabricate. This gave them a reputation for crack sensitivity until the 1960s. During the late 1960s and early 1970s, there was another nickel shortage and pushed the price of austenitic alloys. With the introduction of vacuum and argon oxygen decarburization practices, steel production techniques had improved dramatically, leading to steels with low carbon, sulfur and oxygen contents along with greater control of nitrogen content. The maximum carbon content in the UNS S31500 was 0.03%. The chemical composition was controlled to optimize the ferrite-austenite phase balance and to enhance resistance to SCC. The addition of nitrogen improved corrosion resistance and stability of austenite in the heat affected zone (HAZ). However, they were still susceptible to IGC under certain conditions due to high Cr/Ni equivalent ratio, which led to an almost fully ferritic HAZ after welding. Carbides and nitrides precipitated along grain boundaries because of the very low solubility of carbon and nitrogen in ferrite. Higher levels of nickel and nitrogen were added to overcome this problem and the IGC resistance was significantly improved.

Through the 1970s and 1980s, several duplex grades were developed with emphasis on improved weldability and better resistance to corrosion in aggressive environments. Highly alloyed duplex grades such as the UNS S32550 with 25% Cr and up to 2% Cu, were developed as castings such as pumps and valves, and have been used extensively in the offshore

industry and for sulfuric acid service. The superduplex grades containing about 25%Cr, 6–7%Ni, 3–4%MO, 0.2–0.3%N, 0–2%Cu and 0–2% W have pitting resistance equivalent numbers (PREN) greater than 40. In making superduplex alloys, care was taken to balance the Cr and Ni forming elements and higher levels of nitrogen were added. These factors stabilized the HAZ during welding, but promoted intermetallic precipitation [10].

In recent years duplex grades have emerged as an alternative to austenitic grades such as 316 and 304. Lean DSS are used in bridges, storage tanks and also for construction of transport vehicles. Superduplex grades such as Zeron 100 (UNS S32760) were developed to compete with superaustenitic grades and are used in large quantities in umbilicals for the control of sub-sea systems. DSS have also replaced austenitic grades in flue gas cleaning systems and desalination plants .

In natural gas pre-heaters, S32304 are selected for exchanger tubing where low grade steam is used for heating purposes. For applications where higher chloride contents are present, tubing is made from S31803/S32205. This grade is also used for reactors, storage tanks and heat exchangers in the production of detergents comprising of fatty amines and chlorides, in plastic production, in steam sterilization of bi-products of sodium cyanide production and so on. Cast 32550 is used in phosphoric and sulfuric acid production and also as stud bolts in ammonia injectors and valve internals in urea recycle lines.

Grade S31803/S32205 has been extensively used for the construction of advanced chemical tankers for marine transportation since 1987. Duplex grades are also used as propeller shafts, thrusters, water jet engines and other components subjected to high mechanical loads. Superduplex grades such as S32760 are used in pumps to handle potash at around 80°C and hot bauxite slurry in the Bayer process. Other uses for this grade include pipe work in a titanium dioxide refinery for spent hydrochloric acid lines. Low alloy grades such as S32304 are selected for water heaters, calorifiers and hot water tanks in breweries and similar industries. The cast DSS of the CF series finds applications in nuclear power plants for reactor coolant and auxiliary system piping [10].

3. Metallurgy of duplex stainless steels

During solidification of the DSS melt, the first solid that forms is δ-ferrite. As the temperature drops, austenite formation takes place. After complete solidification, the microstructure is that of austenite islands in a matrix of ferrite. The volume fraction of ferrite-austenite depends on the chemical composition. The large amounts of alloying elements added to DSS results in the formation of various carbides, intermetallics and other secondary phases which form over different temperature ranges at varying rates (**Figure 1**).

3.1. Secondary phases

3.1.1. Sigma phase

The Sigma (ζ) phase is a Cr, Mo rich hard embrittling precipitate which forms between 650 and 1000°C is often associated with reduction in impact toughness and corrosion resistance. Since

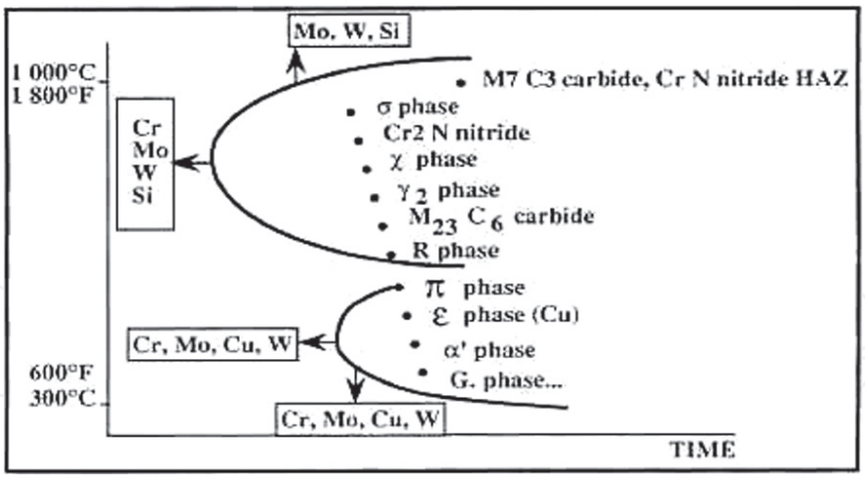


Figure 1. A schematic TTT curve for formation of precipitates in DSS and the effects of alloying elements in the temperature ranges of formation for various precipitates [10].

the mobility and concentration of Mo and Cr in ferrite is higher than in austenite, ζ-phase precipitation generally occurs in the ferrite phase. It also forms in the HAZ during welding. It has a tetragonal crystal structure with 32 atoms per unit cell and 5 different crystallographic atom sites. The morphology of ζ-phase changes with temperature. At around 750°C, it has a coral-like structure; at 950°C it is bigger and more compact [10].

The depletion in Mo content is a lot more pronounced compared to that of Cr, indicating that Mo is the main element controlling the precipitation of ζ-phase. The formation of ζ-phase is rapid and a very high cooling rate is required to avoid it formation during quenching from solutionizing temperature. For a 2205 DSS, a cooling rate of 0.23 K/s is necessary to avoid more than 1% ζ-phase formation [10].

3.1.2. Chi phase

The enrichment of ferrite with intermetallic forming elements during long term thermal exposure at temperatures around 700°C, favors the precipitation of Chi (χ) phase. It often nucleates at the δ/γ interface and grows into the δ matrix. It is difficult to study its influence on corrosion and toughness since it often co-exists with ζ-phase. Increase in aging time causes an enrichment of Mo and depletion of Fe in the χ-phase. During isothermal aging, the χ-phase always precipitates before ζ-phase, but during continuous cooling, χ-phase appears only at low cooling rates [11].

3.1.3. Secondary austenite

The mechanism and rate of formation of secondary austenite (γ_2) may vary depending on the temperature. In the temperature range of 700–900°C, typical mechanism is by the eutectoid reaction, which is facilitated by rapid diffusion along the δ/γ boundaries giving rise to ζ-phase and γ_2 in prior ferrite grains. This also reduces the Cr and Mo content in the ferrite. When Cr2N precipitates cooperatively, γ_2 has been found to be poor in Cr, making it highly susceptible to pitting corrosion. At temperatures above 650°C, at which diffusion rates are higher, γ_2 is

formed as Widmanstätten precipitates. Below 650°C, ferrite transforms to γ_2 by a mechanism quite similar to that of martensite formation. The γ_2 formed in this manner has a similar composition to the ferritic lattice thus indicating that the transformation was diffusionless [12].

3.1.4. R-phase

Isothermal treatment of duplex stainless steels between 550 and 650°C results in the uniform and very fine distribution of R-phase throughout the δ grains [11]. The R-phase is a Mo rich intermetallic having a trigonal crystal structure. Its formation reduces the toughness and critical pitting temperature in DSS. R-phase precipitates may be intergranular or intragranular in nature; the former perhaps more deleterious with regard to pitting corrosion since they may contain up to 40% Mo [12]. With the increase in aging time, R-phase transforms into ζ-phase due to diffusion of Mo from the R-phase into the ζ-phase, which eventually results in the decrease in the volume fraction of R-phase [13].

3.1.5. Chromium nitrides

The solubility of nitrogen at about 1000°C in ferrite is high, but drops on cooling and the ferrite becomes supersaturated in nitrogen, leading to the intergranular precipitation of needle-like Cr_2N. Isothermal heat treatment in the temperature range of 700–900°C usually results in precipitation of Cr_2N either on the δ/δ grain boundaries or the δ/γ phase boundaries. The hexagonal Cr_2N formed under these conditions has a negative influence on pitting corrosion resistance. In HAZ of welds, however, the cubic Cr_2N is the predominant nitride that has been observed [12]. Cr_2N precipitates display film-like or tiny platelet-like morphology.

3.1.6. Carbides ($M_{23}C_6$ and M_7C_3)

M_7C_3 forms at the δ/γ grain boundaries in the temperature range of 950–1050°C but can be avoided by ordinary quenching methods since its formation takes at least 10 min. $M_{23}C_6$ precipitates rapidly between 650 and 950°C, predominantly at the δ/γ boundaries where Cr-rich ferrite intersects with C-rich austenite. Several precipitate morphologies have been recorded including cuboidal, acicular and cellular form; each having an associated Cr depleted zone in its vicinity. Since modern duplex grades contain less than 0.02%C, carbides of either form are rarely seen [10].

3.1.7. Alpha prime

Alpha Prime (α′) is a Cr-rich precipitate that forms in the temperature range of 280–525°C [4]. The main cause for formation of α′ is the miscibility gap in the Fe-Cr system whereby ferrite undergoes spinodal decomposition into Fe-rich δ-ferrite and Cr-rich α′. Within the miscibility gap but just outside the spinodal, classical nucleation and growth of α′ occurs. The α′ precipitate has a body-centered crystal structure and is the main cause of hardening and 475°C embrittlement in ferritic stainless steels [10].

3.1.8. Epsilon phase

In duplex alloys containing copper, the supersaturation of ferrite due to decrease in solubility at lower temperatures leads to the precipitation of extremely fine particles of Cu-rich Epsilon (ε)

phase within the ferrite grains after 100 h at 500°C. This significantly extends the low temperature hardening range for duplex stainless steels. Often, ε-phase has been mistaken for γ2 due to similar temperature ranges of formation [10].

3.1.9. G, π and τ phases

The G-phase develops at α/α′ interfaces between 300 and 400°C after several hours of exposure, due to enrichment of Ni and Si at these locations [10].

The π-nitride is a Cr and Mo rich precipitate with a cubic crystal structure that forms at intergranular sites in DSS welds after isothermal treatment at 600°C for several hours [10].

The η-phase is a heavily faulted precipitate with needle-like morphology that forms due to heat treatment in the temperature range of 550–650°C. It has an orthorhombic crystal structure [11].

4. Effect of alloying elements

4.1. Chromium

The primary role of chromium in stainless steels is to improve the localized corrosion resistance, by the formation of a passive Cr-rich oxy-hydroxide film. This film extends the passive range and reduces the rate of general corrosion. The beneficial effect of adding very high levels of chromium is, however, negated by the enhanced precipitation of intermetallic phases which often lead to a reduction in ductility, toughness and corrosion resistance. Apart from this chromium also stabilizes ferrite [10]. Although, other alloying elements can influence the effectiveness of the passive film, none of them can create the properties of stainless steel, by themselves. However, it is often more efficient to improve corrosion resistance by addition of other elements, with or without increasing the chromium content to ensure that the mechanical properties, fabricability, weldability or high temperature stability remain largely unaffected [14].

4.2. Nickel

Nickel, when added in sufficient quantities, stabilizes austenite; this greatly enhances mechanical properties and fabrication characteristics. Nickel effectively promotes re-passivation, especially in reducing environments and is particularly useful in resisting corrosion in mineral acids. Increasing nickel content to about 8–10% decreases resistance to SCC, but on further increase, SCC resistance is restored and is achieved in most service environments at about 30% Ni [14].

In order to maintain 40–60% ferrite, balance austenite in DSS, the ferrite stabilizing agents need to be balanced with the austenite stabilizers. For this reason, the level of nickel added to a DSS will depend primarily on the chromium content. Excessive nickel contents may enhance intermetallic precipitation when the alloy is exposed to the temperature range of 650–950°C, due to enrichment of ferrite in Cr and Mo. High Ni contents also accelerate α′ formation. Although nickel does have some direct effect on corrosion properties, it appears that its main role is to control phase balance and element partitioning [10].

4.3. Molybdenum

Molybdenum, in combination with chromium, effectively stabilizes the passive film in the presence of chlorides. Molybdenum is effective in increasing the resistance to the initiation of pitting and crevice corrosion [14]. Its effect on ferrite stability is similar to that of chromium. To prevent ζ-phase formation in the hot working temperature range, i.e. above 1000°C, the upper limit of Mo addition of is limited to about 4%, since Mo is the main element controlling the precipitation of ζ-phase.

4.4. Manganese

Although manganese acts as an austenitic stabilizer in austenitic stainless steels, mixed results have been obtained for DSS in which it has little effect on the phase balance. It appears that Mn increases the temperature range and formation rate of ζ-phase. Manganese increases abrasion and wear resistance and tensile properties of stainless steels without loss of ductility. Further, Mn increases the solubility of nitrogen, thus allowing for higher nitrogen contents. However, Mn additions in excess of 3 and 6%, for nitrogen levels of 0.1 and 0.23% respectively, significantly decrease the critical pitting temperature (CPT). Nevertheless, the combination of Mn and N in modern DSS improves the pitting resistance and counteracts the singular problems associated with Mn [10].

4.5. Nitrogen

Nitrogen enhances pitting resistance by retarding the formation of ζ-phase and diminishes Cr and Mo segregation and also raises the corrosion resistance of the austenitic phase in DSS [14]. Nitrogen has also been reported to increase crevice corrosion resistance. Nitrogen strengthens austenite by dissolving at the interstitial sites in solid solution. Addition of nitrogen to DSS, suppresses austenite dissolution and encourages austenite reformation in the HAZ [10].

4.6. Copper

Copper reduces the corrosion rate of high alloy austenitic grades in non-oxidizing environments, such as sulfuric acid. In some DSS with 25% Cr, 1.5% Cu is added to obtain the optimum corrosion resistance in 70% H_2SO_4 at 60°C. For boiling HCl, an addition of 0.5% Cu decreases both active dissolution and crevice corrosion rates. Copper additions in DSS are limited to about 2%, since higher levels, reduce hot ductility and can lead to precipitation hardening. Exposure at temperatures between 300 and 600°C can lead to precipitation of tiny Cu-rich precipitates which do not significantly reduce corrosion resistance or toughness but can be exploited for improving abrasion-corrosion resistance in duplex pump castings [10].

4.7. Tungsten

Up to 2% tungsten additions have been made in DSS to improve pitting resistance. Tungsten also increases crevice corrosion resistance in heated chloride solutions. Tungsten encourages intermetallic formation in the 700–1000°C temperature range, and also encourages γ_2 formation in weld metal. Thermodynamically, it is believed to be equivalent to Mo with respect to ζ-phase formation, but this is not the case in terms of kinetics. Levels between 1 and 3% have

been shown to restrict ζ-phase formation to the intergranular sites instead of phase boundaries; the influence of the large tungsten atom on the diffusion of Mo and W at the phase boundaries is thought to be the reason. Tungsten alloyed weld metal has been shown to form χ-phase more rapidly than in welds without W additions. Generally, the tungsten content is limited to 1% in a 4% Mo DSS, and 2% in DSS with about 3% [10].

4.8. Silicon

Silicon enhances high temperature oxidation resistance and is also beneficial for concentrated nitric acid service. DSS bearing high silicon (3.5–5.5%) have enhanced pitting corrosion resistance and a claimed immunity to SCC. However, it is preferred to limit Si additions to 1% since Si is generally considered to enhance ζ-phase formation [10].

4.9. Carbon, sulfur and phosphorous

The carbon content of most wrought DSS is limited to 0.02 to 0.03%, primarily to suppress precipitation of Cr-rich carbides along the grain boundaries. Sulfur and phosphorous contents are controlled but not eliminated. The presence of S is important for weld bead penetration. Modern steel making processes such as argon oxygen decarburization (AOD) and vacuum oxygen decarburization (VOD) help in controlling the levels of S and C, while P contents can be reduced by using good melting practice [10].

5. Effect of heat treatment

5.1. Solution annealing

Element solubility in ferrite falls with decreasing temperature, increasing the probability of precipitation during heat treatment. During solidification, DSS solidifies completely as ferrite and then undergo solid state transformation into austenite. This is a reversible process and as a result, any large increases in temperature above 1000°C lead to an increase in ferrite and also a reduction in the partitioning of substitutional elements between phases. In addition, ferrite becomes enriched in interstitial elements such as carbon and nitrogen.

Heat treatment in the temperature range 1100–1200°C can have a dramatic influence on the microstructure of a wrought product. Prolonged treatment at high temperatures can lead to equiaxed grains, whereas, cooling at intermediate rates can render the grains acicular, with Widmanstätten morphology. Step quenching, with or without simultaneous mechanical strain can lead to a dual structure, consisting of both coarse and fine austenite grains.

Duplex alloys with high contents of Cr, Mo and W are most susceptible to intermetallic precipitation. Mo and W extend the stability range of intermetallics to higher temperatures. For this reason, higher solution annealing temperatures, i.e. above 1000°C are necessary. In order for the precipitates to re-dissolve, solution annealing temperatures for superduplex grades must be performed at 1050°C and above. For grades such as S32550 and S32750, a few minutes at 1050–1070°C are sufficient, whereas, for tungsten bearing grades such as S32760, 1100°C has been recommended [10]. Li et al. [15], during their investigation of a

hyper duplex stainless steel without W additions, solution annealed the samples at 1100°C for 1 h and obtained a microstructure of ferrite and austenite with no secondary phases. Jeon et al. 2012 solution treated a hyper duplex alloy with high W additions at 1090°C for 30 min and found no secondary phases.

Figure 2 shows the SEM micrograph of the as-received S2205 DSS in the wrought form in which austenitic islands are embedded in the ferritic matrix with some undissolved precipitates. Hence, in order to dissolve these harmful precipitates samples were subjected to solution heat treatment by heating it to 1110°C for 60 min. The solution heat treatment was also done to adjust the austenite and ferrite phase proportions which can be seen in the **Figure 3**. If any macro segregations are present in the sample the solution heat treatment will help to eliminate them [16].

5.2. The 475°C embrittlement

Duplex stainless steels (DSSs) have high strength, excellent corrosion resistance and good weldability, and are thus widely used in primary circuit piping of pressurized water nuclear reactors (PWRs). However, after long-term service at temperatures ranging from 280 to 450°C, DSS are subjected to thermal aging embrittlement. The thermal aging embrittlement has caused the degradation of DSS in impact toughness, corrosion properties, and fatigue properties. So far much attention has been paid to the structural integrity assessment and life prediction of aged DSS components subjected to thermal aging embrittlement.

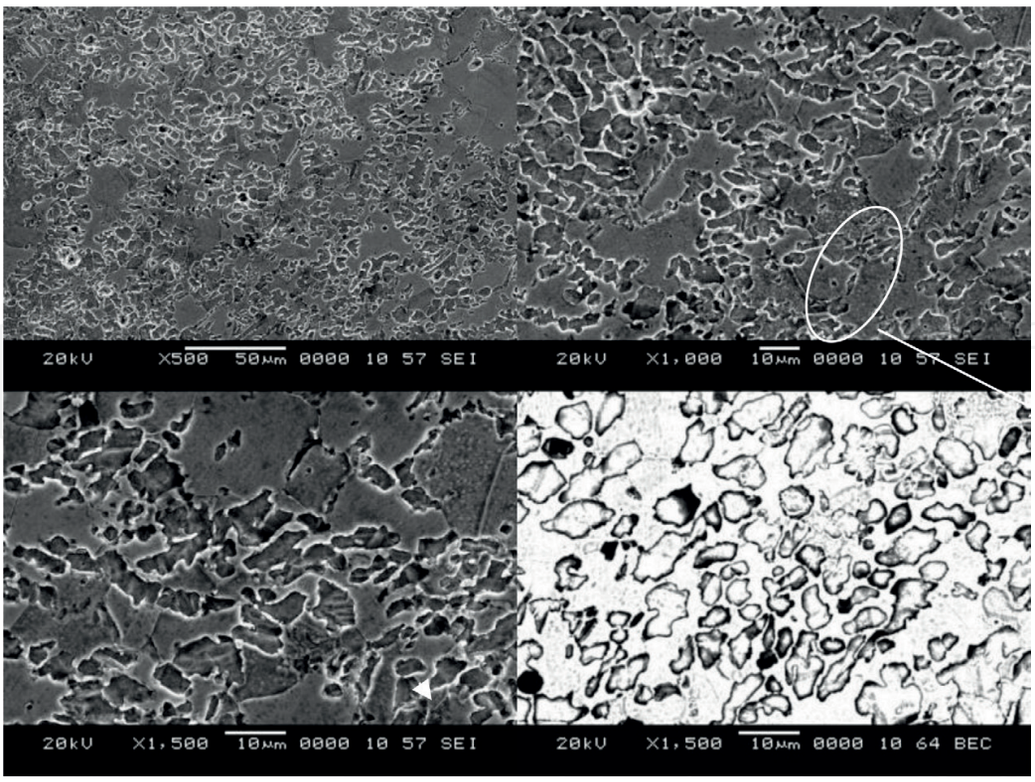


Figure 2. Microstructure of as received S2205 duplex stainless steel sample (Etchant:Beraha's tint etch).

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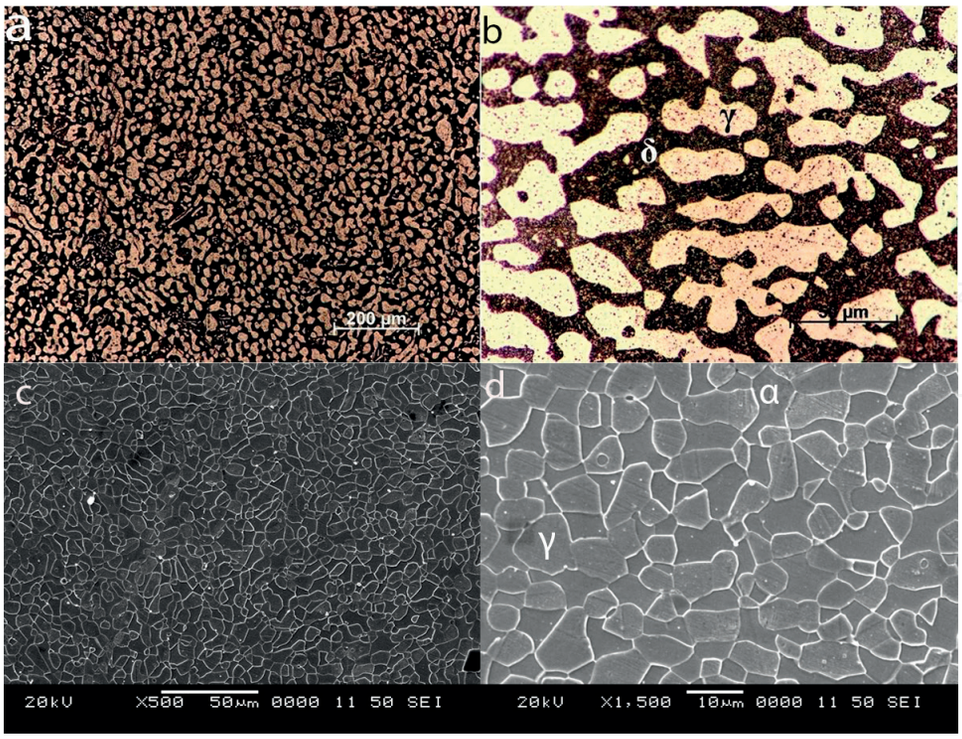


Figure 3. Microstructure of S2205 after solution heat treatment (a) OM image of distribution of austenite grains in the ferrite matrix (magnification: 100×). (b) OM image of phase morphology (magnification: 500×).

Early studies indicate that the thermal aging embrittlement of DSS is due to spinodal decomposition that ferrite phases decompose into coherent Cr-enriched α' and Fe-rich α. It is well known that spinodal decomposition in ferrite of DSS leads to loss in toughness, increase in ferrite hardness and little or no change in tensile properties. In addition, the spinodal decomposition is also accompanied by the chromium nitrides and G-phase precipitation in the ferrite phases.

William [17] was the first to analyze the existence of miscibility gap in iron-chromium phase diagram in the temperature range of 280–500°C because of formation of α' precipitate in the ferritic phase due to the spinodal decomposition as shown in **Figure 4**. According to this phase diagram 475°C embrittlement would occur in the temperatures below 516°C in the composition range of 12–92 at. % chromium in the iron chromium binary alloy system. Blackburn and Nutting [18], Reidrich and Loib [19], completely redissolved the α' in the ferritic steels after 24 h of aging at 550°C. Vintaikin and Loshmanov [20] in his neutron diffraction studies confirmed the clustering and decomposition of ferritic phase in the temperature range of 280–500°C.

Cahn [21] and Hilliard [22] made some critical reviews on the theory of decomposition in metastable ferritic alloys The reviews included the thermodynamical distinction within the miscibility gap in: (a) spinodal decomposition; (b) nucleation and growth of α'. Spinodal decomposition refers to a reaction where two phases of the same crystal lattice type, but different compositions and properties, form due to the existence of a miscibility gap in the alloy system by means of uphill diffusion without nucleation. Thermodynamically this is possible at concentration between the points where the second derivative of the free energy with composition equals zero. This phase separation process occurs at a very fine scale (of the order of

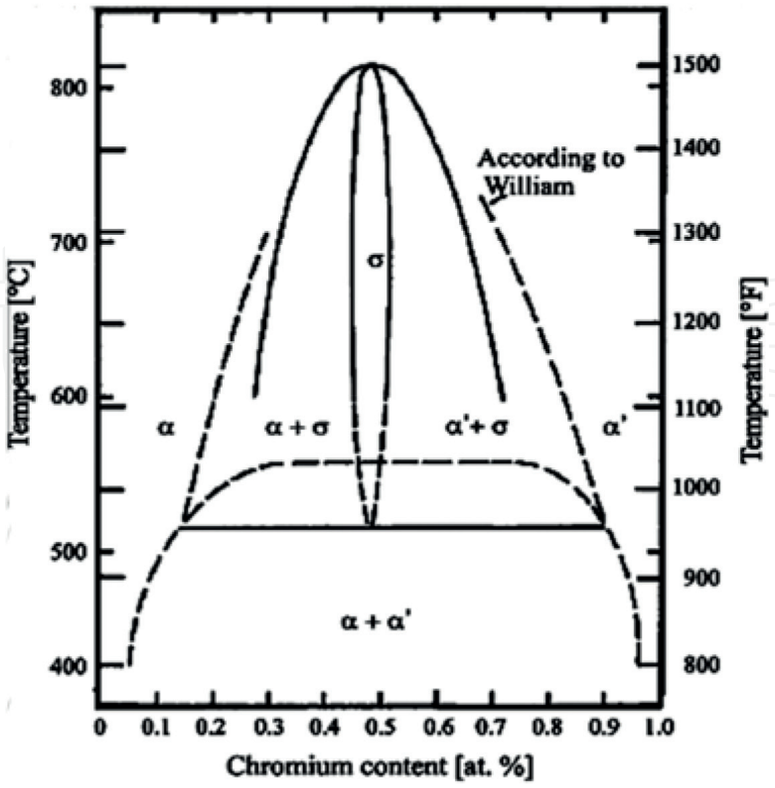


Figure 4. Phase diagram of the iron-chromium binary system.

only a few nanometers) and the presence of the α' phase can only be detected through an atom probe field ion microscope [23, 24]. According to Cahn [20] there should be no change in molar volume with composition in an infinite isotropic solid free from imperfections in order to have spinodal decomposition. So the sustainability of spinodal decomposition is very stringent for a multi component ferritic phase as in DSS, where many alloying elements other than chromium are partitioned to the ferritic phase. Chandra and Schwartz [25] tried to calculate the solubility of chromium in iron in the temperature range of 280–500°C and predicted the boundaries within the miscibility gap for spinodal decomposition, nucleation and growth. The coherent spinodal line in the diagram is the corrected chemical spinodal, taking into account the elastic strain energy due to 0.6% difference in the atomic size of iron and chromium. R.O. Williams. [17] studied the Mossbauer effect of 475°C embrittlement of a series of iron–chromium binary alloys by varying the chromium content and estimated the solubility of chromium in iron to be 12 wt. % at 475°C. They predicted that only alloys with chromium content in excess of 12 wt. % exhibit 475°C embrittlement. Another important observation was that alloys with chromium content 12–30 wt. % decomposed via a nucleation and growth mechanism.

Shamanth et al. found drastic increase in tensile strength and decrease in ductility due to the embrittlement associated with the formation of α and α' precipitates in the ferrite phase for the samples aged at 475°C for 1000 h as depicted in the **Figure 5** where the mottled contrast in the ferrite matrix at nano-scale indicates the presence of Fe-rich α and Cr-rich α' precipitates formed by the spinodal decomposition [5]. It is difficult to distinguish between α and α' precipitate from HR-TEM results even at higher magnifications because both α and α' precipitate had similar lattice parameter as that of Fe [9]. Also in this investigation they found that the α' precipitate associated with the coprecipitation of Cr2N precipitates in the ferrite matrix.

http://dx.doi.org/10.5772/intechopen.80007

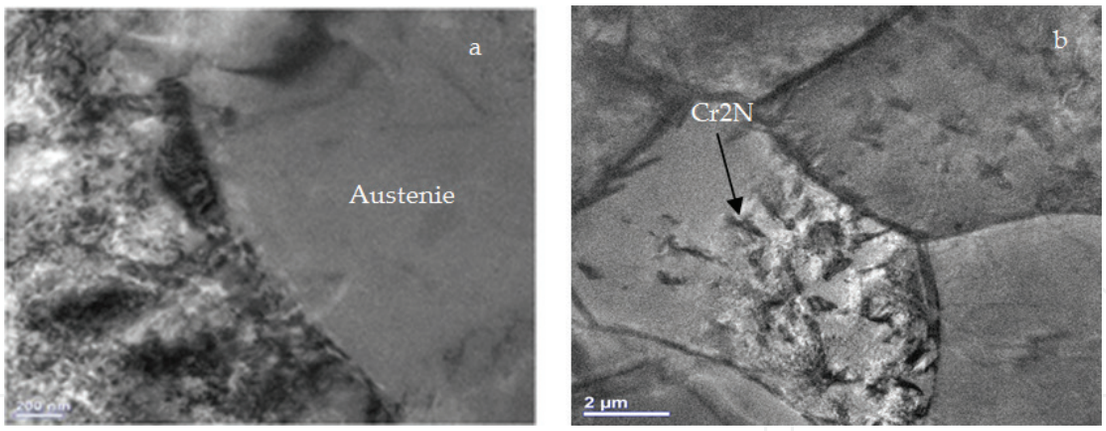


Figure 5. HR-TEM image of 1000 h aged sample showing (a) the mottled contrast ferrite region and precipitate free austenitic phase. (b) the morphology of Cr2N precipitates in ferrite matrix.

5.3. Mechanism of recovery

According to Fe-Cr phase diagram, the spinodal decomposition in ferrite is due to the presence of the miscibility gap in the Fe-Cr system. The spinodal decomposition in the ferrite matrix takes a very long time because of the low atomic mobility at lower temperature (400°C). However the reversion heat treated temperature 550°C is above this ($\alpha + \alpha'$) miscibility gap, the ferrite gets homogenized again or in other words ($\alpha + \alpha'$) will become thermodynamically unstable and dissolve quickly inside the ferrite matrix when they are heat treated at 550°C for shorter duration i.e. maximum of about 60 min. If the time exceeds beyond 60 min there is a possibility for the formation of other intermetallic phases like R-phase, σ-phase or γ-phase. [16]

On subjecting the embrittled specimens to reversion heat treatment at 550°C, it was observed that the strength dropped while the ductility increased, owing to the dissolution of α and α' precipitates into the ferrite matrix as seen in the **Figure 6**. The mechanical properties obtained for Reversion heat treated samples are shown in the **Table 1**. After 30 and 45 min of reversion

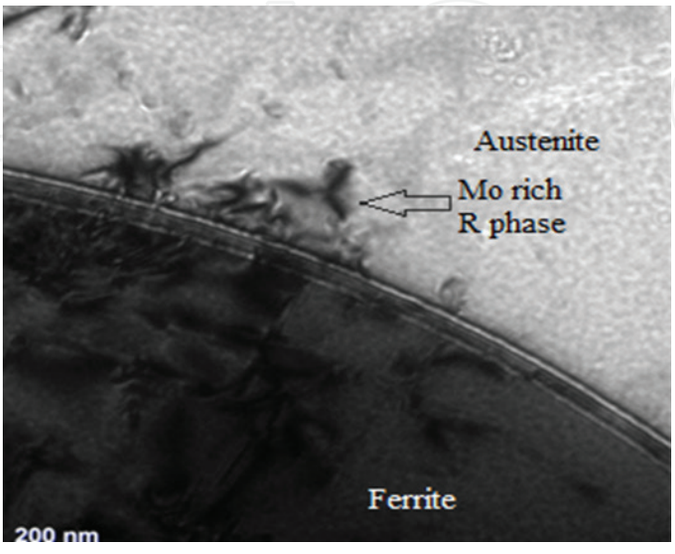


Figure 6. HR-TEM image of 60 min reversion heat treated sample showing clear austenite phase and ferrite phase with R-phase.

Heat treatment	%RE	σ_{ys}(MPa)	%RE	σ_{uts} (MPa)	%RE	Ductility (%)	%RE	Impact value (J)
Solutionized	—	458	—	729	—	42	—	270
Aged-700 h	—	961	—	1261	—	18	—	6
RHT-15 min	20	730	46	935	61.3	31	45.8	140
RHT-30 min	28.9	609	70	842	78.8	38	75	190
RHT-60 min	94.3	528	86	780	90.4	39	80	250
RHT-90 min	36.6	610	69.7	785	89.4	34	96	200
RHT-120 min	26.8	632	65.4	854	76.5	34	96	190
Reaged-25 h	—	502	—	802	—	25	—	90
Reaged-50 h	—	548	—	825	—	24	—	80
Reaged-75 h	—	609	—	892	—	24	—	78
Reaged-80 h	—	861	—	1032	—	19	—	10
Reaged-90 h	—	982	—	1125	—	19	—	6
Reaged-100 h	—	993	—	1208	—	18	—	6

Table 1. Mechanical properties of all heat treatments conducted.

treatment, the decrease in strength was marginal, whereas, the increase in ductility was significant. The material exhibited a further drop in strength and increase in ductility for 60 min of reversion, after which, both the strength and ductility remained more or less constant. The reversion treatment, however, was unable to completely restore the properties of the material back to those corresponding to the un-aged or solution annealed condition. The yield strength was more sensitive to reversion heat treatment, varying much more than the tensile strength with respect to duration of reversion heat treatments. It is because of the further embrittlement that occurred simultaneously with the dissolution of α and α' precipitates, during reversion heat treatment and, as a result, the mechanical properties were not fully recovered. The temperature range of the reversion heat treatment is favorable for the formation of a Mo-rich precipitate called R-phase, which is known to be an embrittling phase [11], and in fact, previous investigators [12], had found unidentified Mo-rich precipitates in super-duplex stainless steels reversion treated for 30 min at the same temperature as in the current investigation. Another possible reason for this behavior could be residual inhomogeneities in the ferrite grains as a result of the Cr and Mo atoms that were part of the precipitates might have been redistributed. This in turn may have resulted in the formation of dislocation substructures in the ferrite grains during deformation. From the results it was also very clear that after 75 min reversion treatment the strength was again increasing and the ductility was decreasing because of the embrittlement caused by the R-phase and secondary austenite which were quantitatively seen in **Figure 6** (TEM micrograph for 120 min reversion heat treated sample). The measured values of ultimate tensile strength and % elongation for re-aged conditions are given in **Table 1**.

6. Conclusion

From the studies we can conclude that the DSS are susceptible for various intermetallic phases when subjected to temperatures of around 300–500 °C. The intermetallic phases formed are Fe-rich α and Cr-rich α' precipitate because of the spinodal decomposition and also some amount of Cr_2N precipitates were seen in the aged ferritic matrix. From the reversion heat treatment technique, the alpha and alpha-prime precipitates was completely dissolved. However, when the embrittled samples are subjected to optimum reversion heat treatment temperature and time, the alpha and alpha-prime precipitates can be completely dissolved.

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