

## **CHAPTER-2**

### **LITERATURE REVIEW**

#### **2.1 EFFECT OF WELDING PARAMETERS ON WELD PROPERTIES**

##### **2.1.1 General:**

DSS and SDSS weld joint properties are mainly based on welding parameters and welding filler wire chemical composition. Welding parameters significantly influence austenite and ferrite phase formation and affect corrosion / mechanical properties of weld metal and heat affected zone (HAZ). Welding parameters include welding current, welding voltage, welding travel speed, heat input (current x voltage / travel speed), shielding gas composition / flow rate and backing gas composition / flow rate, inter-pass temperature, cooling rate etc.

##### **2.1.2 Heat Input:**

The specimen welded with heat input of approximately 0.95 kJ/mm have exhibited better corrosion properties [128] which is due to lack of formation of deleterious

phases such as sigma phases and  $\text{Cr}_2\text{N}$  and balanced ferrite-austenite proportion. Presence of sigma phase and  $\text{Cr}_2\text{N}$  decreases the corrosion potential. It was also reported that an increase in heat input from 0.506 to 0.86 kJ/mm led to a decrease in ferrite percentage and absence of detrimental phases [131]. In addition, low heat input test specimens revealed lower impact strength as compared to higher heat input test specimens. Similarly, high heat input reduces weld defects [132] and results in best quality weld, however higher heat input may alter phase balance and affect corrosion properties. In other studies, welding of duplex stainless steels under high energy conditions mode increases ferrite contents inside the fusion pools resulting reduced corrosion properties [135]. Hence, it is very important to establish appropriate weld parameters range to obtain desired quality weld.

Effect of welding parameters and weld metal chemistry were studied [138]. Apart from welding parameters such as cooling rate, heat input in deciding ferrite / austenite ratio, chemical composition of the weld were found to be more dominant on formation of phases. Henrik Sieurin and Rolf Sandstrom [141] formed a mathematical model of cooling rate and austenite reformation in heat affected zone of duplex stainless steels welded by Submerged Arc Welding. They concluded that slow cooling rate results in higher percentage of austenite formation. It was also quoted that slow cooling rates are necessary to avoid precipitation of intermetallic phases. In another studies, author concluded that the properties of welded joints are remarkably influenced by fusion zone size rather

than the produced austenite–ferrite balance. Low heat input facilitates smaller fusion zone [134].

### **2.1.3 Shielding Gas:**

In general, DSS and SDSS materials are welded using 99.99% Argon shielding / backing gas resulting loss of nitrogen in weld pool leading to ferrite rich weld metal which is inferior for corrosion resistance [22]. Introduction of 2% N<sub>2</sub> in shielding and backing gas will enhance austenite and ferrite phase balance. In addition, shielding gases will protect the molten weld pool from oxidation and detrimental hydrogen. Similar observations were reported [129] that the pitting resistance of a solution heat-treated hyper DSS after welding with argon shielding gas supplemented with N<sub>2</sub>, was greatly increased. It is due to the dissolution of Cr<sub>2</sub>N in ferrite phase, which followed the diffusion of N<sub>2</sub> atoms from the ferrite phase to the austenite phase and an increase of the austenite phase in the weld metal and heat affected zone.

Presence of Hydrogen will reduce fracture toughness properties of the weld (CTOD - Crack Tip Opening Displacement value) [29]. Argon with small amount of N<sub>2</sub> will assist improved mechanical and corrosion properties of the weld. Hydrogen induced cracking in SDSS was studied, and neither crack nor failure was observed on SDSS tubes protected with cathodic protection [36].

#### 2.1.4 Chemical composition of the weld:

Characterization and analysis of a multi pass weld joint of UNS S32750 steel welded with normal industrial standard welding parameters were studied [126]. The root pass was welded with low nickel filler metal and, therefore, resulted with low austenite content. Despite its lower austenite volume fraction (34.2%), the root pass exhibited a higher Charpy impact toughness (57 J) than the filler passes (10 J) at room temperature; this was attributed to finer microstructure of the root pass and high oxygen content of the filler passes. Although, the root pass exhibited higher impact values at the root, cyclic polarization test to measure corrosion resistance exhibited more attack on the root side than the filler passes. This is because of higher ferrite content and chromium nitride precipitates in the root area. In another study, lower Cr and Ni equivalent exhibited better austenite and ferrite phase balance (Cr equivalent:  $\%Cr + \%Mo + 0.7\% Nb$  and Ni equivalent:  $\%Ni + 35\%C + 20\%N + 0.25\%Cu$ ). High pitting resistance equivalent number (PREN) in this chemical composition exhibited lower weight loss and higher critical pitting temperature. When Cr eq. /Ni eq. value decreases, the pitting corrosion resistance after welding increases. Pit morphologies revealed that metastable pits were generated at a lower pitting resistance equivalent number (PREN) phase [130]. The secondary austenite phases seemed to serve as a path for the corrosive environment regardless of the ferrite phase. Impact toughness of the DSS materials were reduced due to lower austenite content in weld metal. It

was also observed that corrosion resistance of the welded specimen reduces in acid solution [139]

### **2.1.5 Cooling rate:**

Recent studies have found that cooling rate is one of the important parameters to achieve desired microstructure [140]. Slow cooling follows diffusion phenomenon, which leads to efficient partitioning of phases. At the same time, there are chances of precipitation of intermetallic phases with slow cooling rates. Rapid cooling leads to equal partitioning of phases (i.e. partitioning coefficient = 1 for all elements) and it may form hazardous chromium nitrides. Cooling rate depends on various parameters like heat input, material thickness, thermal properties of material, etc. Some authors found that cooling rate between 1200 to 800 °C is more critical than cooling rate in lower temperature region. In this temperature region austenite and secondary phase formation takes place [97].

It was found that reheating effect during subsequent weld passes causes formation of acicular type secondary austenite, which leads to reduction of pitting resistance [153]. It was noted that continuous network of grain boundary of austenite formed in fusion zone after faster cooling in ferrite region restricts the corrosion propagation [140].

Pitting corrosion resistance of 2304 DSS with different cooling rate have been studied [133] with potentiostatic critical pitting temperature (CPT) in 1 M NaCl. When cooling rate is decreased from 100 to 10 °C/s in the temperature range of 1350–800 °C, the austenite fraction increases from 27.8% to 35.7%, and the CPT value increases from 14 to 19 °C. Pitting occurred preferentially in the ferrite phase for all specimens. When cooling rate is increased, CPT of the specimen tends to decrease indicating a deterioration of pitting corrosion resistance. Cooling rate to toughness and corrosion resistance of GTAW welds of UNS S31803 DSS is correlated [140]. The mechanical properties are affected by cooling rate. Faster cooling rates increase hardness value but decrease toughness values. The pitting corrosion and intergranular corrosion resistance are improved for fast water-cooled welds than air-cooled ones. Ferrite region is more susceptible to pitting corrosion and corroded preferentially, while austenite is found to be more sensitive to intergranular corrosion. Henrik Sieurin and Rolf Sandstrom [141] formed a mathematical model of cooling rate and austenite reformation in heat affected zone of duplex stainless steels welded by Submerged Arc Welding. They concluded that slow cooling rate facilitate, higher percentage of austenite formation and avoid precipitation of intermetallic phases.

Generally, DSS and SDSS welding is not be subjected for post weld heat treatment. In order to stabilize phase balance, certain application may call for PWHT like solution annealing treatment. It is concluded that DSS materials

subjected for annealing between 800-1000 °C causes formation of intermetallic phases and reduced mechanical and corrosion properties [136]. The optimal combinations of mechanical properties and phase balance are achieved when solution annealing treatment is carried out above 1050 °C. Thermal cycles may promote precipitation of sigma phase formation [30]. Temperature ranges from 828 to 1028 °C to be avoided between each weld pass. Precipitation of Chromium Nitride ( $\text{Cr}_2\text{N}$ ) has been observed while cooling from 1250 to 1100 °C and is found in interior of the high density ferrite grain especially with the faster cooling rate and an increased austenite spacing [32]. Weld passes (thermal cycles) need to be established based on the material thickness. Stringer bead without weaving will reduce heat input.

## **2.2 EFFECT OF INTERMETALLIC PHASES ON MECHANICAL AND CORROSION PROPERTIES OF DSS AND SDSS**

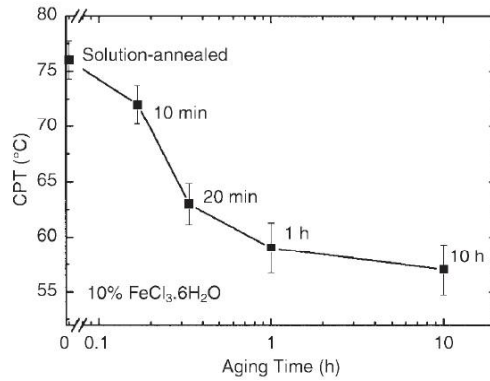
### **2.2.1 Corrosion Properties:**

In a duplex microstructure, Cr and Mo partition to ferrite, Nitrogen and Ni partition to austenite, results in different PREN values for two phases. Hence, the alloying elements should be in appropriate content to get similar PREN values. Effect of nitrogen on pitting resistance of DSS was studied [76]. It is noticed that austenite is more prone to pitting than ferrite, as the weight % of N is not enough to get as high PREN value as ferrite. Therefore, N content can be increased up to 0.4% to get higher PREN value. Beyond this limit, PREN for austenite increases

but PREN for ferrite decreases. This is due to the fact that, N reduces partitioning ratio for Cr, Mo in ferrite, leading to reduction in PREN value. Hence, adjustment of alloying elements is important to get equal PREN values for both phases. The Critical Pitting Temperature (CPT) is the lowest temperature at which stable pit formation is initiated.

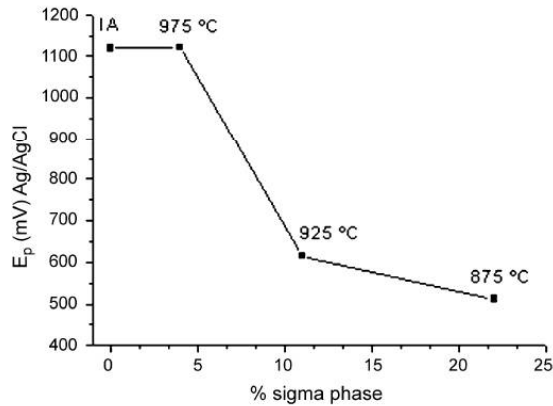
During Eutectoid reaction,  $\alpha$ -ferrite converts into Sigma ( $\sigma$ ) and secondary austenitic phase ( $\gamma_2$ ). This  $\gamma_2$  phase is depleted in Cr and Mo content, which decreases the corrosion resistance [94]. Sigma ( $\sigma$ ) phase is rich in Cr and Mo content, which are ferrite stabilizers in DSS. The precipitation of  $\sigma$  phase causes consumption of Cr and Mo from surrounding ferrite and austenite, which leads to reduction in corrosion resistance of DSS [59]. Effect of sigma phase precipitation on DSS in 10% Fe<sub>3</sub>Cl 6H<sub>2</sub>O solution was carried out. They allowed sigma phase precipitation by different aging treatments and found that CPT value decreases with increase in  $\sigma$ -phase precipitation. After sufficient aging time,  $\sigma$ -phase grew with depletion of Cr and Mo around it and corrosion resistant alloy became susceptible to metastable pitting. The effect of aging time on CPT is shown in Figure 2.1.





**Figure 2.1: Effect of aging time on CPT in 10% FeCl<sub>3</sub>-6H<sub>2</sub>O solution at 850 °C [59]**

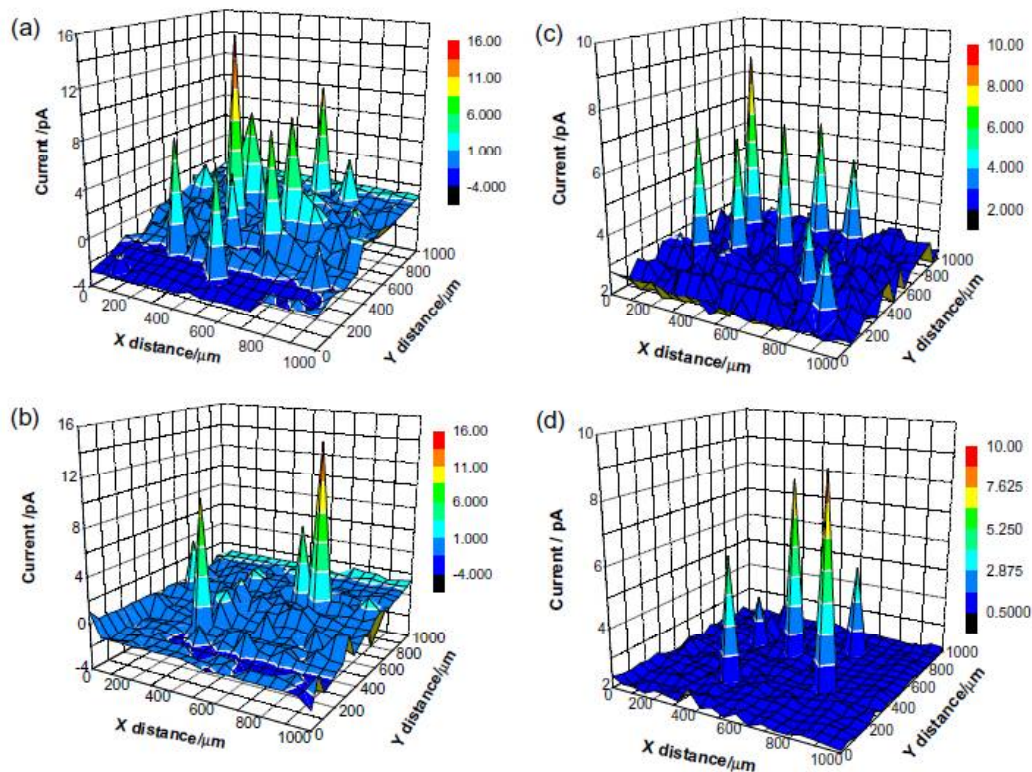
Potential-dynamic polarization studies were carried out in a three electrodes cell [143]. The platinum electrode was used as a counter-electrode and specimen as working electrode and Ag/AgCl as reference electrode. The testing was done at 875, 925 and 975 °C. The root cause of pitting corrosion was found to be the formation of secondary austenite phase at 875 °C. However, at high annealing temperatures (i.e. 925 to 975 °C), high diffusion rate of Cr and Mo replenishes the once depleted zones and the number of sites prone to pitting are reduced. The variation of pitting potential at different aging temperatures is shown in Figure 2.2.



**Figure 2.2: Variation of pitting potential at different aging temperatures**

[66]

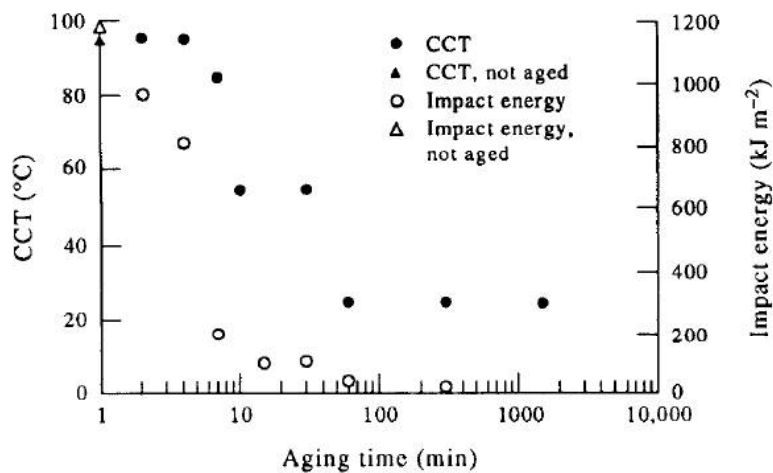
Stress corrosion cracking behavior of 2205 DSS in 26 % NaCl solution at 90 °C was studied. It was found that DSS is immune to stress corrosion cracking [160]. However, at a critical potential coincident with the pitting corrosion potential, susceptibility of DSS to SCC in the solution is observed. Pitting corrosion initiates crack formation and dissolution of alpha phase encourages crack growth. Effect of solution heat treatment at 1100 °C for one hour on the corrosion behavior of DSS was also studied [144]. The authors concluded that alloying elements content in both phases change with solution heat treatment. In addition, number of pitting sites decreases after solution heat treatment. At the open circuit potential, more pitting sites are observed on original sample than solution treated sample as shown in Figure 2.3. In solution treated sample, the pits were found to be larger in size than the pits on original sample. This indicates that the pitting in solution treated sample occur only on the existing pits from original samples rather than forming new pits.



**Figure 2.3: Saturated Calomel Electrode Microscope (SCEM) images of 2205 duplex stainless steel surface after immersion in NaCl at the open circuit potential. (a) Original state (immediately); (b) after solution treatment (immediately); (c) original state (after 1 h immersion); (d) after solution treatment (after 1 h immersion) [144]**

The pitting potential ( $E_p$ ) is defined as the potential at which the anodic current density increases sharply with respect to the background passive current density. Ezuber et al. [145] analyzed seawater pitting caused due to sigma precipitation. They made an interesting conclusion that at room temperature, DSS is immune to

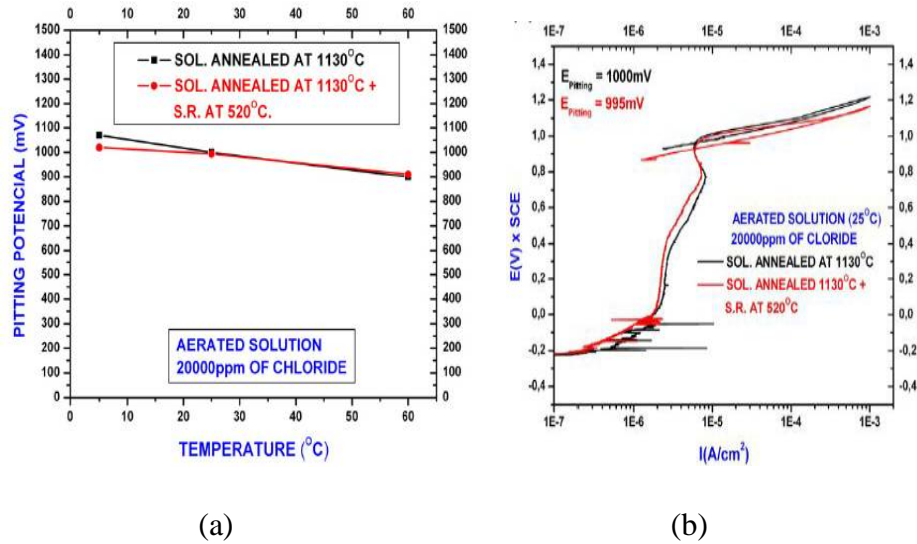
pitting corrosion even in the presence of sigma phase but at 50 °C seawater temperature, it is susceptible to pitting. This is because at high temperatures, cathodic reaction takes place on passive film, which causes reduction in oxygen. This leads to the formation of large number of corrosion cells. Consequences of sigma phase precipitation on seawater corrosion of SDSS were studied [146] and found that localized corrosion starts after 7 min of aging at 800 °C due to formation of Sigma phase and secondary austenite. The sensitivity comparison of pitting corrosion and toughness to sigma phase content is shown in Figure 2.4. This clearly indicates toughness is more sensitive to Sigma phase than corrosion as toughness is affected just after 2 min of aging, much before it affects the crevice corrosion resistance.



**Figure 2.4: Variation of Critical Crevice Temperature and impact toughness with aging time [146]**

Corrosion behavior of super duplex stainless steel castings was studied [147] and concluded that pitting potential decreases with increase in work temperature. In

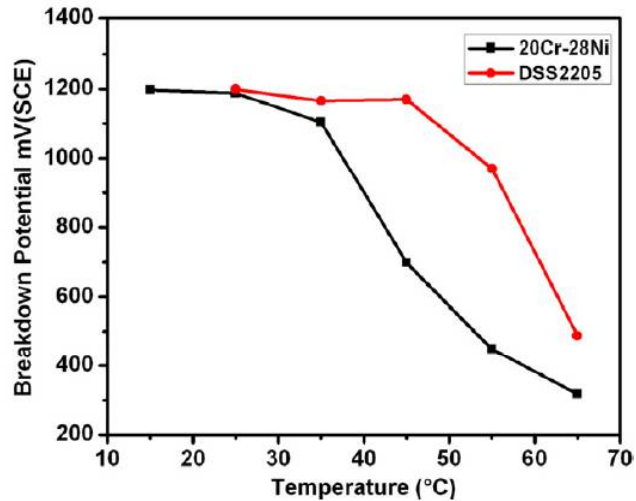
offshore industries where temperatures may go up to 60 °C, material becomes more prone to pitting corrosion. They also pointed that stress relief treatment does not have any effect on pitting potential as shown in Figure 2.5.



**Figure 2.5: Effect of stress relief treatment on pitting a) Variation of pitting potential with test temperature; b) Anodic polarization curves for solution annealed and solution annealed + stress relieved [147].**

For DSS, the breakdown / pitting potential is the potential at which anodic current density reaches a value of 100  $\mu\text{A}/\text{cm}^2$ . Author evaluated the CPT of DSS 2205 in 0.1 M NaCl solution by various techniques [148]. Through potentiodynamic measurements, the authors found that the transition from trans-passivity to pitting corrosion occurs in between 45 to 55 °C. The breakdown potential for DSS was found to be 970 mV at 55 °C. Hence, the passivity domain is decreased from 1200 mV at 45 °C to 700 mV at 65 °C. Figure 2.6 shows variation of breakdown

potential with work temperature for 20Cr-28Ni and DSS 2205 in 0.1 M NaCl solution.

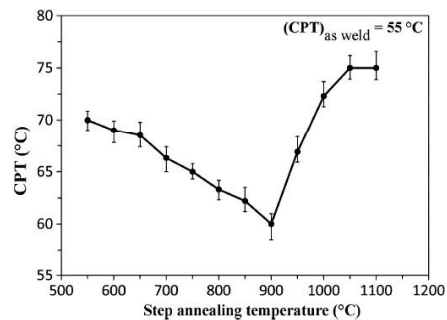


**Figure 2.6: Variation of breakdown potential with working temperature [148]**

During spot welding of 2205 DSS, precipitation of chromium nitrides was observed [149]. The precipitates were dark in appearance and formed due to saturation of N in ferrite grains during rapid cooling. These chromium nitrides cause depletion of Cr in ferrite grains and promote corrosion attack. Experiments were carried out with various grades of 22Cr3Mo DSSs by varying the amounts of nitrogen and nickel [150]. It was found that the nitrogen-bearing specimen has inferior pitting resistance of ferrite phase than other samples due to precipitation of nitrides. It is also concluded that decrease in grain size and cooling rate would decrease nitrides precipitation within ferrite.

There was an evidence of increase in pitting corrosion resistance with high heat input because of slow cooling rates and formation of austenite instead of nitrides. Pitting resistance was significantly reduced by the secondary austenite formation. The morphology of secondary austenite played an important role. The acicular secondary austenite type was found to be more hazardous than polygonal secondary austenite type [153].

Step annealing heat treatments at various temperatures ranging from 550 to 1000 °C for 15 min were carried out on UNS 32760 specimens welded with GTAW process [152]. It was reported that CPT for the welded sample was 55 °C. After step annealing, the CPT values for the entire specimen was increased. In between 550-750 °C, CPT value decreases from 70 °C to 65 °C due to precipitation of chromium nitrides. At high temperatures up to 900 °C, it is further decreased due to precipitation of sigma phase and secondary austenite phase. Above 900 °C, the CPT values increases due to replenishment of ferrite phase. The variation of CPT with annealing temperatures is shown in Figure 2.7.

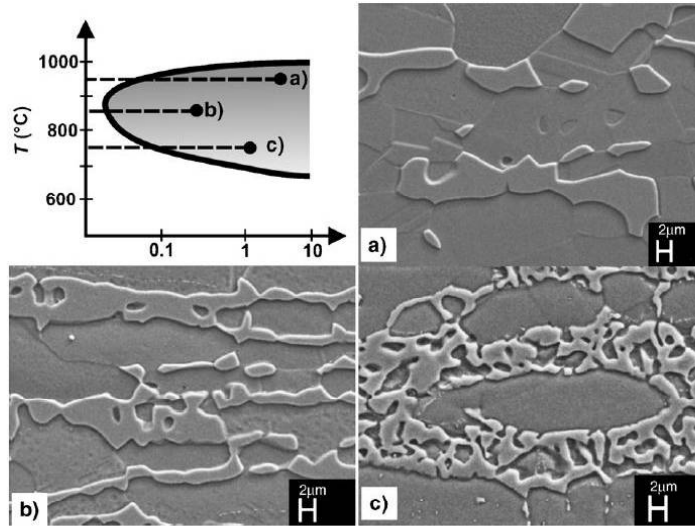


**Figure 2.7: CPT vs annealing temperatures of UNS S32760 weldments [152]**

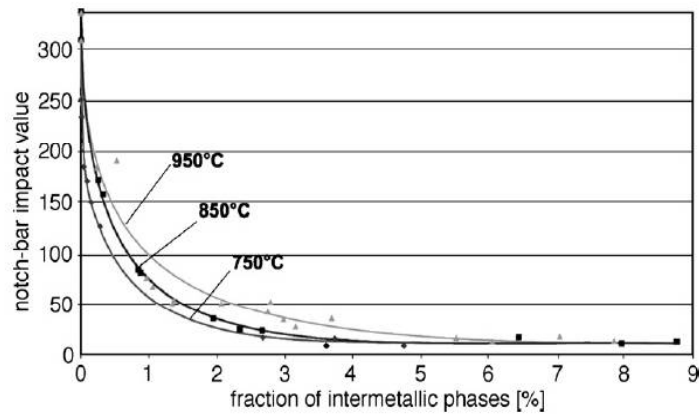
### 2.2.2 Mechanical Properties:

Toughness is severely affected by formation of intermetallic phases and compounds. As metallic binding is weak in case of intermetallic phases, it causes bad-deformability of phases, ultimately deteriorating impact toughness of DSS [94]. In all studies, it was found that even a small volume fraction of Sigma ( $\sigma$ ) phase causes drastic reduction in toughness value. In another study, it was observed that PREN of welded zone was lower than that of base material [154]. This was attributed to the lower contents of CR, Mo and N in ferrite caused by improper weld heat cycle. The Post Weld Heat Treatments (PWHT) improves PREN values due to proper partitioning of elements in two phases and PWHT at 1100 °C gives the best results [155]. At lower temperature, Sigma ( $\sigma$ ) phase morphology shows a net like structure, which causes cracks to propagate over long distances [94]. This results in ferrite phase to cleave and ductile fracture in austenitic phase. At higher temperature, bulk Sigma ( $\sigma$ ) phase is surrounded by larger ferrite and austenite matrix. Hence, ferrite phase shows more ductile fracture as shown in Figure 2.8 and Figure 2.9. In another study, DSS materials subjected to solution annealing treatment at 850°C are noticed with low toughness value due to Sigma ( $\sigma$ ) phase [179]. However, when annealing temperature is above 1100 °C, the toughness value is increased because of increase in ferrite content and phase balance.



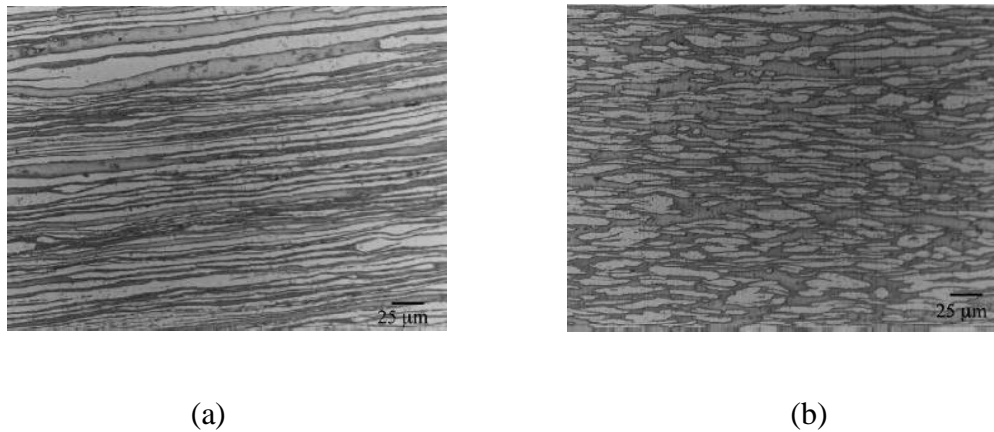


**Figure 2.8: Sigma phase morphology of at various aging temperatures a) 950 °C, b) 850 °C, c) 750 °C [94]**



**Figure 2.9: Impact toughness vs fraction of intermetallic phases [94]**

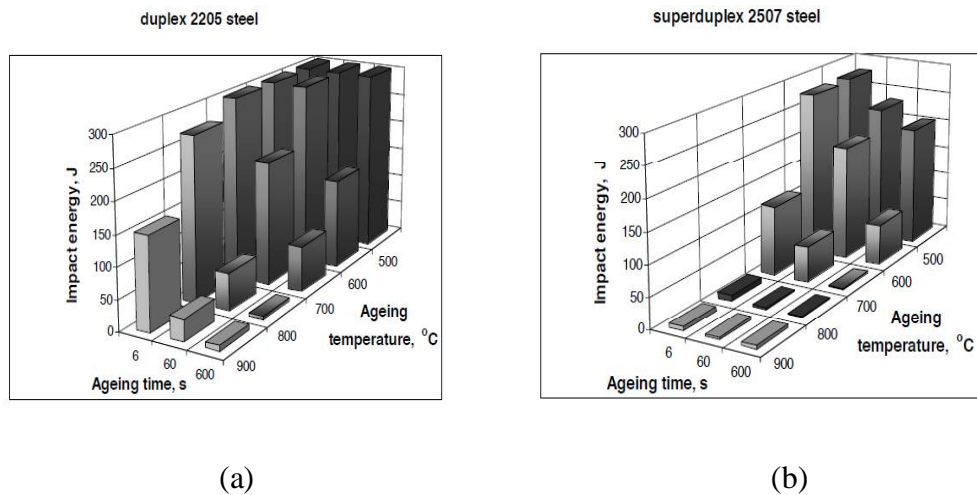
Intermediate annealing treatment on hot rolled DSS at 857 °C has not improved mechanical and corrosion properties however, very low sigma phases in the form of isolated particles were noticed when the annealing treatment was done at 925-975 °C [143]. They concluded that the materials behave anisotropically and material toughness is the most sensitive property with respect to intermetallic phase formation. They also concluded that in transverse direction specimens exhibit better toughness value than that of longitudinal direction specimens. This is because in transverse direction, crack has to propagate through large number of phase boundaries and in longitudinal direction, crack propagation along duplex phases is easier as shown in Figure 2.10.



**Figure 2.10: Grain orientation in rolling in a) Longitudinal and b) Transverse direction [143]**

Toughness behavior of Duplex Stainless Steels and Super duplex stainless steels were compared and concluded that DSS is less sensitive to embrittlement than Super DSS [156]. The results are presented in Figure 2.11. At lower aging

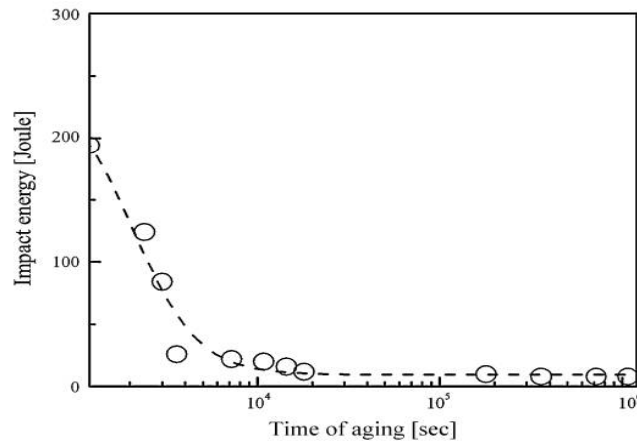
temperatures, DSS retains its toughness value. However, in case of SDSS even at lower aging temperatures and lower aging times i.e. low Sigma phase content, material loses its impact energy absorbing capacity. The authors also claimed that the minimum allowable Sigma phase content in DSS and SDSS is 14 % and 8 % respectively. These values correspond to critical impact energy value of 27 J in industrial DSS applications.



**Figure 2.11: Impact toughness vs aging temperature vs aging time for a) DSS b) SDSS [156]**

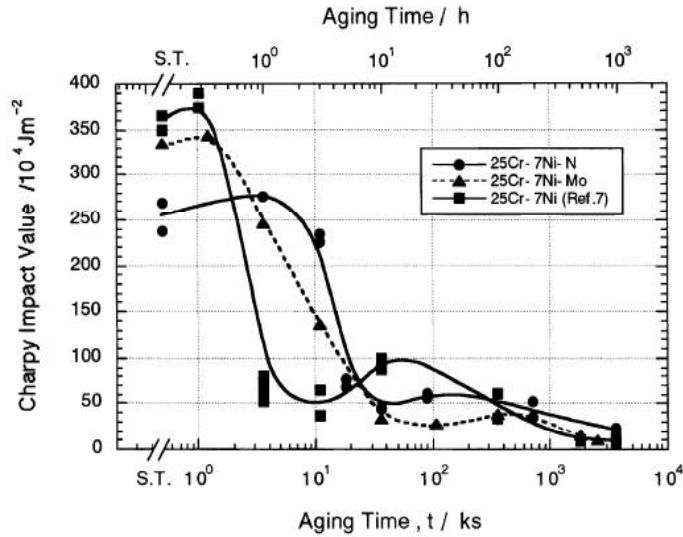
Similar observations were made to evaluate minimum allowable sigma phase content in DSS pipefittings in subsea applications [157]. The authors claimed that the allowable range of sigma phase is up to 5 % and above this level, material will definitely fail due to fracture. Besides  $\sigma$ -phase, other phases like R-phase and 475 °C embrittlement affect the impact toughness of the DSS [106].

Effect of aging at 475 °C on impact energy of DSS 1.4462 was studied [106] and observed that impact toughness energy was deteriorated up to 8J after 100 h of aging as shown in Figure 2.12. On further aging, the impact toughness was plateaued at this value, which indicates, no further reduction in toughness values.



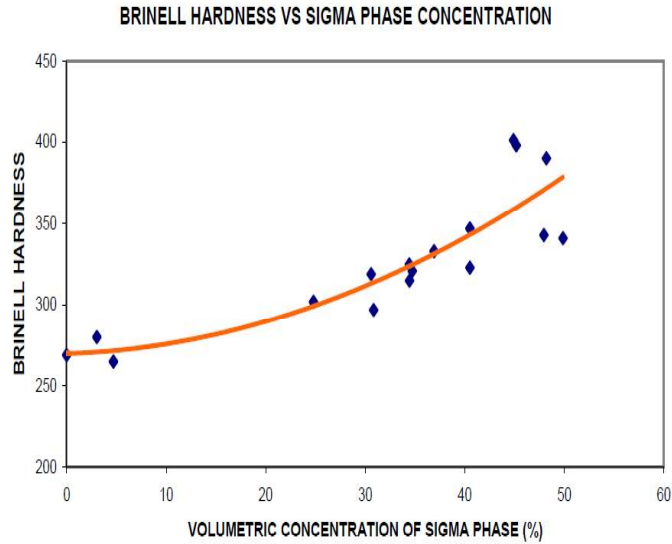
**Figure 2.12: Impact energy vs time of aging at 475 °C [106]**

It is noticed that deterioration of impact toughness energy takes place due to the formation of R-phase in DSS with high nitrogen content [103]. The formation of R-phase took place after aging at 500 °C. The high nitrogen content retards formation of  $\sigma$ -phase in DSS. It can be seen from Figure 2.13 that the R-phase is found to be dominant in degradation of impact energy after aging time of 6 hrs and 10 hrs for 25Cr–7Ni–N and 25Cr–7Ni–Mo respectively. Hwang et al. [104] studied the effect of R-phase on impact toughness of Super DSS. They found that at initial stage of aging at 600 °C, R-phase is formed and later it is transformed to sigma phase. The reduction in toughness with R-phase was found to be drastic.



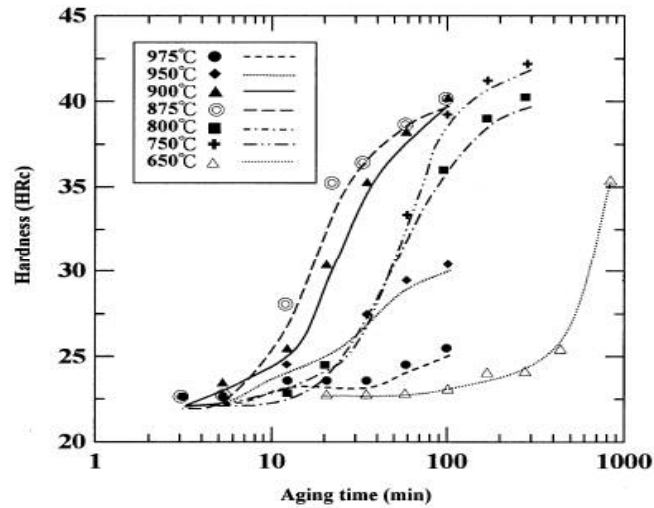
**Figure 2.13: Charpy impact value vs aging time at 500 °C [103]**

The intermetallic phases that occur in duplex stainless steel are hard and fragile. When the content of intermetallic phases increases, that will remove almost all ferrite content. It was reported that embrittlement of material is due to increase in volume fraction of intermetallic phases and decrease in ferrite content [158]. Similar studies with Super Duplex Stainless Steel revealed that increase of Sigma ( $\sigma$ ) phase content promotes hardness values [159] as shown in Figure 2.14. From the figure, it is clearly visible that hardness increases in parabolic manner with increase in sigma phase content. However, a significant increase in hardness value is observed only at higher sigma phase content.



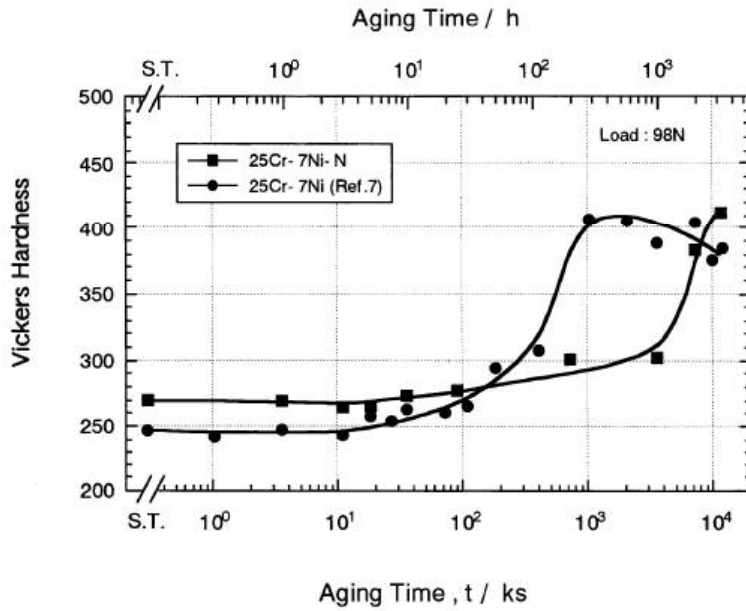
**Figure 2.14: Brinell hardness vs sigma phase volume fraction [159]**

Effect of different aging temperatures between 650-975 °C and aging times on microstructure and mechanical properties of DSS was studied [60]. They found that hardness increases with increase in aging time for all temperatures as shown in Figure 2.15. However, hardness shows sharp increase only after longer aging times of 30 min whereas in case of toughness, only 5 min aging is enough to make a drastic reduction. This indicates hardness is not a measure of low volume fraction of Sigma phase. Similar conclusions were made that toughness is more sensitive and affected by percentage of intermetallic phases than hardness [158].



**Figure 2.15: Hardness variation with aging time at different aging temperatures [60]**

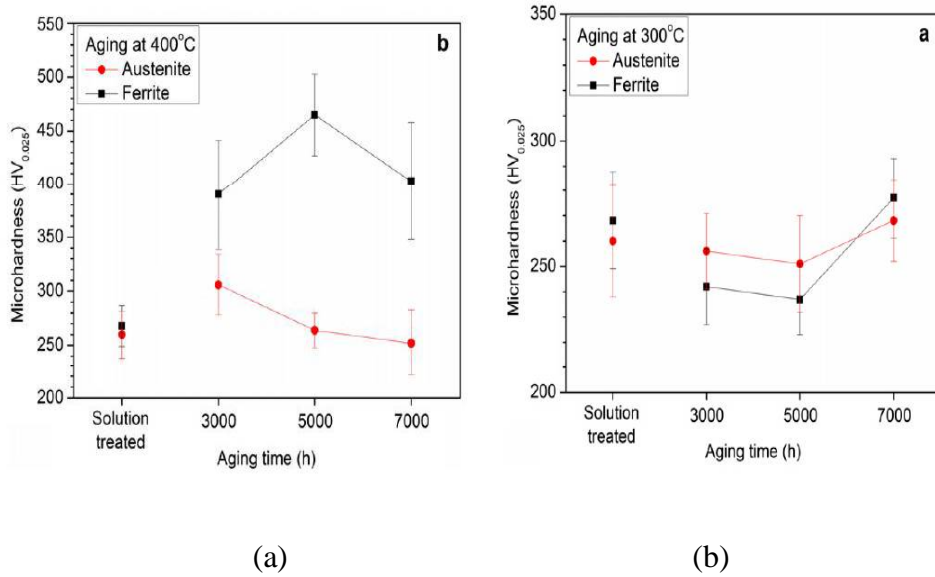
Increase in aging time increases hardness gradually after 14 hrs and 8.3 hrs for both 25Cr-7Ni-N and 25Cr-7Ni duplex stainless steels as shown in Figure 2.16 [103]. The significant increase in hardness value is found to be at aging time of 1400 hrs for 25Cr-7Ni-N and 100 hrs for 25Cr-7Ni respectively. This reflects that increase of aging time increases hard sigma phase content and thus increases hardness of the material. After 2700 hours aging time, hardness starts decreasing for 25Cr-7Ni-N DSS because high nitrogen content retards the formation of Sigma phase.



**Figure 2.16: Vickers hardness Vs aging time at 873 K for alloys 25Cr–7Ni and 25Cr–7Ni–N [103]**

Effect of prolonged aging (up to 7000 hrs) at 300 °C and 400 °C on 2205 DSS as shown in Figure 2.17 was studied [161]. At 300 °C aging, hardness values do not vary significantly, but hardness value of ferrite increases at 400 °C. However, austenite remained unaffected even after aging. The spinodal decomposition of ferrite causes embrittlement of phase. After 5000 hours aging at 400 °C, hardness value decreases due to coarsening of phases or loss of their coherent nature.

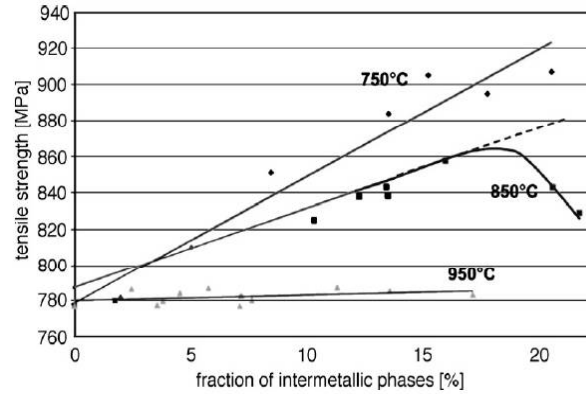




**Figure 2.17: Hardness variation with aging time at a) 400 °C and b) 300 °C**

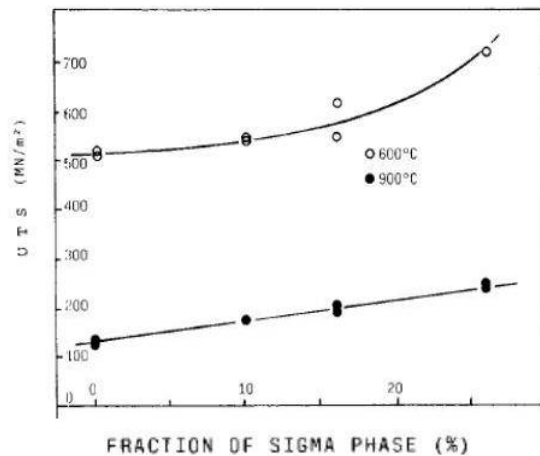
[161]

Sigma ( $\sigma$ ) phase formation causes increase in tensile and yield strength between temperatures 750-850 °C [94]. This is because of net like structure that is obtained at low temperatures. Variation of tensile strength due to percentage fraction of intermetallic phases with different solution annealing treatment is presented in Figure 2.18. At 850 °C, internal brittle micro-cracking of Sigma ( $\sigma$ ) phase causes reduction in strength beyond general material yield level known as ‘low stress failures’. However, at higher annealing temperatures tensile strength hardly shows any change with increase in Sigma ( $\sigma$ ) phase volume fraction.



**Figure 2.18: Tensile strength variation with % intermetallic phases [94]**

Influence of Sigma ( $\sigma$ ) phase on tensile properties of SDSS was studied. They observed that tensile strength increases with the increase of Sigma ( $\sigma$ ) phase content from 0 to 26 % at 600° C however, at higher temperatures of 900 °C, the effect of Sigma ( $\sigma$ ) phase is negligible [162]. The results are plotted in Figure 2.19.



**Figure 2.19: UTS vs fraction of sigma phase at different aging temperatures**

[162]

## 2.3 RESEARCH GAP

There is no clear method reported by earlier researchers to achieve a balanced microstructure of 50% ferrite and 50% austenite after welding.

Welding process is associated with uncontrolled heating rate and cooling rate. DSS and SDSS weld properties depends mainly on microstructure and presence of any detrimental inter-metallic phases, which is directly affected by alloying element and heating/cooling rate. No literature is available to control the formation of the detrimental inter-metallic phases.

Chromium Nitride and secondary austenite formation is another critical issue in welding of DSS and SDSS and there is no literature available related to set of optimum parameters to avoid these phase formations.