CHAPTER - 2

LITERATURE REVIEW

2.1 History of duplex stainless steel

Duplex stainless steels, meaning those with a mixed microstructure of about equal Proportions of austenite and ferrite, have existed for more than 60 years. The early grades were alloys of chromium, nickel, and molybdenum. The first wrought duplex stainless steels were produced in Sweden in 1930 and were used in the sulphite paper industry. These grades were developed to reduce the intergranular corrosion problems in the early, high-carbon austenitic stainless steels. Duplex castings were produced in Finland in 1930, and a patent was granted in France in 1936 for the forerunner of this grade was eventually be known as Uranus 50.1 One of the first duplex grades developed specifically for improved resistance to chloride stress corrosion cracking (SCC) was 3RE60. AISI type 329 became well established after World War II and was used extensively for heat exchanger tubing for nitric acid service [1,4,5].

2.2 Introduction of duplex stainless steel

Duplex stainless steels (DSS) are finding abundant use in the petrochemicals and refining industry, mainly because they do offer very good economical combination of strength and corrosion resistance in sour service atmosphere.

It is well documented in various literatures that the desirable properties of the duplex stainless steels can be achieved for phase balances in the range of 30 to 70% ferrite and rest austenite. However, duplex stainless steels are most commonly considered to have proportionately equal amounts of ferrite and austenite. Current commercial production aiming for slightly improved composition favouring the austenite for best toughness and processing characteristics. The interactions of the major alloying elements particularly, chromium, molybdenum, nitrogen, and nickel, are quite complex. To achieve a stable duplex structure that responds well to processing and fabrication, care must be taken to obtain the correct level of each of these elements.

Besides the phase balance, there is a second major concern with duplex stainless steels and their chemical composition is the formation of detrimental intermetallic phases at elevated temperatures. Sigma and Chi phases form in high chromium, high molybdenum stainless steels and precipitate preferentially in the ferrite. The addition of nitrogen significantly delays formation of these phases. Therefore, it is critical that sufficient nitrogen be present in solid solution. [1, 4, 5]

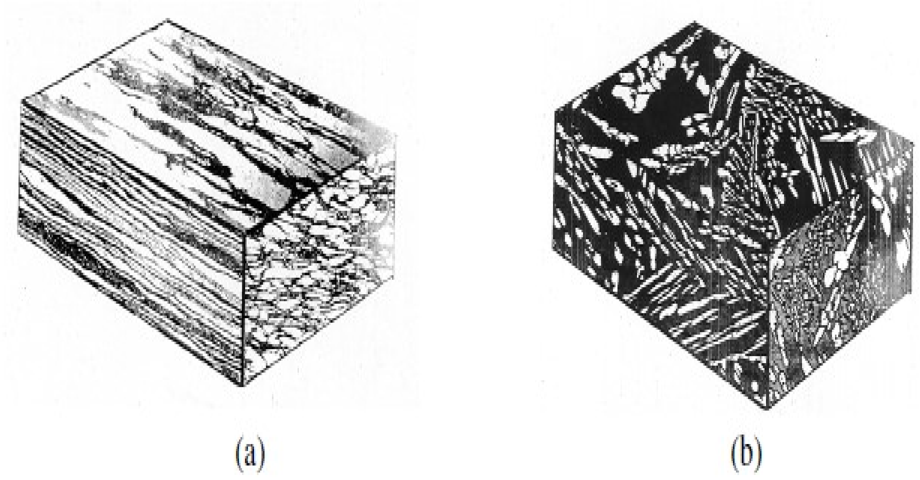

Figure 2.1 Typical microstructures of duplex stainless steel

DSS typically have an annealed structure consists of half ferrite and half austenite, although the ratios can vary from approximately 35/65 to 55/45. Fig. 2.1 & 2.2

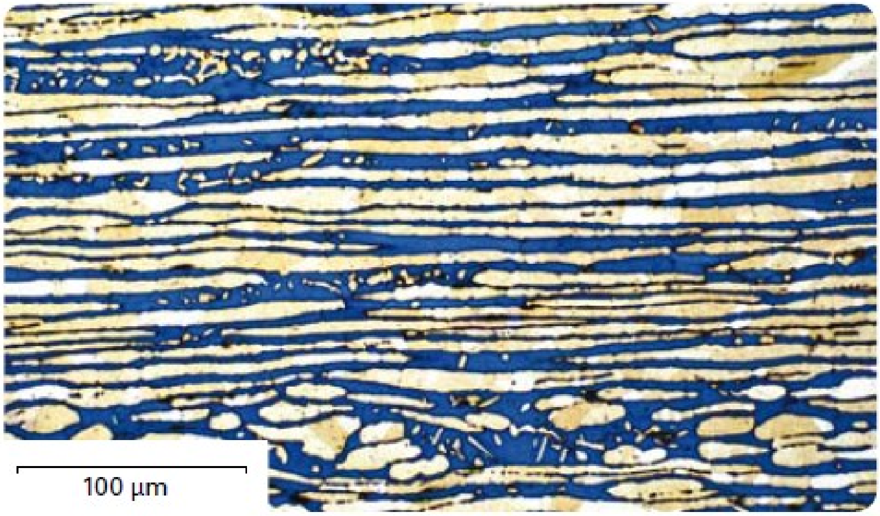

Figure 2.2 Typical transverse section microstructure of a duplex stainless steel, showing continuous ferritic matrix, etched dark, and austenite bands running parallel to the rolling direction of the plate. Source 76

Combining characteristics of both ferritic and austenitic stainless steel (SS) when welded correctly.

When welded incorrectly, the tendency to form detrimental intermetallic phases significantly increases, which could lead to a catastrophic failure.

Duplex Stainless Steels typically comprise approximately equal amounts of body-centered cubic (BCC) ferrite, α-phase and face-centered cubic (FCC) austenite, γ-phase, in their microstructure.

It is well documented through various research that optimum corrosion resistance and mechanical properties throughout a DSS weldment are achieved when the phase balance of ferrite to austenite is 50:50. However, achieving a 50:50 phase balance of ferrite to austenite ($\alpha \rightarrow \gamma$) in a weldment practically has proven to be difficult due to many variables involves such as composition of the base metals, filler metal, welding processes, and thermal history of the steel.

Various research outcome on Welding of Duplex stainless steels have suggested that optimal corrosion resistance and set of mechanical properties are achieved when 35 to 60% ferrite content is maintained throughout the weldment.[6]

DSSs have been existed since the 1930s. However, Type 329 (UNS S32900 the first generation steels), had very poor and unacceptable corrosion resistance and toughness at weldments. [4,7,8]

Hence, the early applications were almost limited to material for heat exchanger tubing, mainly in corrosive cooling water services, and rotary components like shafts and to some extents forgings.

During 1980s, second generation DSSs have become commercially available with improved composition to address problems occurs in welding.

These new grades had nitrogen additions and better austenite/ferrite balances, along with this gradual development in welding technologies for the DSSs, results in improved mechanical (strength and toughness) and corrosion properties as good as annealed duplex Stainless steel base metal.

The three basic variety of DSS includes, low-alloy, intermediate alloy, and highly alloyed, or super duplex stainless steel (SDSS) grades, grouped according to their pitting resistance equivalent number (PREN) with nitrogen and are shown in Table 2.1. The most widely used alloys are DSS-grade 2205+ and SDSS-grade 2507[6].

25 Cr duplex such as Alloy 255 with PREN* less than 40

Super duplex (PREN 40-45), with 25-26Cr and increased Mo and N compared with 25 Cr grades, such as 2507[6].

PREN * = Pitting resistance equivalent number

$$= \%Cr + 3.3(\%Mo + 0.5\%W) + 16\%N$$

The DSSs most commonly used today in refineries include those with 22 %, 25 % and 27 % Cr. The 25 % Cr (super duplex grades) and 27 % Cr (hyper duplex grade) usually also contain more molybdenum and nitrogen, and so have higher PREN values than the 22 % Cr duplex steels.

Table No. 2.1 Chemical compositions of commonly used Duplex SS and other alloys Source [9, 10]

Composition, Wt. % (Single Value Max.)													
UNS No.	Common Designation	C	Mn	S	P	Si	Cr	Ni	Mo	Cu	W	N	PREN
Low –alloy grades (PREN <32)													
S31500	3RE60	0.03	0.2-2.0	0.03	0.03	1.4-2.0	18.0-19.0	4.25-5.25	2.5-3.0	-	-	0.05-0.20	28
S32001	19D	0.03	4-6	0.03	0.04	1.0	19.5-21.5	1.0-3.0	0.6	1.0		0.05-0.17	23.6
S32304	2304	0.03	2.5	0.04	0.04	1.0	21.5-24.5	3.0-5.5	0.05-0.6	0.05-0.06		0.05-0.2	25
S32404	UR50	0.04	2.0	0.01	0.3	1.00	20.5-22.5	5.5-8.5	2.0-3.0	1.0-2.0	--	0.2	31
Intermediate-alloy grades (PREN 32-39)													
S31200	44LN	0.03	2.0	0.03	0.045	1.00	24.0-26.0	5.5-6.5	1.2-2.0	….	…	0.14-2.0	33
S31260	DP3	0.03	1.0	0.03	0.03	0.75	24.0-26.0	5.5-7.5	2.5-3.5	0.2-0.8	0.10-0.5	0.10-0.30	38
S31803	2205	0.03	2.0	0.02	0.03	1.00	21.0-23.0	4.5-6.5	2.5-3.5	..	..	0.08-0.20	34
S32205	2205 +	0.03	2.0	0.02	0.03	1.00	22.0-23.0	4.5-6.5	3.0-3.5	..	..	0.14-0.20	35-36
S32550	255	0.03	1.5	0.03	0.04	1.00	24.0-27.0	4.5-6.5	2.9-3.9	1.5-2.5	..	0.10-0.25	38
S32900	10RE51	0.06	1.0	0.03	0.04	0.75	23.0-28.0	2.5-5.0	1.0-2.0	..	…	…	33
S32950	7-Mo Plus	0.03	2.0	0.01	0.035	0.60	26.0-29.0	3.5-5.20	1.0-2.5	…	…	0.15-0.35	35
Superduplex grades (PREN>40)													
S32520	UR52N+	0.03	1.5	0.02	0.035	0.80	24.0-26.0	5.5-8.0	3.0-5.0	0.5-3.0	…	0.20-0.35	41
S32750	2507	0.03	1.2	0.02	0.035	1.0	24.0-26.0	6.0-8.0	3.0-5.0	0.5	…	0.24-0.32	>41
S32760	Zeron100	0.03	1.0	0.01	0.03	1.0	24.0-26.0	6.0-8.0	3.0-4.0	0.5-1.0	0.5-1.0	0.30	>40
S32906	Safurex	0.03	0.8-1.5	0.03	0.03	0.5	28.0-30.0	5.8-7.5	1.5-2.6	0.8	…	0.30-0.4	>41
S39274	DP3W	0.03	1.0	0.02	0.03	0.8	24.0-26.0	6.0-8.0	2.5-3.5	0.2-0.8	1.5-2.5	0.24-0.32	42
S39277	AF918	0.025	….	0.002	0.025	0.8	24.0-26.0	4.5-6.5	3.0-4.0	1.2-2.20	0.8-1.2	0.23-0.33	>41

Table 2.2 Standard compositions of some commonly used Duplex Stainless steels.

LDX (Lean Duplex), DX (Duplex), EN (European Standard), No (Number) , UNS(Unified Numbering System for Metals and alloys)[9,10]

Grade	EN No./UNS	Type	Approx. Composition					
			C	Cr	Ni	Mo	N	Mn
2101 LDX	1.4162/S32101	Lean	0.04	21.0-22.0	1.35-1.70	0.3-0.8	0.2-0.25	4-6
LDX 2202	1.4062/S32202	Lean	0.03	21.5-24.0	1.0-2.8	0.45	0.18-0.26	2.0
2304	1.4362/S32304	Lean	0.03	21.5-24.5	3-5.5	0.05-0.6	0.05-0.2	2.5
2205	1.4462/S32205	Standard	0.03	22-23	4.5-6.5	3.0-3.5	0.14-0.2	2.0
2507	1.4410/S32750	Super	0.03	24-26	6-8	3-5	0.24-0.32	1.2

Table 2.3 Physical Properties of Duplex Stainless steels. Source [9,10]

Properties	Unit	20 °C	100 °C	200 °C	300 °C
Density	g/cm2	7.8			
Modulus of elasticity	GPa	200	194	186	180
Poisson ratio	-	0.3	-	-	-
LTE	X 106/°C	-	13.0	13.5	14.0
Thermal conductivity	W/m°C	15	16	17	18
Thermal capacity	J/Kg°C	500	530	560	590
Electric resistivity	µ Ohm	0.80	0.85	0.90	1.00

2.3 Mechanical Properties Source [9,10]

Table 2.4 As per ASTM & EN Mechanical property limits for Duplex SS Plate

	ASTM				EN			
Grade	UNS No.	Y.S 0.2% Mpa(Ksi)	T.S in Mpa(Ksi)	% E.L 2". %	EN No	Proof Strength Rp0.2 Mpa(Ksi)	Tensile Strength Rm Mpa(Ksi)	EL As %
2304	S32304	400(58)	600(87)	25	1.4363	400(58)	630(91)	25
2205	S32205	450(65)	655(95)	25	1.4462	460(67)	640(93)	25
2507	S32750	550(80)	795(116)	15	1.4410	530(77)	730(106)	20

Impact Toughness

Table 2.5 Min values according to EN 10028, Transverse direction, J

Test Temperature	LDX 2101	2304	LDX 2404	2205	2507
20 °C	60	60	60	60	60
-40 °C	27	40	40	40	40

Source. [9, 10]

Johan Pilhagen (2014) et al, investigated on Lean LDX material that the fracture toughness at sub-zero temperatures increases with increasing nickel content in the range from 1 to 9 wt. % Nickel [9,10]

Duplex Stainless Steel Applications [9,10]

-Flue Gas desulphurization
-Desalination
-Oil and Gas
-Biofuels
-Food and Drink
-Architecture

2.4 Physical Metallurgy

The iron-chromium-nickel ternary phase diagram is a roadmap of the metallurgical behaviour of the duplex stainless steels. A section through the ternary at 68% iron (Figure 2.3 a & b) illustrates that these alloys solidify as ferrite, some of which then transforms to austenite as the temperature falls to about 1000°C (1832°F) depending on alloy composition. There is little further change in the equilibrium ferrite–austenite balance at lower temperatures. The effect of increasing nitrogen is also shown in Figure 2.2 Thermodynamically, because the austenite is forming from the ferrite, it is impossible for the alloy to go past the equilibrium level of austenite. However, as cooling proceeds to lower temperatures, carbides, nitrides, sigma and other intermetallic phases are all possible microstructural constituents [1].

Small changes in the nickel and chromium content have a large influence on the amount of austenite and ferrite in duplex stainless steel. Duplex stainless steel base metals have higher ratio of ferrite promoting element to austenite promoting element than do nominally austenitic stainless steel. This accounts for the fact that duplex stainless steel solidify as virtually 100% ferrite [1].

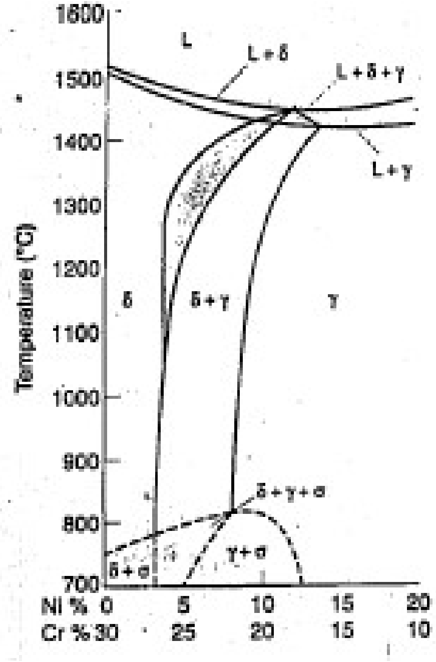

Figure 2.3 (a) Section through the Fe-Cr-Ni ternary phase diagram at 68% Iron

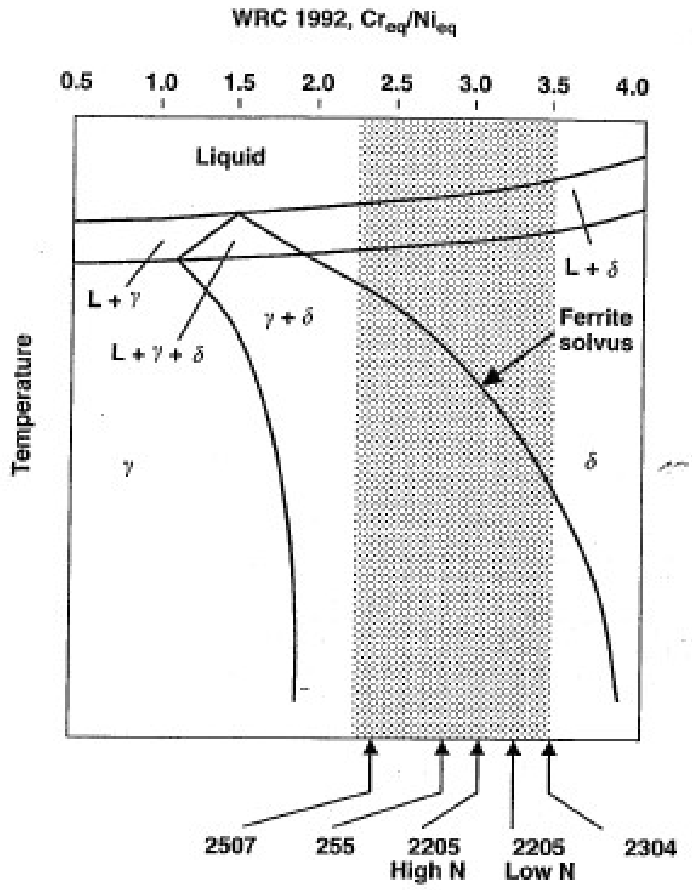

figure 2.3 (b) Elevated temperature region of a pseudo binary phase balance diagram for duplex stainless steel. Shaded region represents the range for commercial alloys. Source [1]

Figure 2.3(b) indicates those alloys whose WRC 1992 chromium equivalent have 1.85 times their nickel equivalent, or more, will solidify as 100% ferrite. The duplex stainless steel base metal typically have ratio between about 2.25 and 3.5.At high temperature (above the ferrite solvus line), the alloy remain 100% ferrite. Austenite can only nucleate and grow below ferrite solvus. Annealing and hot working operation of this steels are generally performed at temperature below ferrite solvus, where ferrite and austenite are coexist in equilibrium [1].

However, because the cooling rate determines the amount of ferrite that can transform to austenite, cooling rates following high temperature exposures influence the phase balance. Because fast cooling rates favour retention of ferrite, it is possible to have more than the equilibrium amount of ferrite.

It can be seen from Fig.2.2 that equilibrium structure at room temperature does not contain ferrite but the hard and embrittle phase , In addition to the equilibrium phases other unwanted detrimental second phases and intermetallic also form, if the alloy is slowly cooled Nitrogen is one such element that shifts the solvus line to a higher temperature[1].

CCT Diagram for DSS

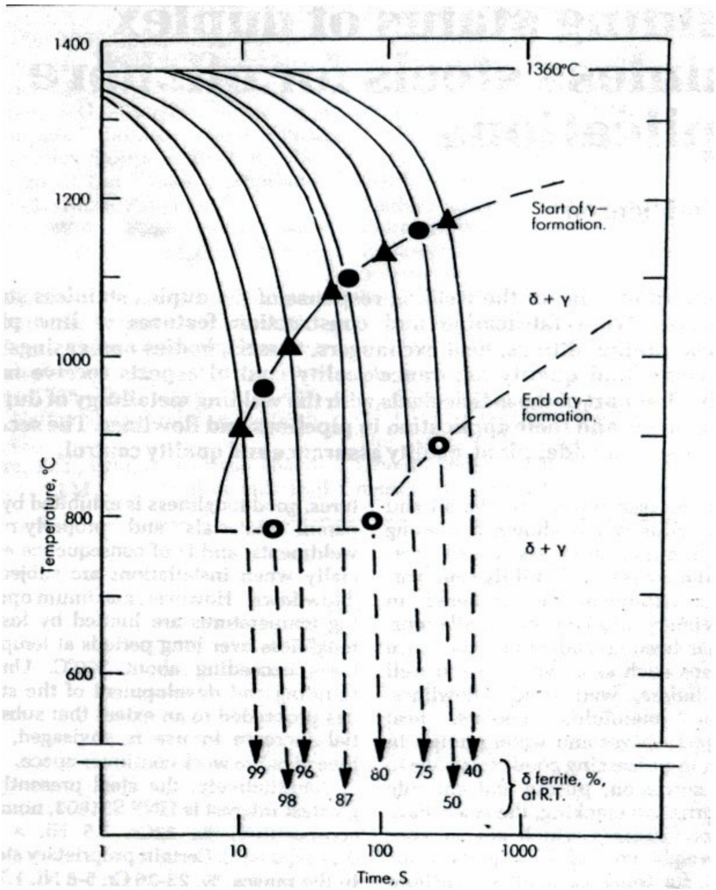

Figure 2.4 CCT diagram for a cast DSS containing 0.02%C, 23.0% Cr and 7.6% Ni with superimposed cooling curves. Source [1]

Hoffmeister and his co-worker (1978) have superimposed cooling curves on the TTT

diagram of a duplex stainless steel, as shown in Fig. 2.4, to predict the ferrite content as influenced by the cooling rate and shown that the faster the cooling rate higher the ferrite content. Thus the effect of cooling rate on ferrite content restricts the lowest heat input that can be employed in welding of DSS[1].

2.5 Alloy Design and Alloying additions of Duplex Stainless Steels

Duplex alloy is produced using Induction furnace with high purity charge materials or high alloyed scrape in Electric Arc furnaces often followed by AOD, VOD or VARP Converters. [11] In either practice Careful selection of Scape material and composition and purity of charge material is always maintained [11].

Overall, the objective is to minimize sulphur and phosphorus, in order to increase corrosion resistance. [11]

Besides deoxidation, the additions of SiCaMn, SiCaCe,REM, AI, Ti, Mg, Nb, Zr etc result in precipitation of microscopic size oxides which becomes nucleation sites for ferrite crystals for grain refinement.[12,13]

Alloying additions

Chromium

The purpose of adding Chromium to steel is to improve the corrosion resistance by the formation of passive chromium- rich oxy-hydroxide film. As per the Fig 2.5 passive range can be extended by adopting Electro-chemical process thereby reducing the rate of general corrosion. (I pass)

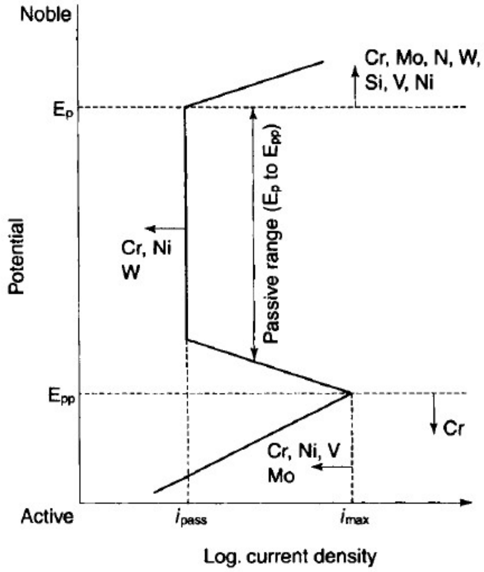

Fig 2.5 Schematic summary of the effects of alloying elements on the anodic polarisation curve. Source [14]

However, addition of chromium can be done up to certain limit as beyond certain limit precipitation of intermetallic phases like Sigma (Fe-Cr) happens that results in loss in ductility, toughness and corrosion resistance. The elements promoting and stabilizing ferrite phases are Mo and Nb besides Cr. As per the Creq as under:-

Creq = %Cr + %Mo + 0.7 x %Nb

Molybdenum

Molybdenum addition in stainless steel has beneficial role as improving pitting and crevice corrosion resistance in Chloride solutions. In the presence of chromium, molybdenum extends the passive potential range and reduces the corrosion current density (I max) in the active range, as shown in Fig.2.5. This is the reason why Molybdenum is included in PREN relationship and besides this as ferrite stabilizer in addition to Chromium. But upper limit 4 % Mo is reported as threat to sigma phase formation during hot working above 1000° C. [4, 5, 16]

Nickel

In Duplex alloys, the ferrite phase is stabilized with Cr, Mo and Nb. In order to balance the Austenite phase, following group of elements are used to stabilize Austenite:

Ni eq = % Ni + 35X %C + 20 X % N + 0.25X % Cu

As per manufacturing specifications, 40 % to 60% ferrite, balance austenite is balanced by the above equations.

With excessive Ni content above 50 %, Austenite phase increases, causes partitioning and enrichment of Cr and Mo in remaining ferrite. As a consequence ferrite transformation to intermetallic phases may be enhanced as reported by Roscoe CV, et al (1986) [15].

When alloy is in temperature range of 650 to 950 °C. More Nickel content produces alpha prime formation, an embrittlement intermetallic phase.

So Nickel does have critical role and remarkable effect on corrosion properties[17].

D. J. Kotecki (1986)[2] experimented on alloy 2205 and 225 in as welded conditions, using self-shielded flux core arc welding electrodes of 8.5% and 10 % Nickel, he found that weld deposit below 60 EFN for alloy 2205 and 255 provides sufficient ductility and toughness that a side bend test, Charpy V-notch energy of better than 20 ft-lb (14.7) at -50°F (-46°C). Ferrite content above 30 FN result in yield strength and tensile strength in the weld metal matching to base metal strength. Addition of 4% Moly deliberately added to Alloy 255 for improving corrosion resistance, adversely shown possibility of embrittlement.

S.K. Seshadri b, S. Sundaresan et al (2003)[18] work on effect of weld metal chemistry & H.I on structure and properties on DSS Welded joints showed that Nickel is very effective in controlling the ferrite / austenite ratio than the cooling rate. Differences in ferrite /austenite ratio has little effect on Hardness but the toughness is highly depended on ferrite content in addition to other factors such as residual stresses, precipitation morphology.

They practically showed possibility of EBW Welding Technique for joining DSS provided with care of Nickle enrichment to control effect of cooling rate by high energy density processes.

S.A. Ta´vara a, M.D. Chapetti et al (2001)[19] work on Influence of nickel on the susceptibility to corrosion fatigue of duplex stainless steel welds.

They have tries Ni 2.8, 4.7, 6.8 and 9.8 wt% and measured by three point bending fatigue tests in air & normalised environments accompanied by with anodic polarisation. Research outcome was Electrode with 4.7% Ni provided very satisfactory Corrosion Fatigue properties

Nitrogen

Nitrogen has a numerous effect on Stainless steels by enhancing pitting resistance, austenite formation and solid solution strengthening.

Nitrogen addition does similar effect on pitting as Cr and Mo, Moving Ep in noble direction and increasing passive potential range. As shown in Fig. 2.5

As per literature survey proposed factor for Nitrogen in the PREn relationship is ranging from 13 to 30, but the most accepted value for duplex alloys is 16.[4]

Nitrogen has high solubility in austenite so it partitions preferentially to the austenite besides it concentrates on metal-passive film interface.[20,21]

Enriched Surface nitrogen on passive film haven been reported during prolonged passivation of stainless steels in acid solutions. [22, 23]

Nitrogen has also been noted to increase the crevice corrosion resistance as investigation in the work by Osozawa K et al and Clayton et al and Fukuzaka T et al.[24,25] Another property of nitrogen is its ability to stabilise duplex alloys against the precipitation of intermetallic phases," as reported by Charles J et al.[26] Such as sigma and chi, by reducing Cr-partitioning is also reported.[27].

The addition of N strengthens austenite by dissolving at interstitial sites in the solid solution, similar work is also done by carbon but due to sensitization problem, use of Carbon as strengthening element is restricted in Stainless steels.

Besides this Nitrogen is a strong austenite stabilizer it suppresses austenite dissolution and encourage austenite reformation in HAZ as reported by Irvine KJ et al.[28]

Manganese

Although Mn has been reported as austenite stabilizer but due to its very little effect on duplex phase balance, it is excluded from Creq nd Ni eq equations.

Usually Mn additions to stainless steels result in increase in abrasion and wear resistance. However, Mn additions in excess of 3 to 6% , for nitrogen level s of 0.1 % and 0.23 % , significantly decrease Critical pitting temperature, due to MnS inclusion formations which act as initiation sites for pits. As reported by Sedriks eta al[29]

Copper

Copper additions to high alloy austenitic stainless steel reduces the corrosion in environment such as sulphuric acid. In some of 25% Cr dupex alloys, approximately 1.5 % Cu is added to improve corrosion resistance in upto 70 % H2SO4 at 60 C as reported by Guha P et al[30].

Tungsten

W additions of up to 2% to duplex alloys imrove pitting resistance by extending the passive potential range and reduce I pass. In the same way W also increase crevice corrosion resistance.

W tends to form intermetallic formation during 700 to 1000 °C temperature range and secondary austenite formation in weld metal.[31]

Silicon

Addition of Silicon is meant for enhancing the high temperature oxidation resistance and use of steel for concentrated nitric acid service conditions High silicon (3.5-5.5%) bearing duplex stainless steels have been developed with increased pitting resistance and a claimed" immunity to stress corrosion cracking (SCC). although as Si is generally considered to enhance sigma formation (Fig.2.6), so it is generally Preferred to limit its addition to the 1% level.[32]

Carbon, sulphur and phosphorus

The carbon content of most wrought duplex stainless steels is limited to 0.02% or 0.03%, principally to avoid the precipitation of Cr-rich carbides (as shown in Fig. 2.6) which can act as initiation sites for pitting corrosion and intergranular attack.[4] Similarly, S and P contents are controlled, although not eliminated as the presence of some sulphur is important for weld bead penetration." Current modern steel making processes, such as ADD and VOD, level of C and S can be very well controlled while phosphorus contents can be reduced using good melting.[4,33]

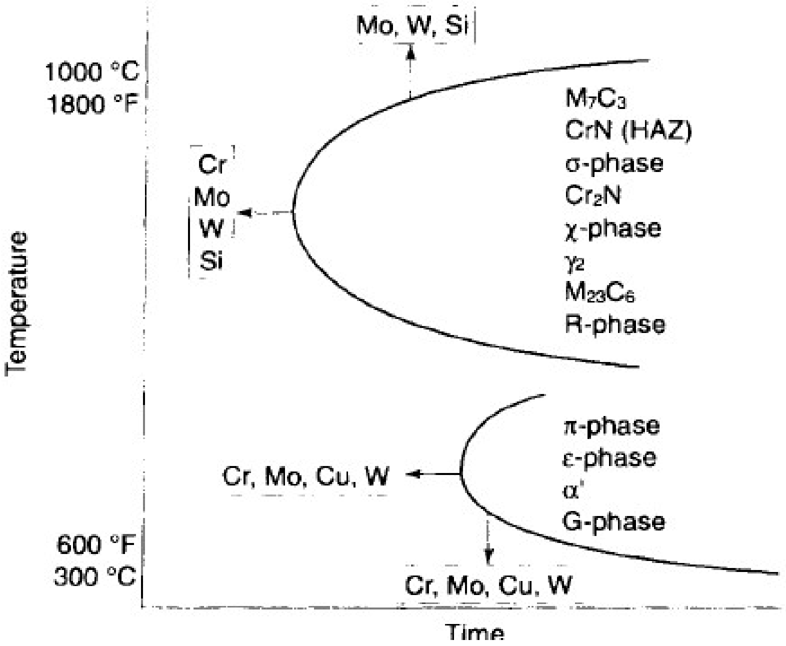

Fig 2.6 Schematic summary of the effects of alloying elements on the formation of various precipitates reference / source[34]

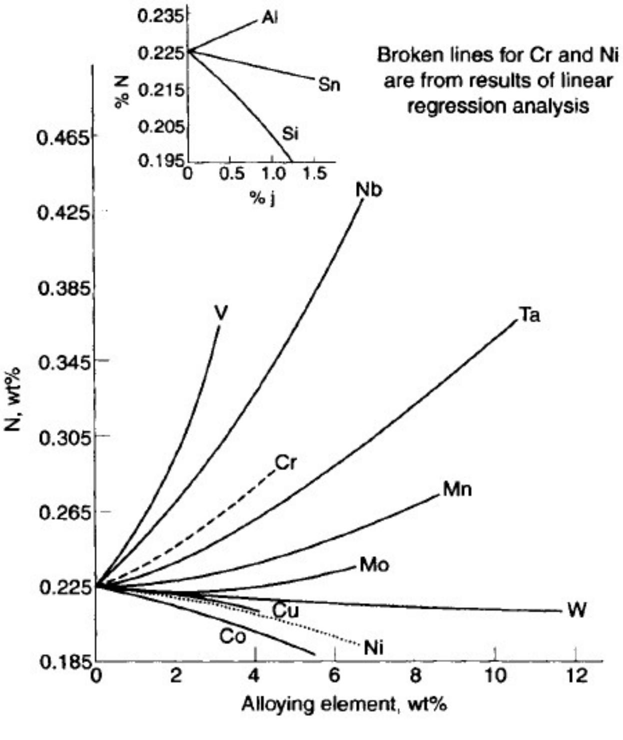

Fig 2.7 Effect of alloying elements on the solubility of Nitrogen in liquid Fe-18%Cr-8%Ni alloys at 1600°C at 1 atm N2. Source[35]

Table 2.6 The role of alloying elements in Duplex Stainless Steels can be summarized as below. Source[6]

Element	Wt %	Element Role	Alloying Characteristics
Cr	18-30%	Ferrite former	Improve corrosion resistance Ferrite content increase with increase in Cr, Higher Cr disturbs phase balance
Ni	4-8%	Austenite former	Changes Crystal Structure from ferrite to austenite Slowing down formation of intermetallic detrimental phases.
Mo	<5%	Ferrite former	Improved Pitting resistance. Increased tendency to form detrimental intermetallic phases if Mo content is too high.
N	0.14%	Austenite former	N causes austenite to form from ferrite at elevated temperatures, allowing for restoration of an accepted balance of austenite to ferrite after a rapid thermal cycle in the HAZ later welding. Additions of N increase pitting and crevice corrosion resistance and strength. Delays the formation of intermetallic phases. Offsets the formation of sigma phase in High Cr, High Mo Steels.

2.6 Welding of duplex stainless steel (General Welding Guidelines)

2.6.1 Cleaning before welding

Clean all regions that are to be heated prior to welding applies not just to duplex stainless steels, but to all stainless steels. The chemistries of the base metal and the filler metal have been developed assuming that there are no additional sources of contamination. Dirt, grease, oil, paint, and sources of moisture of any sort will interfere with welding operations and adversely affect the corrosion resistance and mechanical properties of the weldment. No amount of procedure qualification is effective if the material is not thoroughly cleaned before the weld.

2.6.2 Preheating

As a general rule, preheating is not recommended because it may be detrimental. It should not be a part of a procedure unless there is a specific justification. Preheating may be beneficial when used to eliminate moisture from the steel as may occur in cold ambient conditions or from overnight condensation. When preheating to deal with moisture, the steel should be heated to about 95°C (200°F) uniformly and only after the weld preparation has been cleaned. Preheating may also be beneficial if the weld is one of those exceptional cases.

2.6.3 Heat Input

Heat input and inter pass temperature are the two main welding parameters majorly influencing the cooling rate.

Heat input (KJ/mm) = $(V * A) / (S * 1000)$

Where V = voltage (volt)

A = Current (ampere)

S = travel Speed (mm/s)[5]

High weld heat inputs and high preheat and inter pass temperature promote coarse grained weld deposits and heat affected zones, extend the width of the HAZ and encourage precipitation. These structural changes may affect adversely the properties of the weldment. On the other hand, low heat inputs leads to rapid cooling that restricts grain growth and precipitation effects; however , the fast cooling suppresses the delta-gamma transformation and the consequent reduction in austenite content may also be undesirable in many respects.[6,37]

Lundquist et al. [1986][38] studied the effects of welding heat input 0.5 to 3.0 KJ/mm on the resistance of 2205 and 2304 DSS against pitting corrosion. The effect of H.I in the range from 0.5 to 3.0 kJ/mm was examined for Tungsten Inert Gas (TIG) welded bead-on-tube welds with and without the addition of a filler metal. The pitting resistance was seen improved with increasing value of heat input.

J. Nowacki et al, (2006)[37] investigated that increase in the heat input from 2.5 kJ/mm up to 5.0 kJ/mm has no negative influence on properties of the DSS 2205 welded joints prepared by SAW process

B. Gideon et al (2008)[39] studied on GTAW Weld samples at different weld heat input 1.5 to 2.0. They reported not much difference in ferrite -austenite proportions in root, Fill and Cap region. Substitution element do not have scope to partition in low heat input conditions. Hardness level as correlation with ferrite content. Impact testing correlations with H.I Shows that control of heat input was not a big role in influencing the weld metal mechanical properties within the conditions.

D.J.Kotecki (2010)[40] in his publications provided Recommendations for use of DSS 2205 with at least 0.14% N added, proper H.I & Inter pass Temperature for obtaining desired microstructure & Mechanical & corrosion performance.

Cleiton C. et al, (2013)[41] in their experimental work on AWS E309MoL austenitic stainless steel covered electrode and the AISI 410S ferritic stainless steel an overlay of equipment in the petroleum and gas industries explained effect of H.I on amount of delta ferrite production & subsequent effect on corrosion rate.

Ghusoon Ridha Mohammed et al, (2017)[42] reviewed significance of solidification mode on cooling rate & ferrite formation. The ratio of the ferrite to austenite is dependent on the Heat Input. High H.I. results in sufficient time for austenite formation at high temperature, while low H.I. result in less amount of austenite production and severe precipitation of deleterious phases like chromium nitrides. Author mentions that Susceptibility to SCC and the resistance against intergranular corrosion did not affect from high Heat inputs.

General heat input recommendations:

2304 or lean duplex 0.5–2.0 kJ/mm (15–50 kJ/in)

2205 0.5–2.5 kJ/mm (15–65 kJ/in)

2507 0.3–1.5 kJ/mm (8–38 kJ/in)[6]

2.6.4 Inter pass temperature. [6]

To avoid problems in the HAZ, the weld procedure should allow rapid cooling of this region after welding. The temperature of the work piece is important because it provides the largest effect on cooling of the HAZ. As a general guideline, the maximum interpass temperature is limited to 150°C (300°F). That limitation should be imposed when qualifying the weld procedure, and the production welding should be monitored to assure that the interpass temperature is no higher than that used for the qualification. Electronic temperature probes and thermocouples are the preferred instruments for monitoring the interpass temperature. It would not be conservative in the welding procedure qualification to allow the trial piece for a multipass weld to come to a lower interpass temperature than can be reasonably or economically achieved during actual fabrication. When a large amount of welding is to be performed, planning the welding so there is enough time for cooling between passes is good,economical practice.

2.6.5. Desired phase balance.[6]

The phase balance of duplex stainless steels is often said to be “50-50”, equal amounts of austenite and ferrite. However, that is not strictly true because modern duplex stainless steels are balanced to have 40-50% ferrite with the balance being austenite. It is generally agreed that the characteristic benefits of duplex stainless steels are achieved when there is at least 25% ferrite with the balance austenite. In some of the welding methods, particularly those relying upon flux shielding, the phase balance has been adjusted toward more austenite to provide improved toughness, offsetting the loss of toughness associated with oxygen pickup from the flux.

2.6.6 Post weld Heat treatment (PWHT)

PWHT is not recommended for Duplex Stainless steels weldments due to the fact that the heat treatment causes harmful intermetallic phases precipitation in the temperature range of 800 to 500 °C[6]

The well documented phenomena is alpha prime (475°C/885°F) embrittlement causing a loss of toughness and corrosion resistance.[6]

Postweld heat treating temperatures in excess of 315°C (600°F) can adversely affect the toughness and corrosion resistance of duplex stainless steels. Any post weld heat treatment should include full solution annealing followed by water quenching. [6]

2.6.7 Dissimilar metal weld

Duplex stainless steels can be welded to austenitic stainless steel, to carbon and low alloy steels. Duplex stainless steel filler metals with increased nickel content relative to the base metal are most frequently used to weld duplex stainless steels to other duplex grades. AWS E309L/ER309L is commonly used to join duplex stainless steels to carbon and low alloy steels. If nickel-base filler metals are used, they should be free of niobium (columbium). Because austenitic stainless steels have lower strength than duplex grades, welded joints made with austenitic filler metals will not be as strong as the duplex base metal

P. Bala Srinivasan et al (2006)[43] studied the impact strength & corrosion behaviour of SMAW Welded dissimilar weldments between UNS 31803 and IS 2062 steels. Results have shown that general corrosion resistance of the weld metal with E309 is superior whilst the welds with E2209 electrodes exhibit better passivation behaviour.

Welds produced with E309 electrodes have the highest Susceptibility to pitting in chloride solution. But E2209 electrodes for joining DSS and CS is most suitable for achieving better mechanical and corrosion properties.

Table 2.7 Welding Consumables Used for Dissimilar Metal Welding

	2304	2205	25 Cr	Super duplex
2304	2304 E2209 E309L	E2209	E2209	E2209
2205	E2209	E2209	25Cr-10Ni-4Mo-N	25Cr-10Ni-4Mo-N
25 Cr	E2209	25Cr-10Ni-4Mo-N	25Cr-10Ni-4Mo-N	25Cr-10Ni-4Mo-N
Super duplex	E2209	25Cr-10Ni-4Mo-N	25Cr-10Ni-4Mo-N	25Cr-10Ni-4Mo-N
304	E309L E309MoL E2209	E309MoL, E2209	E309MoL, E2209	E309MoL
316	E309MoL E2209	E309MoL, E2209	E309MoL, E2209	E309MoL, E2209
Carbon steel Low alloy steel	E309L E309MoL	E309L, E309MoL	E309L, E309MoL	E309L, E309MoL

2.6.8 Welding Process Selection

All of the common arc welding processes are applicable and suitable for welding Duplex Stainless steels. The selection of process is based on Materials, joint configurations, thickness, productivity and quality requirements agreed between the manufacturers and the clients.

Having selected any process, it is subsequently optimized for improving quality and productivity.

Gas tungsten arc welding (GTAW), shielded metal arc welding (SMAW), submerged arc welding (SAW), flux cored arc welding (FCAW), gas metal arc welding (GMAW) and plasma arc welding (PAW) are commonly used with success for most DSS grades.

Koray Yurtisik1 et al, (2013)[44] in his research work, combined the Plasma Arc Welding (PAW) & of GMAW Welding processes to take advantage of deep penetration capability & higher metal deposition capability . This Hybrid welding process achieved less heat input compared to GMAW while, the precipitation of secondary phases, which can adversely affect toughness and corrosion resistance of DSS, was significantly suppressed in both FZ and HAZ. Secondly, with keyhole techniques, suitable cooling time and weld metal composition were developed, resulted in a suitable microstructure, Mechanical & corrosion properties.

Autogenous welding and high power density welding processes such as electron-beam welding , laser-beam welding, stud welding, resistance welding to some extent, are not recommended in many literatures, because fast cooling associated with this Low Heat Input (High Power density processes) promotes Cr2N precipitates due to rapid super saturation of nitrogen in the ferrite upon quenching[1] in general for welding Duplex Stainless steels, one of the reasons, being autogenous process & not being able to use Ni enrich filler wires there will be many issues pertaining with weld strength & Corrosion performance as high ferrite content in Weld Metal & intermetallic precipitations in the WM & HAZ, In many literatures, Solution Annealing treatment is recommended to dissolve back all precipitates & revert back in to solution and avoiding re-precipitation by adopting suitably fast cooling rates. but this practice often compromises with the Mechanical Strength of the joints as reported in many literatures[1].

J.M. Pardal et al (2007) reported effect of multi pass (GTAW Root pass & SMAW fill & cap pass) welded SDSS 32750 on toughness -Mechanical & Pitting Corrosion Behaviour as Low Nickel filler metal employed in root pass result in low austenite formation & deleterious phases while SMAW Fill & Cap Pass resulted in low toughness.

The Table 2.8 & 2.9 provides the recommendation for the common arc welding techniques along with the selection of gas & consumables.

Table 2.8 Suitable Welding process recommendations. Source[6]

Welding Process	Gas Types
GTAW	99.996%Ar, Ar+2%N2, Ar+5%N2
GMAW	Ar+1%O2, Ar+30%He+1%O2, Ar+2%CO2, Ar+15%He+2%CO2
FCAW	Ar+1% O2, Ar+20%CO2, Ar+2%CO2
PAW	99.996%Ar

Table 2.9. Recommendations for DSS welding consumables. Source[6]

Alloy	Process	AWS specification	BS EN specification
DSS	GTAW	ER 2209	W 22 9 3 N L
	GMAW	ER 2209	G 22 9 3 N L
	SMAW	ER 2209-15/16/17	N 22 9 3 N L B/R
	FCAW	ER 2209 t0-1/4, ER 2209 t1-1/4	T 22 9 3 N/L RP
	SAW	ER 2209 + FLUX	S 22 9 3 N/L RP
SDSS	SMAW	E2594-15	BS EN 25 9 4 N L B
		E2594-16	BS EN 25 9 4 N L R
	GTAW	AWS ER2594	
	FCAW	AWS E2594T0-4 AWS E2594T1-4	

2.6.9 Shielded Metal Arc welding [45]

In Shielded Metal Arc Welding (SMAW) process, the heat is generated by an electric arc maintained between base metal and a consumable electrode. In this process electrode movement is to be controlled manually controlled so it is termed as manual metal arc welding (MMAW). As shown in Fig. 2.8

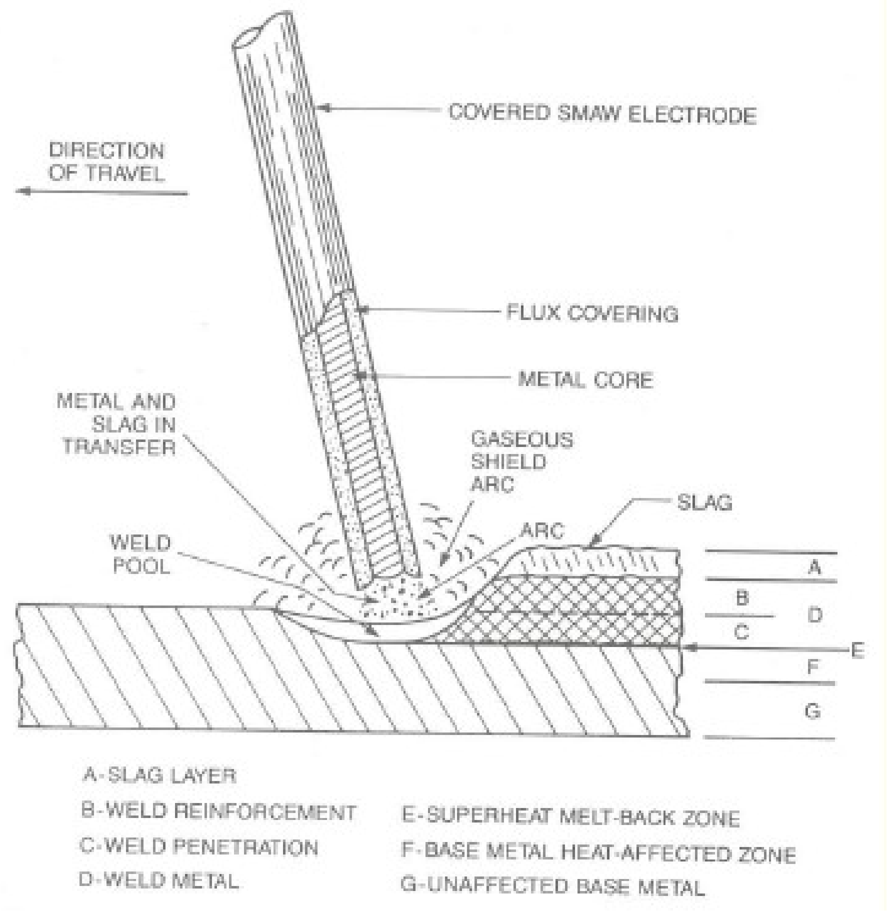

Fig. 2.8 Diagrammatic sketch of the shielded metal arc welding process (SMAW) using a consumable flux coated covered electrode. Source[45]

This process is widely used for depositing weld metal because it is easy to deposit the molten weld metal at the desired place where it is required and it doesn’t need separate shielding.

SMAW electrodes consist of a metal core wire and a flux covering surrounding the core wire.

As the electrode melts, the coated flux covering disintegrates, generates vapours that protect the weld area from oxygen and other atmospheric gases. In addition, the flux provides molten slag which floats to the surface and protects the weld from contamination as it solidifies. The Arc and the weld are shielded by gas and slag.[45]

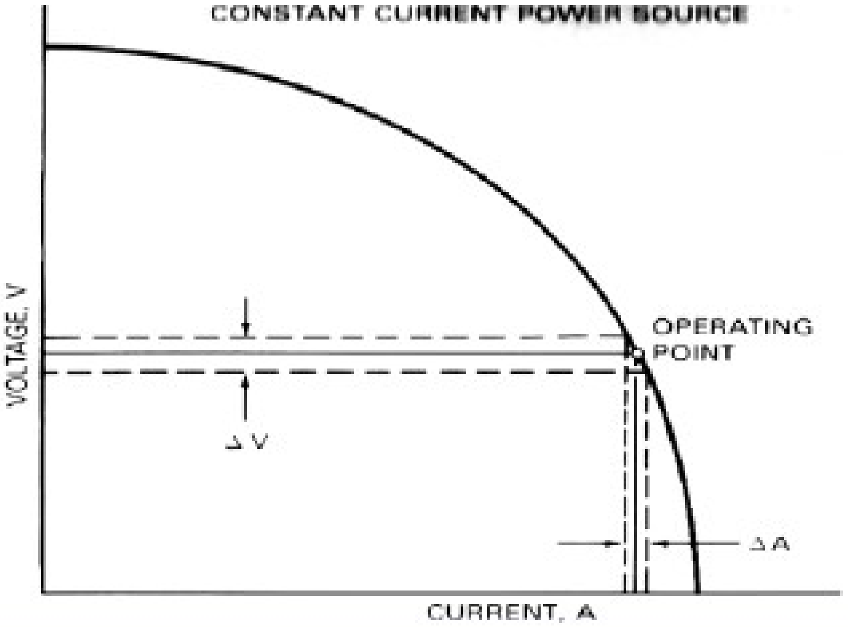

Fig.2.9 Constant Current Power Sources (Drooping Characteristics)

Drooping characteristics power source (Constant Current Characteristics) is preferable for this process (as shown in Fig. 2.9) since it is manually controlled and so power source is designed to give stable operation where the electrode moves up and down with the welders hand eg. MMAW and GTAW processes.

As any small Variation in arc voltage with movement of the welders hand results in very little change in current as shown in figure. So Stable current gives consistent arc heat and weld pool.

Open circuit voltage (OCV) is the voltage across the output terminals of the power source when it is under no load condition.

In case of AC welding plays an important role in ensuring easy arc starting and good arc stability. Higher is the OCV better is the arc stability. However higher OCV poses danger of electric shock and hence its value is restricted to 100 V max

Commercially available transformers generally have OCV values 60 V to 70 V While rectifiers generally have OCV values 65 V to 80 V.

Electrode coatings can consist of a number of different compounds, including rutile, calcium fluoride, cellulose, and iron powder.

Coating offers the smooth Arc characteristics such as Stability, Striking & Re-striking, Force, Capability to work in positions, in AC & DC Power Source sets

The function of the Slag is to provide sufficient shielding to the molten weld pool from the atmospheric gases and to bring impurities out of molten weld metal, Good detachability, Flow ability as well as quick freezing nature.

Additionally, the Flux coating also serves functions such as Stabilisation and maintenance of Arc so as to improve metal transfer and reduce spatters. So overall operating Voltage for the electrodes also reduces.

Shielding can be ensured in two ways: (i) by gases produced by the flux and (ii) slag covering during welding.

Slag fluidity determines the ease of positional welding so Weld pool control is a function of composition of Flux. It is well documented that Fast freezing slag is more suitable for welding in vertical and overhead positions.

Flux also contains alloying elements to improve mechanical properties of the joint. □

Coating Constituents include Arc stabilisers, Slag formers, Deoxidisers, Gas forming materials, Binders, Alloying elements, Extruding/slipping agents etc.

There are typically five Coating types such as Rutile, Basic, Cellulosic, Acid, Acid-rutile and Oxidising

Types of Electrodes as per AWS based on application:

Carbon-manganese steel electrodes AWS A5.1

Stainless steel electrodes A5.4

Low alloy steel electrodes A5.5

Copper & Copper alloy electrodes A5.6

Aluminium & Aluminium alloy electrodes A5.10

Nickel & Nickel alloy covered electrodes A5.11

Basic Coated Low Hydrogen Electrodes Coating contains Metal Carbonates & Calcium Fluoride. It Releases CO2 in arc atmosphere, often Fluxing by Calcium Fluoride. (Fluorspar) so Moisture bearing materials are restricted in coating.

It offers the advantages such as adequate penetration, easy Slag removal, enhanced iron powder for improving productivity & good mechanical Properties.

Technologically it is very important to achieve Weld metal integrity, Weld joint produced is of very high radiographic quality.

There are certain applications demand for high toughness at sub-zero temperatures so Hydrogen Level has to be controlled very carefully so that Basic Coated Low Hydrogen Electrodes allows Low amount of diffusible hydrogen content of weld metal (< 5 ml/100g deposited weld metal)

Alloy transfer efficiency is also reported high compared to other class of electrodes because of Iron powder /alloying additions in the composition.

An electric arc is maintained between the end of a coated metal electrode and work piece.

The flux covering melts during welding and forms gas and slag to shield the arc and molten weld pool.

2.7 Welding metallurgy of duplex stainless steel [45]

The Mechanical & Corrosion performance of the Duplex Stainless Steels weldments is depended on ferrite/austenite ratio, developed features of the microstructure which in turn depended on the phase transformations during associated weld thermal cycles during welding.

The iron-Chromium-nickel ternary equilibrium diagram is a roadmap to foresee the metallurgical behaviour. Fig 2.10 shows a 65 % rich Iron portion of Fe-Cr-Ni ternary alloys. Alloys with composition in band 1 will undergo solidification as either fully austenitic or austenitic with small amount of residual ferrite content which becomes susceptible to Hot Cracking during welding.

Alloys with compositions in bands 2, 3 and 4 will undergo solidification as ferrite; on further cooling part of the ferrite transforms to austenite at temperature below ferrite solvus.

In band 2 about 20-30% of vermicular ferrite is retained at room temperature. In band 3 about 50% of the acicular ferrite can be retained. The Duplex Stainless steels composition falls in band 3. In the high Chromium equivalent band 4 almost 80-100% of the ferrite will be retained.

The transformation sequence on cooling from the liquid state can be represented as follows

$L \longrightarrow L + \delta \longrightarrow \delta \longrightarrow \delta + \gamma$

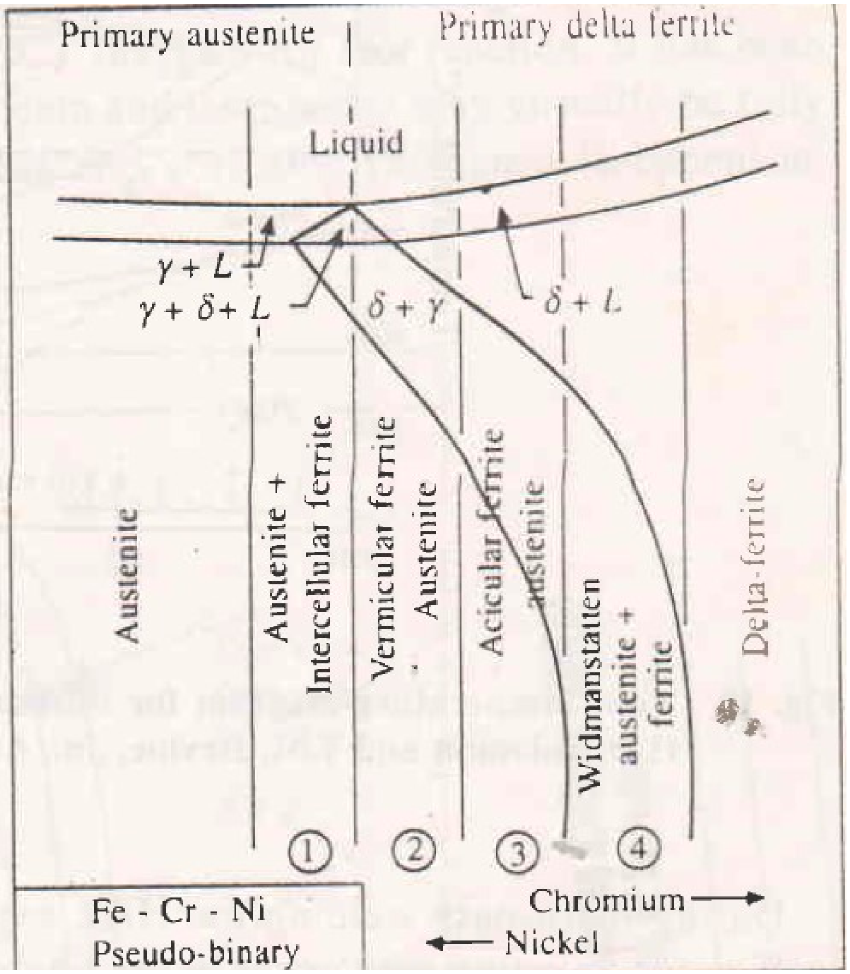

Fig 2.10 Schematic constant iron section at 65% iron of the Fe-Cr-Ni ternary diagram, source[45]

Showing variation of solidification mode of ferrite morphology with composition

$L \longrightarrow L + \delta \longrightarrow \delta \longrightarrow \delta + \gamma$

The duplex stainless steels are preferably welded after solution treatment in the range 1000- 1100º C the temperature and time being decided by steel composition and section size, respectively. This heat treatment would result in nearly equal proportions of austenite and ferrite in a typical DSS[45].

During welding in the heat affected zone (HAZ) austenite is transformed to ferrite on heating whenever the ferrite solves temperature is exceeded. On consequences is the austenite dissolution is the growth of ferrite grains [45]

Coarse grain regions are commonly observed adjacent to the fusion line. Which is a similar type of phenomena occurs in ferritic stainless steels [45].

During cooling the austenite forms again along the prior ferrite boundaries and at intergranular sites. Degree of reverse formation of austenite is a function of composition, temperature and time. Like the austenite these precipitates form along the ferrite boundaries or within the ferrite grains. Regions surrounding either grain boundaries or intergranular austenite are free from precipitation. The precipitates include carbides, carbonitrides, nitrides, alpha prime and other hardening phases such as intermetallics sigma, chi and eta as reported by Kiessling 1984. See Fig. 2.6.[45,5]

During multi pass welding HAZ experiences additional thermal cycles. So reactions like dissolutions or precipitations may take place as a function of temperature and time, but the net effects is always towards increasing the amount of austenite formation in the weld metal as reported by Stephenson, 1987[45,5]

The austenite forms also, particularly when its percentage is high as Widmanstatten side plates nucleating from the grain boundaries austenite and growing along specific crystallographic orientations in the ferrite matrix as reported by Southwick and Honeycombe 1980. Precipitation reactions and structural changes during multi-pass welding are similar to those in the HAZ[45,5]

There can be different morphologies of austenite possible, first which it forms along ferrite grain boundaries by nucleation and growth mechanism, below ferrite solvus temperature.

Ferrite to austenite transformation is solid state transformation so it depends on cooling rate predominantly [45,5]

Additional austenite may form as Widmanstatten side plates off the grain boundaries austenite or intergranularly within the ferrite grains[1]

2.7.1 Role of Nitrogen in Solidification Mechanism

Nitrogen in the range of 0.08 to 0.35 wt. % is deliberately added in all modern duplex stainless steels this is because, Nitrogen, an austenite stabilizer, is added as both a solid-solution hardener and resistance promoter against pitting corrosion in chloride-containing media.

Duplex Stainless steels solidify as 100 % ferritic structure and then with further cooling below ferrite solvus, some part of the ferrite phase transforms to austenite phase within the ferritic structure. Nitrogen raises the temperature (ferrite solvus temperature) at which the austenite formation initiates. This mechanism permits the equilibrium level of austenite and the desired phase balance, even at relatively rapid cooling rates.

Another favourable effect occurs during solidification, as in welding, reduces the risk of excess ferrite in the HAZ.

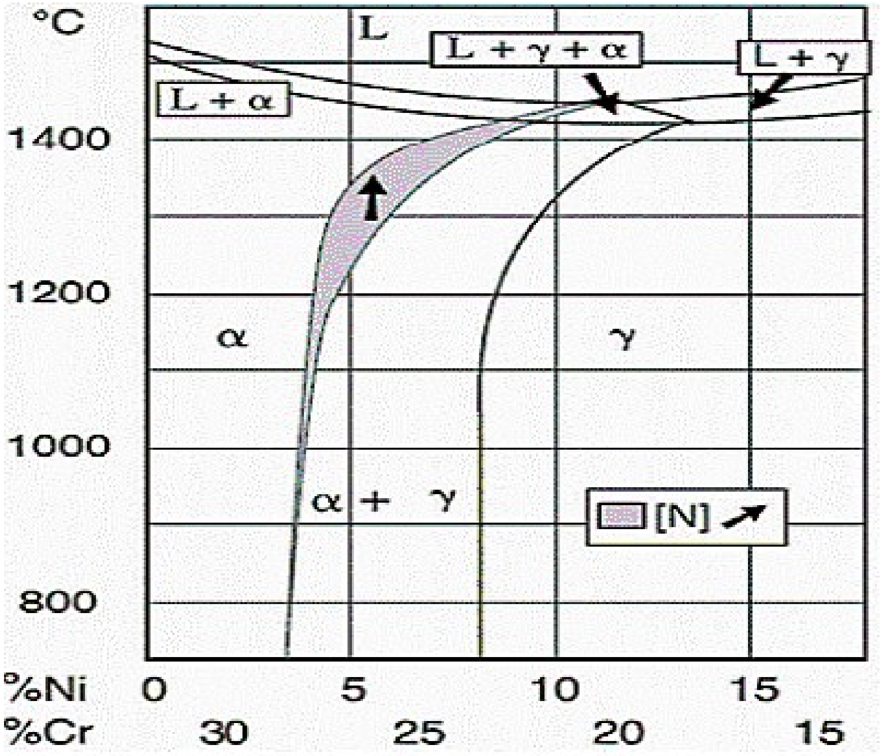

Fig 2.11 Pseudo-binary Fe-Cr-Ni phase at 70% Fe section illustrating areas of detrimental phase formation Source.[46]

It is clear from the above Fig 2.11 that the beneficial effect of nitrogen that it raises the ferrite solvus temperature below which the austenite begins to form from ferrite through solid state transformation.

Carlos Roberto et al (2015)[47] in their experimental work with GMAW on Bead on Plate on DSS 2206 have found through experimental & Numerical methods that High HI can cause Ferritic Grain growth & Less Austenite production in High Temp HAZ (HTHAZ), effect of Nitrogen is not only as Austenite former in FZ but it keeps cooling rate above Sigma Phase Precipitations.

Under actual cooling conditions, which is at rapid rate, balance amount of austenite would be formed. Nitrogen is deliberately added in the latest DSS second generations DSS like UNS 32205, UNS 32550 Compositions to minimize the problem of additional ferrite level in the WM & HAZ.[5,6,46]

As can be seen from the solubility limit versus temperature relationship (Fig.2.12) above about 1000 °C due to difference in solubility limit of Nitrogen in ferrite and in austenite below 1000 °C, Nitride precipitation is occurring. Nitrogen partitions between ferrite and austenite and remain in solid solution when microstructure is balanced nearly 50/50[1]

If the ferrite content is high, in WM & HAZ, under rapid cooling conditions, an increase in nitride precipitation occurs upon cooling since the solubility limit is of the ferrite is surpassed and the nitrogen has sufficient time to partition to the austenite.

In most cases, these nitrides are Cr-rich and are thought to be primarily Cr2N. as reported by Brandi S.D, Ramirez et al & Brandi S.D. & Lippod et al, results in loss of ductility, toughness & Corrosion resistance[1].

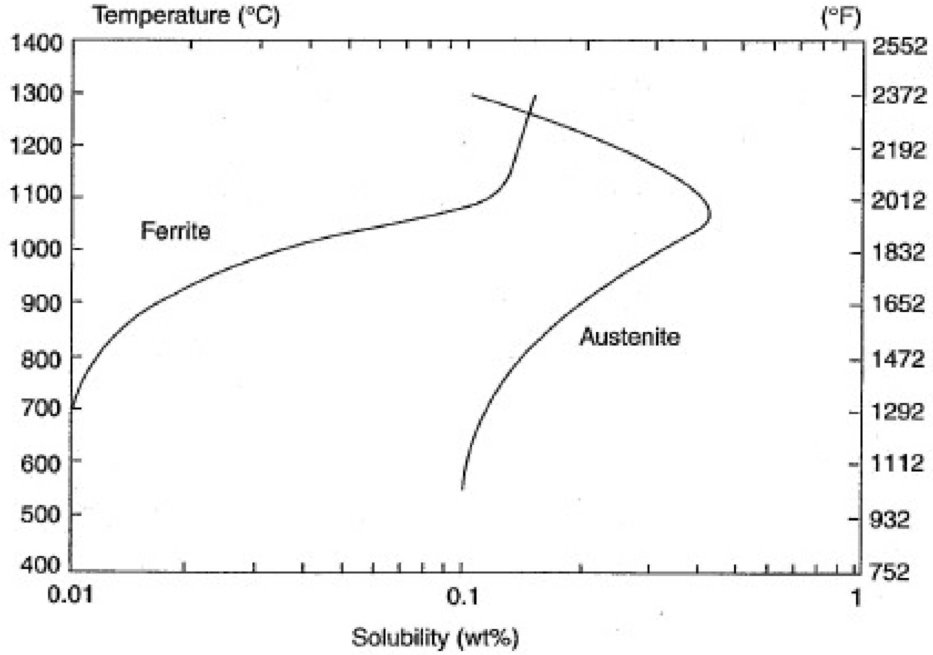

Fig 2.12 Nitrogen solubility in ferrite and in austenite. (Constructed by J.C.Lippold, based on several literature sources.) Source[1]

Due to rapid cooling effect, from near the ferrite solvus temperature, there is a higher tendency for ferrite in the WM & HAZ than in the Base Metal.

Ferrite austenite ratio phase balance in DSS Weldment is a function of diffusion phenomena, compared to all the alloying elements, Carbon and Nitrogen being smaller interstitial atoms have high diffusion rate. Nitrogen has tendency for lowering the effective quench temperature so that phase balance almost becomes equals to wrought base metal.

Ogawa & koseki et al have explained that Nitrogen has higher solubility in austenite than ferrite phase. During cooling below ferrite solvus temperature, nitrogen diffuses from ferrite towards, austenite. If the cooling is too rapid for the nitrogen to partition into austenite, some of the nitrogen will become trapped within the ferrite phase and subsequently precipitate as chromium nitride. Cr, Mo, Ni have less mobility below ferrite solvus while N has mobility below ferrite solvus.

Jingqiang Yang et al,[48] conducted weld failure analysis of 2205 duplex stainless steel nozzle with a root cause that Localized uneven distribution of ferrite/austenite with 80-90% ferrite in weld responsible for the cleavage fracture by crack propagation mechanism along columnar grains.

2.7.2 Intermetallic and secondary phases

Detrimental sigma, alpha prime, and carbides and nitrides can form in a matter of minutes at certain temperatures. Consequently, the thermal treatments required for processing and fabrication, as well as the service cycles, must take reaction kinetics of phase formation into account to ensure that desired corrosion resistance and mechanical properties are obtained.[6,7]

An isothermal precipitation diagram for 2304, 2205, and 2507 duplex stainless steels is shown in Figure 2.13 .The start of chromium carbide and nitride precipitation begins at the relatively “slow” time of 1–2 minutes at temperature.

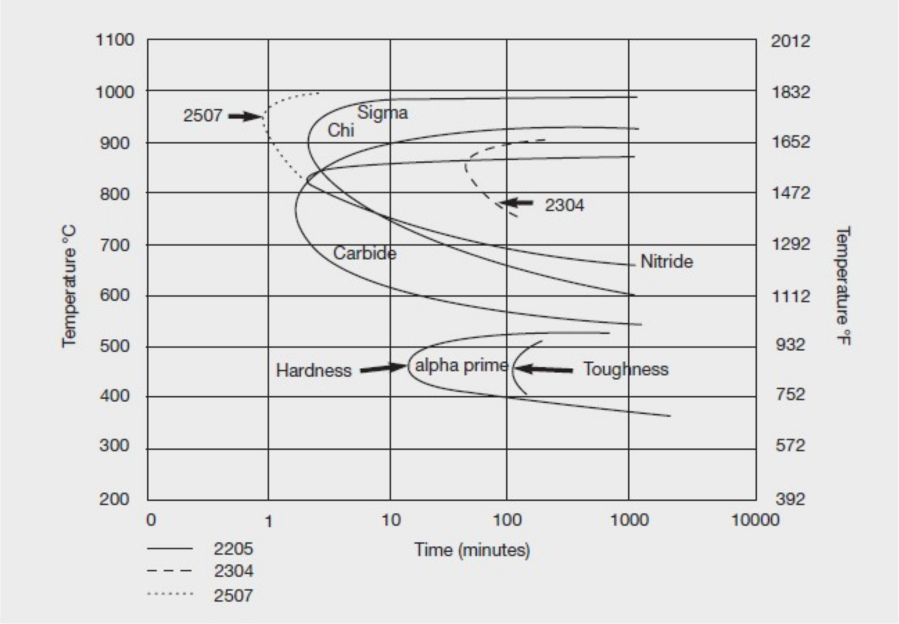

Fig.2.13 isothermal precipitation diagram for 2205 duplex stainless steel, annealed at 1050 ºC (duplex grades 2307 and 2507 are shown for comparison)

The use of nitrogen as an alloying element in these stainless steels means that chromium nitrides may be present on ferrite-ferrite grain boundaries and on austenite-ferrite boundaries in the heat-affected zone of welds. If formed in large volume fraction.[6,7]

Under conditions in which the chromium-depleted areas do not have time to homogenize during annealing, these chromium nitrides may adversely affect corrosion resistance. However, because higher nitrogen promotes austenite, which has a high solubility for nitrogen, the second-generation duplex stainless steels seldom contain significant amounts of chromium nitrides.[6,7]

The precipitates free zone (PFZ) is believed to occur because the austenite acts as a sink for the fast-diffusing interstitial elements carbon and nitrogen, thus inhibiting precipitation in the vicinity of the austenite crystal[1].

2.7.2.1 Alpha prime (α’)

Alpha prime is also a stable phase in duplex alloys, developing in the ferrite phase below about 525°C (950°F) in the same manner it forms in fully ferritic alloys. Alpha prime causes the loss of ambient temperature toughness in ferritic stainless steel after extended exposure to temperatures centred in the range of 475°C (885°F); this behavior is known as 475C / 885F embrittlement.

2.7.2.2 Sigma phase (σ)

The deleterious Cr, Mo rich sigma (**σ**) phase, which is very hard and embrittle in nature, forms in the temperature range between 970°C-650°C. The minimum time required for **σ** formation at 800°C is about 15 minutes in DSS. After 200 hours at 800oC, the amount of **σ** phase is estimated to be 50%. **σ** Phase nucleates both on the intergranular M23C6 carbides and at the interface of **σ** -ferrite with the austenite.

2.7.2.3 Carbides M23C6 and M7C3

M7C3 forms between 950 and 1050°C at the ferrite-austenite grain boundaries (Solomon and Devine, 1982). However, as its formation takes 10 minutes, it can be avoided by normal quenching techniques. Further, as modern duplex grades contain less than 0.02%C, carbides of either form are rarely if ever seen (Gunn, 1997). If carbon levels are about 0.03%, M23C6 17 rapidly precipitates between 650 and 950°C, requiring less than 1 minute to form at 800oC. Precipitation predominantly occurs at ferrite-austenite boundaries, where Cr-rich ferrite intersects with carbon rich austenite.

The temperature limits for these pressure vessel design codes for various duplex stainless steel is summarized in Table 2.10

Zhiqiang Zhang et al (2016)[52] In their research work, investigated the relationship between microstructure developed by Flux-cored arc welded metal for corrosion behaviour using Electrochemical potentiokinetic reactivation technique to study selective corrosion and concluded selective corrosion of secondary austenite over primary austenite & ferrite. Apart from this Localised corrosion possibility around Cr2N and sigma phase in HAZ.

A review paper on “Welding of Duplex SS” by Jatandeep Singh et al (2013)[53] explained the importance of balancing ferrite to austenite, way of avoiding & minimizing formation of deleterious intermetallic and non-metallic phases, deleterious effect of hydrogen on duplex stainless steel and measuring technique of ferrite contents in Duplex SS Weldments.

2.7.2.4 Secondary Austenite[54,1]

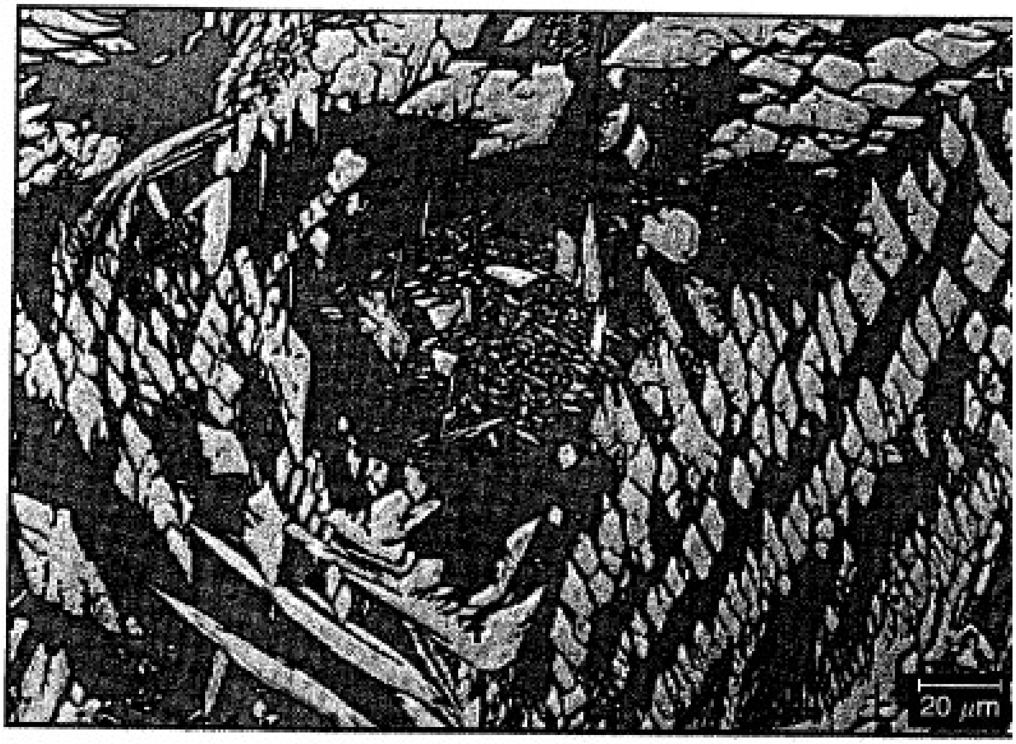

Fig. 2.14 Secondary austenite in a simulated HAZ n alloy 2205. Secondary austenite is fine light etched phase in the centre of a prior ferrite grain. (From Ramirez)[54,1]

Under rapid cooling conditions, in DSS WM & HAZ, the F/A Phase balance tends to be higher than equilibrium for a given composition, as a result, Reheating of the weldment allows for additional diffusion takes place. Further growth of existing austenite or nucleation of new austenite, termed as secondary austenite. See Fig. 2.14 to 2.16.

Secondary austenite is most prevalent in the WM & HAZ during multi pass welding.

The mechanism of secondary austenite has been studied in great detail by Ramirez et al**[54,55,1]** as per this are two distinct forms of secondary austenite. As shown in Fig. 2.16.

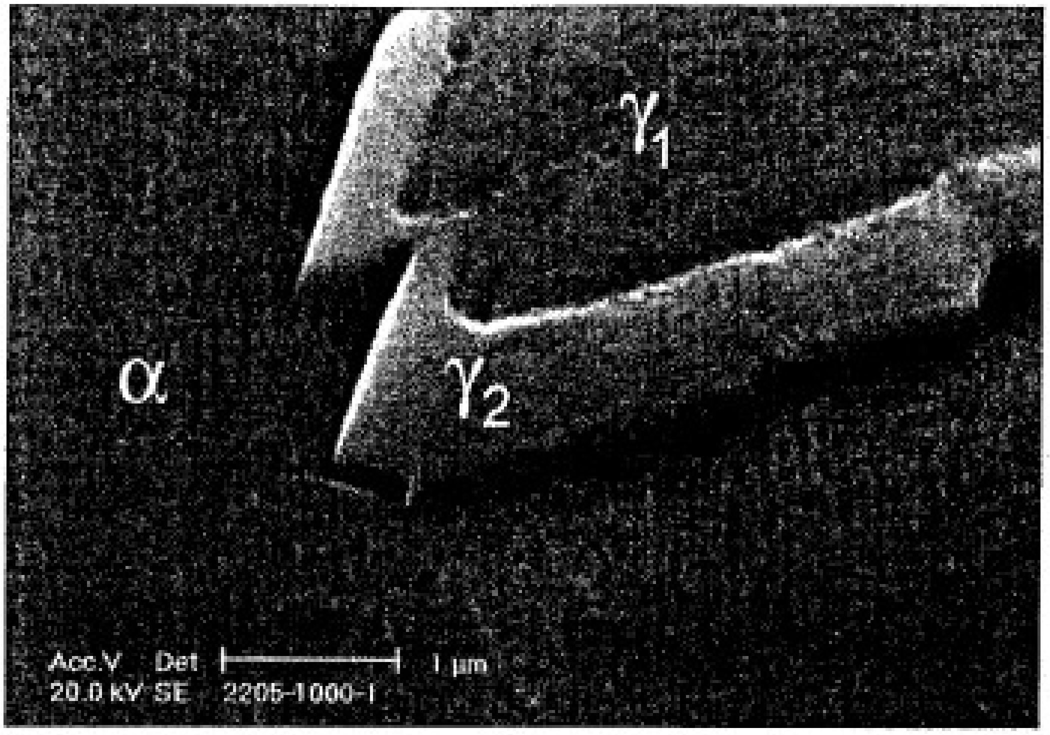

Fig 2.15 Secondary austenite (gamma 2) resulting from growth off of primary austenite (gamma1) in Alloy 2205. (From Ramirez eta l.[55,1]

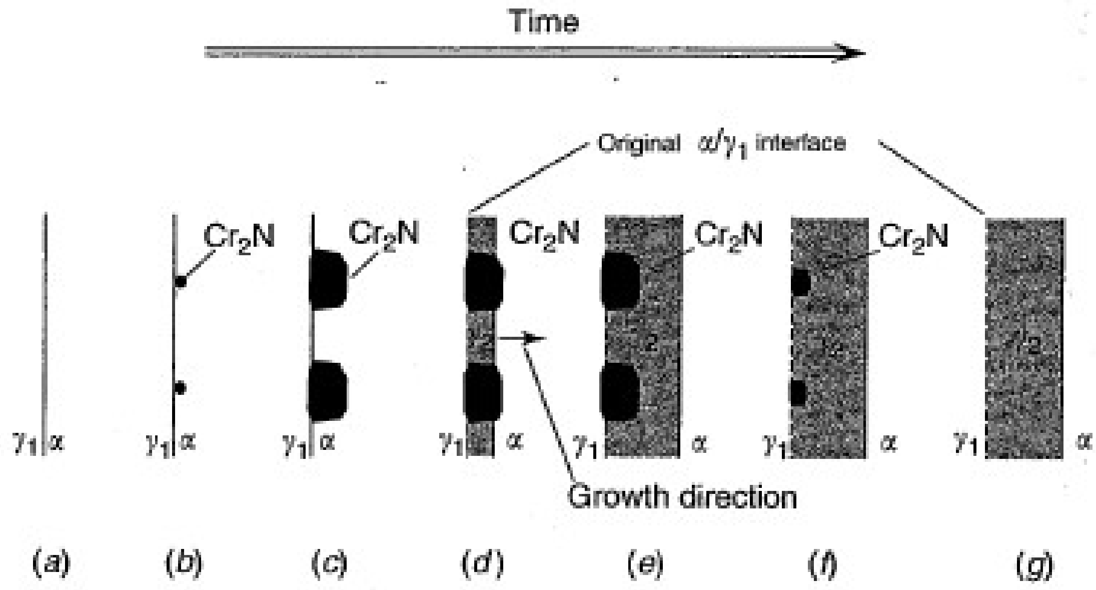

Fig 2.16 Cooperative growth mechanism for formation of secondary austenite. (From Ramirez et al [54,55,1]

Secondary Austenite improves toughness. But Secondary Austenite result in loss in pitting resistance as pitting nucleation prefer ɣ 2/ ferrite Interface and low content of N in secondary austenite than primary austenite.

Cr2N first nucleates at the interphase interface, resulting in a local depletion of ferrite-promoting elements Cr and Mo. This local depletion then leads to the nucleation of Gamma 2 at the interface and subsequent growth.

In time region 1, Austenite transforms to ferrite and precipitate dissolution.

In time region 2, above the ferrite solvus, ferrite grain growth occurs since there is no second phase (austenite) or precipitates to inhibit growth.

In region 3 austenite reformation and precipitation reactions (carbides and Nitrides) From Varol eta [1,56]

Table 2.10 the temperature limits for duplex stainless steel Precipitation temperature for DSS. Source [6]

Solidification range	1445 to 1385 °C
Scaling temperature in air	1000 °C
Sigma Phase formation	700 to 975°C
Carbide precipitation	450 to 800°C
475° embrittlement	350 to 525°C

2.8 Ferrite measurement [99,100]

There are several different techniques for the measurement and determination of δ-ferrite; however, magnetic determination is the most extensively used in the industry because it is Non destructive and provides an immediate result. Ferrite Number can be measured directly on weld deposits, because ferrite being magnetic in nature.

The volume fraction of ferrite can be quantified by three experimental techniques

- **Magnetic measurement by ferritoscope**: after polishing of the specimens, usually five measurements of on each weld test coupons are taken with a calibrated ferritoscope; the equipment has to be calibrated with appropriate standards, with detection limit of 0.1% ferrite. The measurement method is based on magnetic induction in which a magnetic field is generated by a coil that interacts with the magnetic phase of the sample. Any changes in the magnetic field induce a voltage proportional to the ferromagnetic phase content in a second coil. This voltage is then evaluated in terms of Ferrite % OR Ferrite Number (FN).

Several instruments are available commercially, including the Magne Gage, the Severn Gage, the Inspector Gage and the Ferritscope which can be calibrated to AWS A4.2 or ISO 8249 and provide readings in Ferrite Number. The amount of ferrite normally should not be greater than necessary to prevent hot cracking with some margin of safety. The presence of ferrite can reduce corrosion resistance in certain media and excess ferrite can impair ductility and Toughness [1] (Ref. Damian Kotecki, (2003); Stainless Steel Welding Guide, the Lincoln Electric Company)

• **Quantitative optical metallography Method ASTM E562**: after polishing and etching of the weld test coupons, measurements of phase contents are made by the point counting technique prescribed in ASTM Standard E562-02, using an image analysis software, connected via digital high resolution camera to a optical microscope. Usually ten fields per sample are analyzed at 500X magnification.

• **X-ray diffraction**: to confirm the existence of ferrite and austenite, X-ray diffraction patterns are obtained using an XRD- diffractometer.

The principle is based on exposure of the stainless steel sample to a monochromatic X-radiation source and, depending on the crystal structure of the phases present (BCC ferrite, FCC austenite), Characteristics peaks will be reflected for each phase whose intensity will be related to the composition of each phase in the sample.

According to the published literatures [101-103], it is reported that the quantitative determination of ferrite content in duplex stainless steel welds has not been satisfactory, possibly because the fine dispersed morphology of the ferrite - austenite matrix in duplex stainless steels matrix make the diffraction patterns diffuse.

The equipment is expensive and it has only been used in laboratory studies. Moreover, ASME SEC II C Code does not recommend XRD Method.

2.8.1 Introduction to Schaeffler, WRC De-Long & WRC 1992 Diagram

These diagrams are useful tool to predict the resultant weld metal composition & Microstructure and particularly susceptibility to Hot Cracking in Austenitic stainless steels & dissimilar steels welding.

2.8.1.1 Schaeffler diagram

The introduction of the Schaeffler diagram (1949) provided the first method to calculate ferrite percent in a non-destructive manner. Under non-equilibrium cooling conditions, as experienced in welding, the Schaeffler diagram (Fig. 2.17) can be used for predicting the relative amounts of phases present for Fe-Cr-Ni steels that do not contain nitrogen.

Schaeffler mathematically correlated chromium and nickel equivalents, which were readily calculated based upon the alloy chemistry, to the amount of ferrite present. Based upon the amount of nickel, carbon, manganese, chromium, molybdenum, silicon and niobium (columbium) present, a brief reference to this diagram quickly estimated the amount of ferrite present

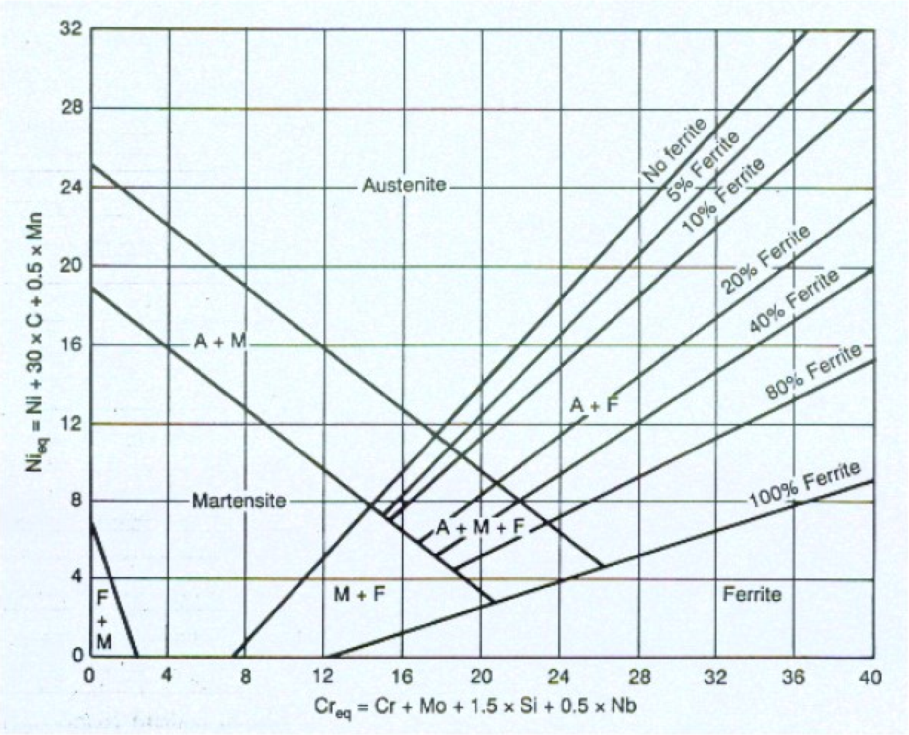

Fig 2.17 Schaeffler Diagram source [1, 42]

2.8.1.2 WRC-1992 diagram [1]

WRC-1992 diagram is now latest and more accurate for higher alloys and some special grades like Manganese-austenitic or duplex, austenitic-ferritic alloys.

Although, similar results can be obtained with WRC-Delong Diagrams (Fig. 2.18) but for low alloy routine grades like 304, 316, 308 etc. reduction of the weld metal properties from the composition of the base material and filler material with the use of any of several constitution diagrams. (Ref: - Damian Kotecki, (2003); Stainless Steel Welding Guide, the Lincoln Electric Company)

The oldest of these is the 1948 Schaeffler Diagram which contained empirical relationship as The Cr equivalent (% Cr + % Mo + 1.5 x % Si + 0.5 x % Cb) is plotted on the horizontal axis and the nickel equivalent (% Ni + 30 x % C + 0.5 x % Mn) on the vertical axis.

Despite long use, the Schaeffler Diagram is now obsolete because it does not take into account effect of Nitrogen as Austenite former and because it has failed to provide consistent result among several measures.

These limitations associated with the Schaeffler Diagram is taken care of in the development of 1973 WRC-DeLong Diagram, which can be used to predict ferrite level. The main differences are that the DeLong Diagram includes nitrogen (N) in the Ni equivalent (% Ni + 30 x % C x 30x % N + 0.5 x % Mn) and shows Ferrite Numbers in addition to “percent ferrite.” Ferrite Numbers at low levels may approximate “percent ferrite.”

As per the Kotecki, D.J 1997 [57], approximately 100 FN can be approximated to 70 Ferrite.

The most recent diagram, the WRC-1992 Diagram, Figure 2.18, is considered to be the most accurate predicting diagram at present. The WRC-1992 Diagram has replaced the WRC-DeLong Diagram in the ASME Code with publication of the 1994-95 Winter Addendum.[57]

Its Ni equivalent (% Ni + 35 x % C + 20 x % N + 0.25 Cu) and Cr equivalent (% Cr + % Mo + 0.7 x % Cb) quite differ from those of Schaeffler and WRC-DeLong[57].

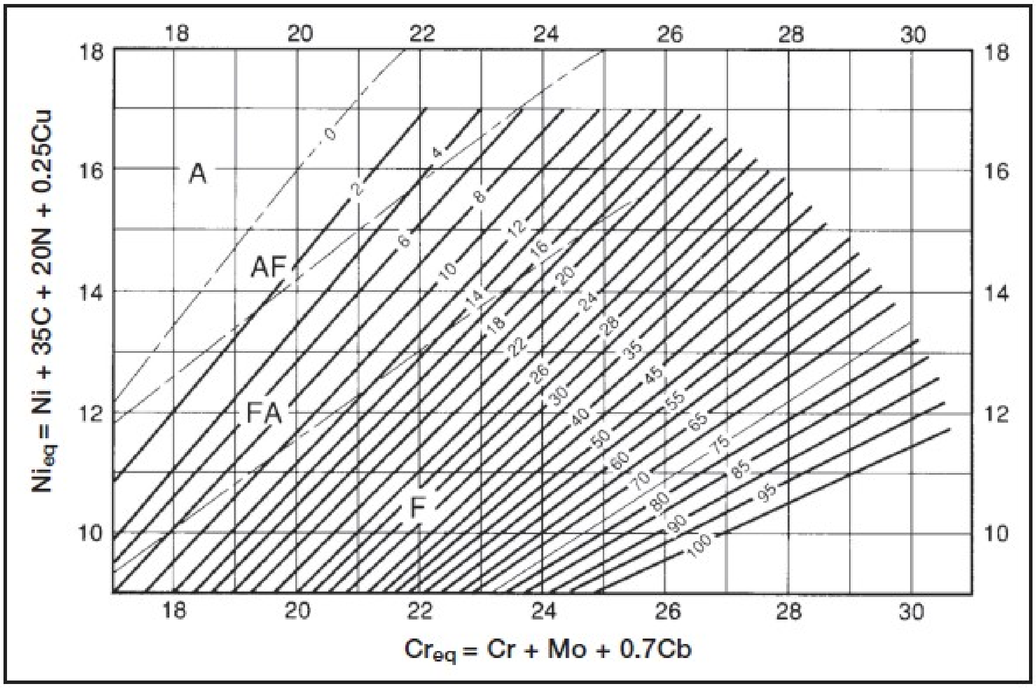

Fig 2.18 New 1992 WRC diagram including solidification mode boundaries. (Updated from T.A. Siewert, C.N. McCowan and D.L. Olson – Welding Journal, December 1988 by D.J. Kotecki and T.A. Siewert - Welding Journal, May 1992.) Source Damian Kotecki, (2003); Stainless Steel Welding Guide, the Lincoln Electric Company

2.9 Weldability of duplex Stainless Steels

2.9.1 Weld solidification cracking [1]

Weld solidification cracking depends on the composition. Basically all of the duplex alloys solidify in the ferrite mode and have obviously higher solidification cracking susceptibility than the austenitic alloys that solidify in the ferrite-austenite mode, this increase is due to the existence of ferrite-ferrite boundaries at the terminal stage of solidification that becomes easily wet by liquid films than ferrite-austenite boundaries. The susceptibility to solidification cracking is very much lower than austenitic alloys that solidify in the austenitic mode.

In practice, the Duplex Stainless Steels are resistance to Weld solidification cracking due to comparatively low level of impurity levels and discrete grain boundaries due to two phase structure. So grain boundary liquid films is small and not continuously networked.[1]

J. C. Lippold, I. Varol And W. A. Baeslack Ii et al (1989)[58] evaluated solidification cracking tendencies of two different alloys SAF 2205 & Ferralium 255. According to their research work, SAF 2205 shows weld solidification cracking susceptibility somewhat less than that duplex alloy Ferralium 255. See Fig. 2.19

While comparing with Austenitic Stainless steels, Cracking in the duplex alloys was found to be intermediate between Type 304/FN 8 (ferrite solidification) and Type 304/FN 0 (austenite solidification). Thereby there is a big role of ferrite & primary mode of solidification in Solidification cracking tendencies.

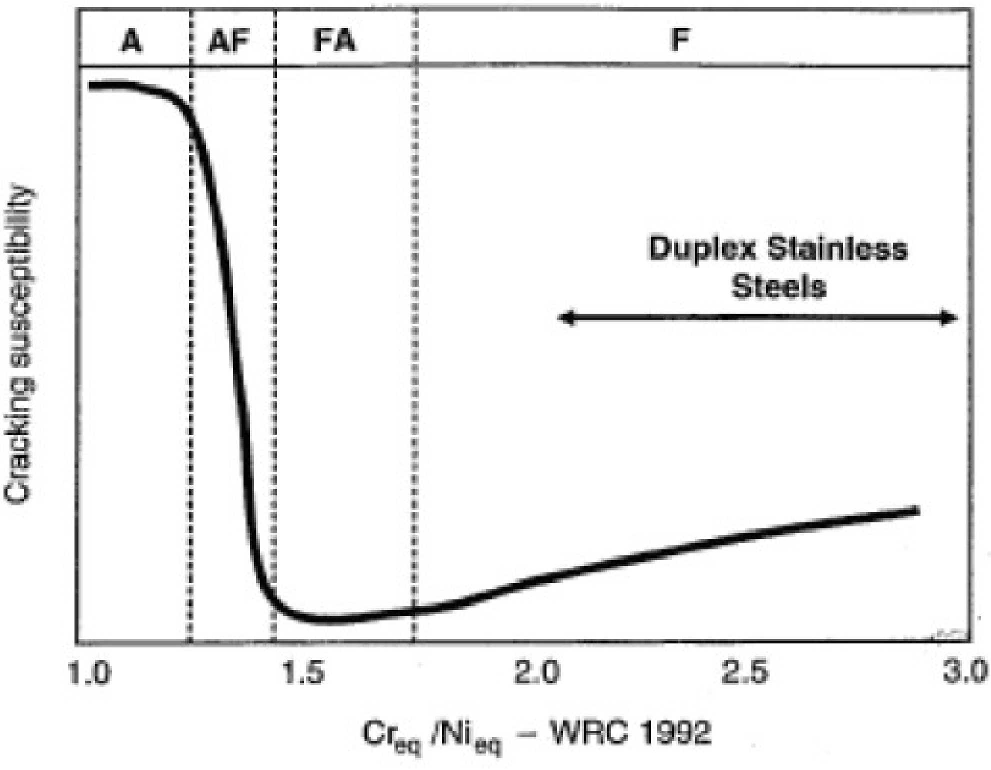

Figure 2.19 Variation of weld solidification cracking susceptibility with respect to Creq / Nieq source [1]

Use of austenitic filler metal will improve cracking resistance but reduce corrosion resistance of weld compare to base metal.

2.9.2 Hydrogen induce cracking [1]

Usually DSSs are considered to be resistant to hydrogen-induced cracking, however, number of costly failures have occurred in DSS weldments due to combination of high hydrogen level and poor microstructure control. More amount of ferrite presents in weld increases risk of hydrogen cracking, provided sufficient hydrogen and stress are present. Welding procedures are recommended with Low-hydrogen involvement. Use of hydrogen additions to argon gas shielding for GMAW, is generally inadvisable for DSS due to cracking possibilities.[1]

Best way to avoid hydrogen cracking in DSS is to control the deposition of ferrite in weld. Austenite provides a sink for the hydrogen and obstructs crack growth. With sufficient amount of austenite in weld structure, not only along grain boundaries but also within ferrite grains, effectively limiting hydrogen diffusion.

2.10 Corrosion behaviour of Duplex stainless steel

Oluwatoyin Adenike Olaseinde eta al, (2013)[59] in their research work conducted a comparative study of corrosion behaviour of the 2101, 2205 and 2507 duplex SS using potentiostat. In depth Scanning Electron Microscopy (SEM) with EDX and X-ray diffractometry (XRD) revealed phases of austenite and ferrite without any intermetallic phase. The elemental analysis of the phases showed that the various Ferrite forming & Austenite forming elements partitioned more into the phases that they promoted. Comparison made in the two media, their corrosion resistance is in order of: 2507 > 2205 > 2101 in terms of corrosion resistance.

O. A. Olaseinde et al (2014)[60] studied the electrochemical behaviours of 316 and 2205 stainless steelin 1 M sulphuric acid contaminated by sodium chloride at different temperatures, the corrosion potential measurements indicated that the corrosion potential of Alloy 2205 was nobler than alloy 316 at 25˚C, 40˚C and 80˚C. The passivity range in 316 was longer than for 2205 at the understudy temperatures. The increase in temperature result in increase in corrosion rates for the 2205 and 316 stainless steels. The 2205 Duplex stainless steel exhibited better corrosion resistance in ambient temperature. (Source Outokumpu Duplex Stainless Steel Material safety data Sheet)

The duplex stainless steels provide a wide range of corrosion resistance in various corrosive environments.

2.10.1 Uniform corrosion

Uniform corrosion is occurs on the steel surface by coming in contact with a corrosive medium. Corrosion rate is less than 0.1 mm/year is said to be acceptable uniform corrosion resistance.

Due to rich Cr in the composition, duplex steels offer excellent corrosion resistance in many atmosphere. Lean Duplex steels in most cases, a better resistance than Austenitic 304L steel (4307) and in some cases as good as 316 L (4404).

(Source Outokumpu Duplex Stainless Steel Material safety data Sheet)

2.10.2 Corrosion behaviour in Sulphuric acid

The iso corrosion diagram in sulphuric acid is shown in Figure. In sulphuric acid contaminated by chloride ions, 2205 shows much better resistance than 4404 and a similar resistance to that of 904L, Figure.2.20 & 2.22 (Source Outokumpu Duplex Stainless Steel Material safety data Sheet)

2.10.3 Corrosion behaviour in Hydrochloric acid

Duplex Stainless steel grades 4307 and 4404 have very limited application in hydrochloric acid due to risk of uniform and localised corrosion. High-alloyed steels such as 2507 and to some extent also 2205 can be used in dilute hydrochloric acid, Figure. 2.21. Pitting is not an issue in the region below the boundary line gram but crevices may be a problem. As can be observed from the diagram. (Source Outokumpu Duplex Stainless Steel Material safety data Sheet)

2.10.4 Corrosion behaviour in Nitric acid

It is observed that non molybdenum alloyed steels perform better than the molybdenum alloyed steels with strong oxidising acids like Nitric acid.

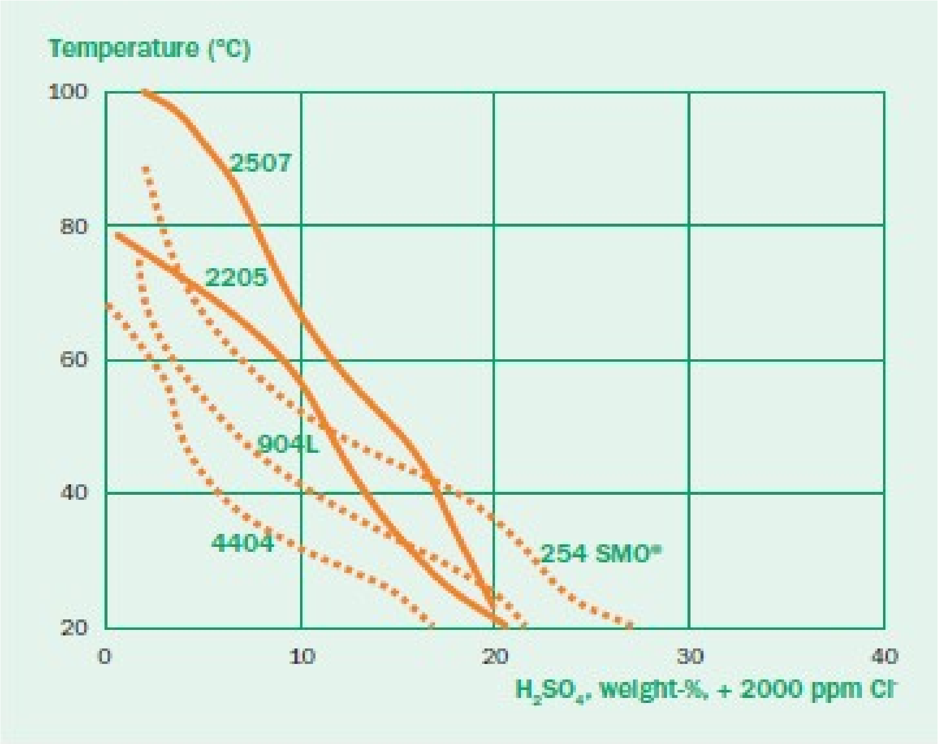

Fig. 2.20 iso corrosion curves, 0.1 mm/year, in sulphuric acid containing 2000 ppm chloride ions. (Source Outokumpu Duplex Stainless Steel Material safety data Sheet)

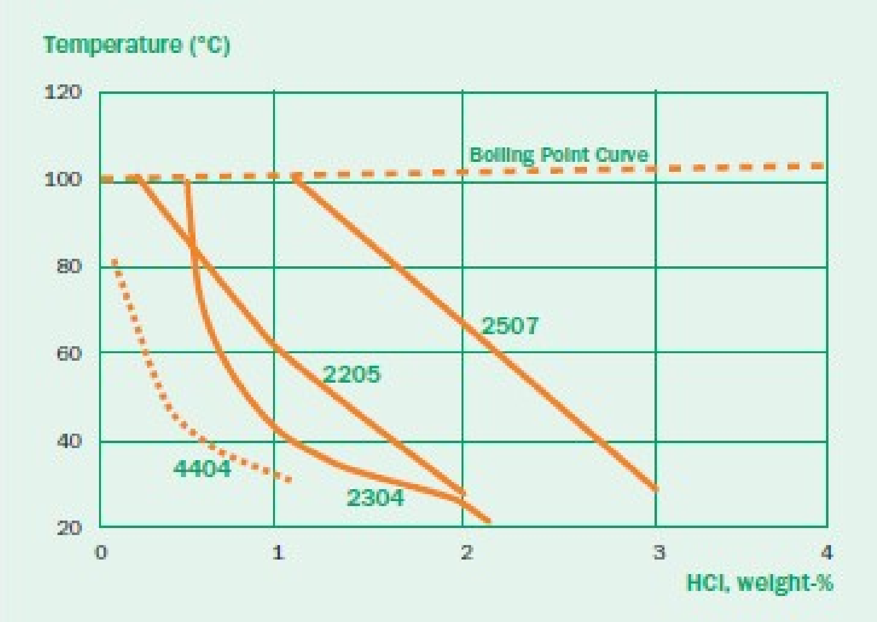

Fig 2.21 Iso-corrosion curves 0.1 mm/year, in hydrochloric acid. (Source Outokumpu Duplex Stainless Steel Material safety data Sheet)

Fig 2.22 Iso corrosion curves, 0.1 mm/year, in sulphuric acid. (Source Outokumpu Duplex Stainless Steel Material safety data Sheet)

2.10.5 Pitting and crevice corrosion [45]

The practically proven, empirically formula suggested by (Clerk et al, 1986) for the pitting resistance equivalent (PREN) for the Duplex Steel material, can be represented as: PRE = %Cr + 3.3 x %Mo + 16 x %N. PRE values given for different grades are presented in Table 2.1 From the above formula it is clear that the resistance to pitting and crevice corrosion increases with the content of chromium, molybdenum and nitrogen in the composition of steel[45]

For a given chloride environment, each grade of Duplex stainless steel can be characterized by a temperature above which pitting corrosion will initiate and propagate to a visible scale within about 24 hours. Below this temperature, pitting initiation will not happen for indefinitely long times. This temperature is known as the critical pitting temperature (CPT) in the same context, Critical Crevice Temperature (CCT) can be calculated[45]

As per literature findings, CCT will be 15 to 20°C lower than the CPT for the

Same steel for the same under corrosion environment.

The PRE value can be used as an estimate for selecting candidate material for the given application, it also gives comparison of different materials. According to many literature & research papers, critical pitting temperature (CPT). Is a much more reliable way of ranking steels is according to its resistance to pitting corrosion, There are several methods available to measure CPT[45] See Fig. 2.24 for CPT Values for Duplex stainless Steels.

Lundqvist et al [38] also studied on SMAW welding on 20 mm-thick 2205 plate butt plate configuration by using H.I. from 2.0 to 6.0 kJ/mm. investigation have shown that top surfaces of the weld metal shown accepted result in the pitting test done with 10% FeCl3 6HP at 30 °C irrespective of heat input but on the contrarary, weld metal on root side, failed. To further investigate this phenomenon, tests on CPT were conducted under 3% NaCl with different values of H.I result correlated with more formation of austenite at high H.I also precipitated CrN which impaired the pitting resistance

Yinhui Yang et al (2011)[61] studied the Mechanical & Corrosion behaviour of DSS 2205 under High Heat Input conditions using Gleeble 3800 thermo-mechanical simulator, confirmed that more proportions of grain boundary austenite (GBA) and the growth of intergranular austenite (IGA) improves pitting corrosion & intergranar corrosion.

Yiming Jiang et al, (2013) [62] in their research work, using PAW Process, examined on UNS S32304 duplex stainless steel welded joints, variation of Creq/Nieq (value from 2.65 to 3.19) on Mechanical properties & Pitting corrosion resistance.

They discovered that lower the Creq/Nieq value, better the microstructure. High PREN in result in low weight loss rate and high critical pitting temperature for base metal.

There are two standard test methods available as under.

1. ASTM G 150 standard test method for electrochemical critical pitting temperature testing of stainless steels
2. ASTM G 48 standard test method for pitting and crevice corrosion resistance of stainless steels and related Alloys by ferric chloride solution.

Jianyu Xiong et al (2013)[63] studied the Micro electro Polarization Technique in various zones FZ, HAZ1, HAZ 2 of two dissimilar metal joints of SS 316 & DSS 2205 and concluded that DSS & HAZ1 Resistance to Pitting than ASS 316 L & HAZ

J.H. Potgieter et al (2008)[64] in his research work on Influence of nickel additions (5%, 7%, 9% and 13%) on the pitting corrosion behaviour of low nitrogen 22% Cr series duplex stainless steels. Research showed that Uniform corrosion behaviour of the alloys predominantly controlled by phase composition and ratio while pitting resistance is controlled by nickel contents.

Zhiqiang Zhang at al (2016)[65], Use of N2 as shielding gas promote solid solution in the austenite. Pitting corrosion resistance preferentially attack on Secondary austenite than Primary austenite due to less amount of Cr and Mo available in the phase. Presence of inclusion due to use of E2209T1 flux based process result in poor pitting corrosion resistance.

The typical critical crevice corrosion temperatures (CCT) measured in 6% $FeCl_3$ + 1% HCl according to ASTM G 48 Method F, is presented in Figure 2.24. The value CCT values that differ from the tabulated value due to differences in finishing of the surface methods adopted.

Due to their different alloying levels, the Duplex steels show considerable differences in the resistance to pitting and crevice corrosion. LDX 2101® has a resistance in-between 4307 and 4404, 2304 is on a level with conventional molybdenum-alloyed steels of the 4404 type, while LDX 2404® and 2205 is on a level

The effect of welding parameters on the pitting resistance of a DSS has been investigated by Sridhar et al (1984)[66]. A higher heat input was found to be beneficial on account of the lower cooling rate. Through both 1. Increasing the volume fraction of austenite and 2 uniform distribution of various alloying elements between the two phases. Corrosion of the weld metal was observed to occur preferentially in the ferrite along austenite –ferrite boundaries. [45]

Fig 2.23 Typical critical pitting corrosion temperatures (CPT) in 1M NaCl measured according to ASTM G 150 using the Avesta Cell. Test surfaces wet ground to P320 mesh. CPT varies with product form and surface finish

Fig 2.24 Typical critical crevice corrosion temperature (CCT) according to ASTM G 48 Method F. Test surfaces dry ground to 120 mesh. CCT varies with product form and surface finish

As reported by Prof.S.Sunderasan [45] in his article, that Austenitic Steel type 304 weldments pitting corrosion is commonly occurring due to Cr and Mo depleted austenitic phase, because presence of small amount of ferrite, segregation of ferritizing elements Cr and Mo takes place during solidification of the weld.

While, in Duplex SS, primary solidification occurs a 100 % ferrite and subsequent solid state transformation of ferrite to austenite phase, besides this due to faster diffusion of Cr and Mo in ferrite than in austenite. No segregation has been reported responsible for pitting corrosion. [45]

Tamaki et al 1986[67] reported beneficial effect of slower cooling rate to provide sufficient time for Cr to diffuse and heal the Cr-depleted regions surrounding the Chromium Nitride precipitations.[45]

Stephanson et al,1987[69] also reported the beneficial effect of higher heat input i.e slow cooling rate, as it promotes more austenite formation which facilitates Dissolution of large amount of Nitrogen. The interesting fact is that CrN Precipitation does not happen due to this phenomena. But such precipitation result from relative motion of ferrite-austenite phase boundaries.[45]

The effect of heat input on Pitting corrosion resistance has also been investigated by Ume et al (1987)[68] who establish that the pitting resistance improves with increase of heat input and that the pitting itself was due to chromium nitride precipitation but excess heat input would again degrade corrosion performance by forming Nitride precipitation.[45]

2.11 Stress corrosion cracking (SCC)

Stainless steel can be affected by stress corrosion cracking (SCC) in chloride and sulphide containing environment at elevated temperatures. Conventional austenitic stainless steel is particularly susceptible to stress corrosion cracking while duplex stainless steels are less susceptible to this type of corrosion.

R.K. Singh Raman et al (2010)[70] Investigated on Super duplex 2507 grade, effect of Nitrite additions in Mgcl2 SSRT Solution. They have researched out that up to 2800 ppm additions susceptibility of Ch-SCC is suppressed but beyond 5600 ppm Nitrile additions, susceptibility of Ch-SCC rate increases.

A.I. Aljoboury et al (2010)[71], conducted SCC Test in Brine Solution & Electrochemical Analysis Pitting measurement UNS S31603 and UNS S32750 wrought samples and provided recommendations for building brine recirculation pumps. UNS S32750 samples shown superior stress corrosion resistance than UNS31603 material in the same testing conditions

There are various test methods to rank stainless steel grades with respect to their resistance to stress corrosion cracking. The results may show variation depending on the test program adopted & corrosion environment t which it is exposed to. In Table

2.11, a comparison is given of the SCC of commercially used austenitic stainless steels and duplex stainless steels by various accelerated laboratory corrosion test methods. The test specimens are immersed in different chloride solutions.

Slow-strain rate tests (2.2 x 10^{-6} S^{-1}) at 35% boiling water $MgCl_2$ solution and 125 °C is performed to determine the sensitivity to SCC.[72,73]

In one of these methods, Chloride solutions is in state of evaporative conditions in Wick test (ASTM C 692)[74] the results show that while duplex stainless steels are not resistant under very aggressive atmosphere, such as boiling concentrated magnesium chloride, but they withstand stress corrosion cracking under many conditions where conventional austenitic grades are not able to perform. (Source Outokumpu Duplex Stainless Steel Material safety data Sheet)

2.11.1 Chloride and Sulphide induced stress corrosion cracking.

In the presence of hydrogen sulphide (H2S) and chlorides (Nacl, MgCl2) the risk of stress corrosion cracking rises, when parts or components like boreholes for oil & gas wells, underground fittings, etc exposed to lower temperatures.

Duplex grades, such as 2205 and 2507 have demonstrated good resistance, while 13% chromium steels have shown a tendency towards stress corrosion cracking. (Source Outokumpu Duplex Stainless Steel Material safety data Sheet)

According to literature, Conditions with high partial pressure of hydrogen sulphide and presence of internal stress are responsible for this stress corrosion cracking to happen.

2205 and 2507 are both approved materials according to NACE MR0175/ISO 1515 Petroleum and natural gas industries - Materials for use in H2S-containing environments in oil and gas production.[86]

(Source Outokumpu Duplex Stainless Steel Material safety data Sheet)

Table No.2.11 Comparative Stress Corrosion cracking resistance in accelerated laboratory tests.

(Source Outokumpu Duplex Stainless Steel Material safety data Sheet)

Test Solution Temperature load	ASTM G36 45% MgCL 155 °C (b.p) U-bend	40% CaCl2(100 °C) U-bend	40% Cacl2 (100°C) 0.9 X Rp0.2 (4-PB)	ASTM G 123 25% NaCl, pH 1.5 106°C (b.p.) U-bend	25% NaCl 106°C (b.p.) U-bend	ASTM C 692 1500 ppm Cl- 100°C Rp0.2
4307	Expected	Expected	Expected	Expected	Expected	Expected
4404	Expected	Expected	Possible	Expected	Possible	Expected
LDX 2101®	Expected	Not anticipated	Not anticipated	Not anticipated	Not anticipated	Not anticipated
2304	Expected	Not anticipated	Not anticipated	Not anticipated	Not anticipated	Not anticipated
LDX 2404®	Expected	Possible	Not anticipated	Not anticipated	Not anticipated	Not anticipated
2205	Expected	Not anticipated	Not anticipated	Not anticipated	Not anticipated	Possible
2507	Expected	Not anticipated	Not anticipated	Not anticipated	Not anticipated	Not anticipated
254 SMO®	Expected	Not anticipated	Not anticipated	Not anticipated	Not anticipated	Not anticipated

b.p. = boiling point. Expected = SCC is expected to occur. Not anticipated = SCC is not expected to occur. Possible = SCC may occur.

(Source Outokumpu Duplex Stainless Steel Material safety data Sheet)

However, as with many materials, the duplex stainless steels may be susceptible to stress corrosion cracking under high temperature, chloride-containing environments, or when conditions support hydrogen induced cracking (HIC) such as immersion testing of wrought mill annealed Austenitic and Duplex stainless steels in the boiling 42% magnesium chloride test, drop evaporation test shows the value of the stress which causes cracking as parentage of Yield strength as shown in Fig. 2.25

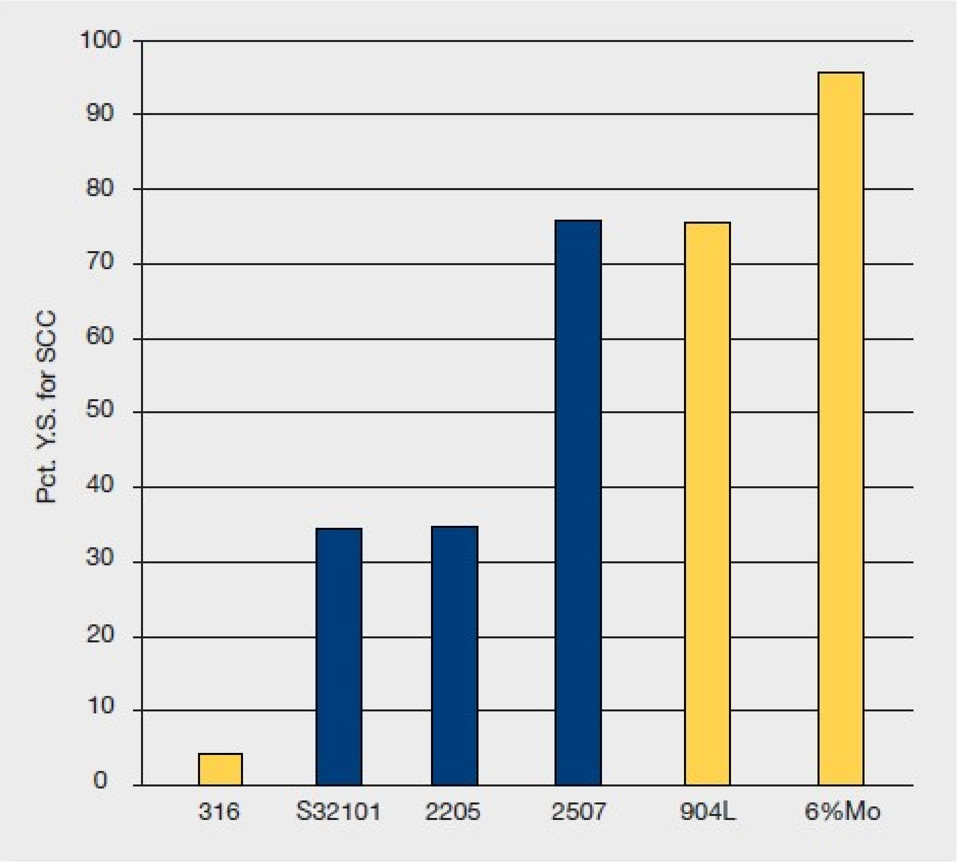

Fig 2.25 Stress corrosion cracking resistance of mill annealed austenitic and duplex stainless steels in the drop evaporation test with sodium chloride solutions at 120°C (248°F) (stress that caused cracking shown as a percentage of yield strength) (Source: Outokumpu)[75,76]