Chapter-1
Introduction and Literature Survey

1.1 Introduction

Application of conventional austenitic stainless steels (S304, S310, etc.) is restricted mainly due to the higher cost of nickel. To lower the cost, nickel is replaced by nitrogen and manganese, in addition attractive combination of properties is achieved. This has resulted in the development of 200 series of stainless steel. In India, these stainless steels have been used extensively since 1980. Although these grades of steel were developed in the 1930s, the first grades which received the AISI label were 201 and 202 grades, in which nickel content was about 4-6 wt% and nitrogen below 0.25 wt% in the 1950s. These grades became popular during Korean War, which restricted nickel to only military applications. 214 grades with lower nickel content (< 1wt%) were produced at the end of the 1950s. Austenitic Cr-N grades containing Mo with improved corrosion resistance were developed in the mid of 1960s in the US and Europe [1, 2]. Based on the application, these classes of alloys are selected. These grades are best suited for biomedical implants because of the absence of nickel. Nickel ions act as allergens which cause cutaneous inflammations such as reddening, swelling, itching, allergy reactions in the human body. Nickel free nitrogen stabilized austenitic stainless steels are important class of engineering material that exhibit a range of properties such as strength, toughness, pitting corrosion resistance and high temperature creep strength. Nitrogen alloying enhances austenitic stability and work hardenability of this class of steel. These alloys exhibit acceptable strength in temperature range from cryogenic to higher temperatures. Ni free grades are considered potential replacement of the existing grade AISI 316L [1].

High nitrogen steels are solid solutions of iron, chromium, nickel, manganese and of nitrogen and carbon as interstitial atoms which strengthen the steel by nitrides/ carbides. According to Speidel [3], steel should be considered high nitrogen, if it contains nitrogen more than that can be retained as solid solution by the material, at atmospheric pressure.

For ferritic stainless steel, this limit is 0.08 wt% N and for austenitic stainless steel, it is 0.4 wt % N [4]. Stainless steels are mainly divided into three categories; ferritic, austenitic, and martensitic. Among these austenitic grades are widely used due to their higher mechanical properties and corrosion resistance [5].

Austenitic stainless steels retain the high temperature austenitic phase at room temperature and are non-magnetic. Generally, nickel is used as an austenite stabilizer in most of the conventional austenitic stainless steels such as the AISI 300 series. Due to high price and scarcity of nickel ores, an alternate AISI 200 series, with low cost and better properties had been developed in past decades. Nitrogen is a very strong austenite stabilizer, replaces the costly nickel, improves mechanical properties, and reduces the overall cost of steel production. Substitution of nickel by Mn increases the solubility of nitrogen, which shows that there is much scope of study of Fe-Cr-Mn-N alloys. Although nickel is an important austenitic stabilizer in austenitic stainless steel, due to its negative effect on nitrogen solubility, Mn is widely used in most of the nitrogen steel. In recent years, effect of nitrogen alloying had been an area of research due to attractive properties of nitrogen containing steel and also their lower cost.

1.2 Why nitrogen instead of nickel in austenitic stainless steel?

Nickel is added to stainless steel to stabilize the gamma phase. The cost of per kg of nickel, according to Economics Times of India, is ₹1570.30 [6] while nitrogen is freely available in the atmosphere. India has no ores of nickel and imports it from Canada, Russia, and South Africa, this results in overall increase in the cost of austenitic stainless steel. Unsustainable use of nickel reserves leads to depletion of extractable resources of nickel by 2190. Therefore, a careful and selected use of nickel is necessary for the austenitic stainless-steel industry which heavily relies upon nickel [7]. At present 73 % of produced

nickel is used by the stainless steel industry which is a very large fraction, and it would lead to scarcity of nickel ores in near future [8].

As mentioned earlier, nitrogen improves mechanical properties and corrosion resistance of austenitic stainless steel. A comparison of mechanical properties of different types of austenitic stainless steel can be seen from the Table 1.1, given below:

Table 1.1: Comparison of mechanical properties of different austenitic stainless steels.

S.No.	Austenitic Stainless Steel	Yield Strength (MPa)	Ultimate tensile strength (MPa)	Elongation (%)	Hardness (H_v)	References
1.	316L	280	616	40	180	[9]
2.	304L	351	667	58	165	[10]
3.	Fe-18Cr-21Mn-0.65N	668	918	57	323	Present study

Table 1.1 shows that high nitrogen and Mn stabilized nickel free stainless steel has an attractive combination of mechanical properties in comparison with its nickel containing counterparts. Nitrogen is a strong austenite stabilizer; 1 kg of nitrogen can replace 6 to 12 kg of nickel in steel making [11], that drastically reduces the cost of produced steel. From an ecological point of view, nickel is allergic to human body; therefore, the use of nickel containing austenitic stainless steel as metallic implants, is restricted.

In spite of attractive combination of properties and cost effectiveness, these steels have often been ignored and less explored for their application in the intermediate temperature range of 300-600°C. There is a wide availability of technical/scientific data for the nickel containing stainless 300 series, for their industrial applications; however, there is no such data base for application of the nickel free austenitic stainless steels at elevated temperatures, therefore their application is mostly limited to room temperature.

1.3 Development of Nickel Free Austenitic Stainless Steel

The important factor in development of nickel free austenitic stainless steel is the retention of austenite at room temperature, without forming δ (delta) ferrite. Schaeffler diagram (Pickering 1976, Schneider 1960) (**Figure 1.1**) reveals various fields of austenitic, martensitic, or ferritic steels [5]. To get a fully austenitic structure and avoid formation of delta ferrite, it is required that:

$$\text{Ni}_{eq}(\text{Nickel equivalent}) \geq \text{Cr}_{eq}(\text{Chromium equivalent}) - 8 \tag{1.1}$$

$$\text{Cr}_{eq} = \text{Cr} + 1.5\text{Mo} + 1.5\text{W} + 0.48\text{Si} + 2.3\text{V} + 1.75\text{Nb} + 2.5\text{Al} \tag{1.2}$$

$$\text{Ni}_{eq} = \text{Ni} + \text{Co} + 0.1\text{Mn} - 0.01\text{Mn}^2 + 18\text{N} + 30\text{C} \ (\text{mass}\%) \tag{1.3}$$

For increasing corrosion resistance, chromium content should be high but at the same time, Ni content should also be increased to get austenitic structure. From the above equations, one can see that nickel can be fully replaced by nitrogen to get a fully austenitic structure. However, N content should be restricted since Cr-Mn-N austenitic stainless-steel shows ductile to brittle transition. The ductile to brittle transition temperature (DBTT) is affected by N concentration as follows:

$$\text{DBTT(K)} = (300 \, C_N - 30) \tag{1.4}$$

Thus, to get DBTT below room temperature, nitrogen should be restricted to a maximum of 0.95% [4].

Apart from nitrogen, alloying elements such as Cr, Mn, and C stabilize the austenite phase. Cobalt is expensive while manganese is cheaper and stabilizes austenite more efficiently. Since high Mn content decreases the corrosion resistance it should be limited to about 18wt%. Carbon content should be kept below 0.1wt% to avoid deleterious effects on corrosion resistance. Cr content should be in the range of 10-24 wt% to get optimum

corrosion resistance and austenitic phase. Typically, a nickel free austenitic stainless steel has Cr (13-24 wt%), Mn (11-21 wt%), Mo(0-2wt%), N(0.4-1wt%), and C<0.1 wt% [5].
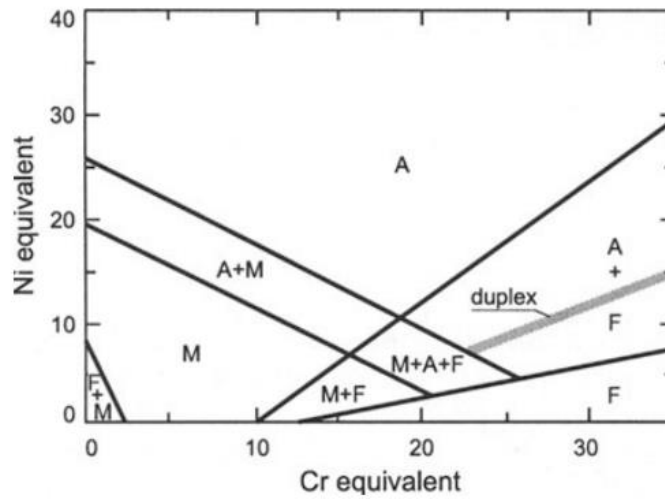
Figure 1.1: Schaeffler diagram ($Cr_{eq}=Cr+l.5Mo+1.5W+0.48Si+2.3V+1.75Nb+2.5Al$ and $Ni_{eq}=Ni+Co+0.1Mn\ 0.01Mn^2+18N+30C$ (mass%), A:austenite, M:martensite, F:ferrite) [5] .

1.3.1 Role of Alloying Elements

Nitrogen and carbon occupy the interstitial (octahedral and tetrahedral) position of a crystal lattice, and in case of austenite crystal lattice both occupy the octahedral site. The largest size of a sphere that an octahedral site can accommodate is $r_6= 0.53$Å for fcc lattice and $r_6=0.29$Å for bcc lattice; For tetrahedral sites, it is $r_4=0.19$Å for fcc and $r_4=0.36$Å for bcc lattice. Atomic radius of carbon and nitrogen depends on the coordination number (CN), for CN:4, the radius of nitrogen and carbon are 0.74Å and 0.77Å respectively and for CN:6, the radius of nitrogen and carbon are 0.84Å and 0.89Å, both the ways nitrogen atoms are smaller in size and from the size of the holes in both, it is clear that nitrogen dissolves more effectively than carbon [1, 5, 11].

Alloying of nitrogen results in change in crystal lattice, such as enhancement of metallic character, change in stacking fault energy affecting dislocation structure, twining, and enhancement of precipitation delaying tendency. Nitrogen has the following advantages:

(1) Better solid solution strengthener than carbon

(2) Greater tendency of solubility than carbon

(3) Stronger austenitic stabilizer than carbon

(4) Beneficial for pitting resistance

(5) Reduces the tendency of precipitation of deformation induced martensite.

Nitrogen in steel increases the concentration of free electrons which promotes intermetallic bonding, as nickel and cobalt do, which significantly improve ductility and toughness. Unlike nickel and cobalt, nitrogen occupies interstitial position causing large lattice distortions. Dissolution of carbon is easier in liquid steel compared to nitrogen but precipitation of deleterious chromium carbides causes reduction in its mechanical strength and corrosion properties [4].

In contrast, solubility of nitrogen is low in liquid iron-based alloys but high in austenitic alloys. It suppresses precipitation of harmful $M_{23}C_6$ precipitates because it has higher Cr-N interactions as compared to Cr-C. The precipitation of chromium-rich M_2N nitrides is delayed although lower segregation of chromium atoms is needed for their formation. The most beneficial property which is imparted by nitrogen addition in steel is resistance to localized corrosion such as pitting, crevice, and intergranular corrosion. Nitrogen has low affinity towards grain boundary; in contrast, carbon has higher towards grain boundary segregation due to smaller value of electric field gradient at iron atom in neighborhood of nitrogen atom compared to carbon atom. Nitrogen atoms result in a higher dilatation of the austenitic crystal lattice, due to a higher concentration of free electrons which have higher energy than localized electrons. Nitrogen atoms carry a negative electric charge whereas carbon atoms are positively charged. The electrostatic interaction with a positively charged dislocation line is attractive for nitrogen and repulsive for carbon atoms. This is the reason

why nitrogen promotes planer slip which increases the low cycle fatigue life and resistance to creep, of nitrogen steel. The solubility of nitrogen is one of the obstacles during the production of high nitrogen steel which is function of temperature and pressure, the solubility limit of nitrogen in liquid iron at 1600°C is 0.045 wt% which is very low [1, 5, 11].

To increase the solubility of nitrogen various strong nitride formers such as Cr, Mn, Zr, V, Nb, and Ti are added to steel, elements such as Al and Ni reduce the solubility. However, strong nitride formers such as V, Nb, and Ti are hardly used, due to low solubility of their resulting nitrides in solid state. Except for Mn, all elements which promote the solubility of N are ferrite stabilizers.

1.3.2 Phases in High Nitrogen Austenitic Stainless Steel

Precipitation of deleterious phases is undesirable during service conditions, excluding special cases. Two kinds of deleterious phases form during high temperature operation of austenitic stainless steel (a) intermetallic phases and (b) carbides/nitrides.

In austenitic stainless steel mainly σ, η, and χ intermetallic phases are formed. These phases precipitate in the temperature range of 600 to 1150°C. σ-phase is most studied due to its harmful effect on the toughness of the stainless steel. It also decreases the resistance towards intergranular corrosion. It is described by formula $(Fe, Ni)_x(Cr, Mo)_y$ and has body centered tetragonal structure. The σ-phase precipitation occurs during long term ageing process, along the grain boundary. In nickel free steels, σ phase precipitation occurs in the range of 700-1200°C. χ phase is a carbon dissolving compound, has a BCC α-Mn type crystal structure and formula $M_{18}C$. Its crystal structure has large holes to in which carbon atoms get accommodated and carbides are formed. Depletion of Cr and Mo form the matrix leads to its precipitation at the grain boundary. η or Laves phase generally forms in Mo containing austenitic stainless steel [4, 5].

Carbides such as $M_{23}C_6$, MC, and M_6C in austenitic stainless-steels, precipitated during ageing treatment, enhances intergranular corrosion as well as embrittlement in the steels. However, in nitrogen stabilized steel precipitation of $M_{23}C_6$ carbides is delayed [4]. Nitrogen also reduces the driving force for the precipitation of M_6C and $M_{23}C_6$ carbides. Intermetallic phases such as σ, χ, and η are also found in nitrogen containing steel. Nitrogen addition to austenitic stainless-steel causes decrease in the activity of Cr and lowering of driving force for the precipitation of these intermetallic phases.

In nitrogen containing austenitic stainless-steel, precipitation of Cr_2N nitride occurs instead of $M_{23}C_6$ carbide. The kinetics and mechanism of precipitation of the Cr_2N nitride were investigated by various researchers [4, 12, 13], it was found that precipitation occurs in thin plate morphology due to discontinuous decomposition of nitrogen stabilized austenite. It is an unsteady process that occurs in two steps, firstly through intergranular diffusion of chromium and then by its bulk diffusion. This results in cellular structure at grain boundaries, these cellular precipitates are also undesirable for mechanical properties.

1.3.3 Production Route

As discussed earlier, nitrogen has higher solubility in austenite compared to carbon, but the addition of nitrogen above 0.15 wt% is a challenging task. Further, nitrogen is volatile and creates problems during the manufacturing of components. The required concentration of nitrogen in steel melt can be achieved by selecting the temperature, pressure, and alloying elements. Nitrogen can transfer into liquid melt by nitrogen uptake, nitrogen molecules from the atmosphere dissociate and adsorbed by the liquid melt. At atmospheric pressure, 0.04% of N can be dissolved into Armco iron. According to Sievert's law, solubility of nitrogen depends on the composition and partial pressure of nitrogen [5] as given below:

$$(\%N) = 0.0396/f_N . p_N^{1/2} \tag{1.5}$$

Where p_N is partial pressure of nitrogen and log $f_N = \Sigma e_N^x$ (%x) for all x (all added alloying elements) with e_N being the interaction parameter used for calculation of nitrogen solubility [14]. The addition of alloying elements, with negative interaction parameters, is the easiest way to enhance nitrogen solubility. An increase in pressure of nitrogen above atmospheric level around the liquid melt, enhances the nitrogen solubility, although this route is costly due to the requirement of special equipment.

Several methods have been explored for the production of high nitrogen nickel free austenitic stainless steel [11], some of them are listed below:

(1) Addition of nitrogen in the form of nitrogen containing master alloys;

(2) Melting in pressurized induction or plasma furnace, pressurized electro slag remelting (PESR), and nitrogen purging. PESR is one of the accomplished methods for high nitrogen steel production in which nitrogen continuously infuses into the melt during remelting, by the addition of nitride additives such as CrN, Si_4N_4, etc. Purging of nitrogen gas is similar to the PESR technique but instead of additives, nitrogen gas is purged from the bottom.

(3) Powder metallurgical routes, where nitrogen is introduced into steel powder by diffusion or by mechanical milling.

(4) Nitrogen alloying in the Indian steel industry is done through the Argon Oxygen Decarburization (AOD) route, in which melting of Ferro nitrided alloys in induction and arc furnace, is followed by AOD process, where nitrogen addition occurs after decarburization. In AOD, argon is replaced by nitrogen gas which ensures a pick of 0.5% of N.

1.4 Applications of Fe-Cr-Mn-N Alloys

Austenitic high nitrogen steels are used in crushing tools, rollers, rings, high pressure hoses, wire and tube for medical application, supporting wire in power transmission, bolts,

suspension, retaining rings, and bio implants (nickel free grades) [1]. These steels are also applicable in marine environments such as in desalination plants and condensers of power plants onshore and firefighting systems on offshore platforms [11]. In paper and chemical industry high nitrogen steels find a wide area of application where strong acidity and halogen concentration are together [15]. At cryogenic temperatures such as in superconducting magnets housing which requires high strength alloys that can withstand large magnetic forces, low thermal conductivity, and excellent fracture toughness, these steels are suitable options. On the other hand, martensitic high nitrogen steels are hard and suitable for temper resistant gears as well as corrosion resistant parts for the food processing industry [1]. The superior performance of high nitrogen steel bearing led to its advanced application in the aviation industry [5]. Some of the important applications of high manganese nitrogen stabilized austenitic stainless steel are given below:

1.4.1 Biomedical Applications

Implants such as artificial joints, bone plates, dental implants are made of high nitrogen nickel free stainless steel, which exhibits high strength, ductility and toughness. Most of the coronary stents were made of AISI 316L due to its excellent combination of properties, but it is a potential allergen. Nickel free austenitic stainless steel may be an alternative material for such applications. A study carried out on biocompatibility of medical grade high nitrogen nickel free austenitic stainless-steel shows better cytocompatibility, blood compatibility, and cell response than that of nitinol alloy [16]. In biocompatibility, porosity plays an important role in cell attachment and platelet adhesion. Porous nickel free austenitic stainless steel by high temperature nitriding process exhibits mechanical properties near to human cortical bone [17]. A study carried out by Kazuhilo Endo et al. on corrosion resistance and cytocompatibility of austenitic steel was simulated in a physiological environment, it showed that pitting resistance was higher than the 316L

because of the formation of CrN in the outer region of the passive film [18]. The cell growth rates were higher as for commercially pure titanium. A study on the effect of varying nitrogen content in high nitrogen austenitic stainless-steel shows that increasing nitrogen content causes higher charge transfer and lower capacitance which results in the formation of thicker and protective passive films. It also enhances biocompatibility due to the reduction of metallic ions which are available for interaction with the biological environment [19]. Effect of nitrogen and cold working on high nitrogen nickel free austenitic stainless steel was also studied by M.Talha et al. which shows that with increasing nitrogen content tensile and yield strength increase but ductility gets reduced [20]. In comparison with nickel containing stainless steel 317L, high nitrogen nickel free austenitic stainless steel shows better blood compatibility [21]. High nitrogen nickel free steels are also attractive material for coronary stent manufacturing. On comparing high nitrogen austenitic stainless steel with 316L and Co-28Cr-6Mo alloy, high nitrogen austenitic stainless-steel possesses better corrosion resistance. It also shows longer clotting time and less platelets conglutination on the surface of steel [22]. Bioimplants undergo cyclic loading, corrosion, wear and erosion due to relative movements; high nitrogen austenitic stainless steel is a better substitute of conventional alloys, as they have good wear resistance and corrosion fatigue strength. A study on cavitation erosion behavior of annealed high nitrogen austenitic stainless-steel showed that annealing improved the resistance against cavitation erosion, by reducing the hardness [23]. A biocompatibility study on Fe-18Cr-21Mn-0.65N and 316 stainless steel showed that nickel free austenitic stainless steel can replace conventional nickel containing stainless steel. Surface modification through ultrasonic shot peening enhances the cell adhesion and proliferation [9, 24].

1.4.2 Other Applications

From the above literature, it is clear that a lot of data on biocompatibility and corrosion behavior is available for high nitrogen nickel free austenitic stainless steel. Since this class of alloys contain an appreciable amount of chromium, they can also be applicable in the intermediate temperature range of 400-700°C. Nickel free high nitrogen stainless steel is a candidate material for the vessel of fusion bed reactor. Structural material in a fusion bed reactor should have resistance to the flux of energetically charged particles, gamma radiation, and Bremsstrahlung. In addition, these materials should have low neutron adsorption, adequate mechanical strength after irradiation, applicability in a wide range of temperature, resistance to atomic displacement, low activation property, and high thermal conductivity. Further, fabrication of the material should be easy and the cost should be low, for these reasons austenitic stainless steels are preferred and they also have a large technical database on the operation in fusion bed reactors. Various austenitic grades such as AISI 304, AISI 316, AISI 321, etc. are being used in different nuclear reactor systems as well as in fast breeder reactors and light water reactors. Recent studies show that austenitic stainless steel, that contains Ni, Mo, Co, and Nb exhibits residual activity after decommissioning. Nickel present in the nickel containing stainless steel undergoes activation due to neutron radiation in two modes, one by direct displacement - by knocking out the atom, resulting void formation and the other by transmutation of atoms causing generation of alpha and proton radiation. The first one results in reduction in ductility during service conditions and the other creates problems in disposal of the components after decommissioning [25]. This is the reason for the replacement of nickel containing stainless steel with low nickel high Mn nitrogen stabilized stainless steel. Masanori Onozuka et al. developed and proposed seven types of Mn-Cr based austenitic stainless steel for fusion reactor, as structural material. They found that 24.5Mn-13.5Cr-0.02C-0.2N alloy exhibits the best combination of properties such as hardness, strength, thermal and

magnetic properties [26]. M.M. Eissa et al. carried out research on attenuation capability of high manganese austenitic stainless steel for fusion reactor system and concluded that manganese modified steel possesses good mechanical properties as well as attenuation properties in comparison with SS316L [27]. Y Suzuki et al. successfully developed 24.5Mn-13.5Cr steel which has extremely low activation compared to other structural materials such as SS316, and concluded that it could be an effective candidate material for vessel fusion reactor[28]. Structural materials used for the construction of fission reactor are exposed to high temperatures (290-1000°C) and suffer from microstructural changes and surface oxidation [29]. High manganese nitrogen stabilized austenitic stainless steel can encounter the oxidizing and reducing atmosphere, in combination with the erosive and corrosive environment at 400-700°C in various applications.

1.5 High Temperature Oxidation

Global crude steel production was 1869 MT in 2019 that showed growth of 3% over the year 2017. India became the second largest producer of crude steel in 2019. Production of total finished steel comprising of stainless steel and un alloyed steels was 102.62 MT. Crude steel in form of ingots in conventional mills or as semis in continuous casting mills are reheated so that can be formed into useful shapes such as bars, rods, plates, etc. Generally, reheating operations are carried out in direct dried furnaces where gases or natural gas are combusted with oxidizing gases for generating heat. This combination of heat, time, and oxidizing gas results in formation of a thick oxide layer or oxidation of surface of the parts, and is highly unavoidable in such conditions. The amount of steel that is consumed as scale is about 1-2% of the total weight of parts, also the removal of oxide layer adds up to the cost of production. This is one example, there are many other examples where oxidation is unavoidable such as after the welding process the assembles are subjected to stress relieving post weld heat treatment in the temperature range of 400-700°C

for 2 to 40 h for removing the peak stress and to maintain dimensional stability. In these condition oxidation causes problems, such as depletion of alloying elements, pits formation at the surface, surface roughening, etc. [30].

1.5.1 Thermodynamics of Oxidation

Oxidation is a phenomenon that occurs when a metal or alloy is exposed to oxygen from the atmosphere or from any other source that causes reaction between surface of the alloy or metal with oxygen and results in formation of oxide layer at room to high temperature. Generally, high temperature alloys are subjected to duty cycles of weeks, months, or years depending on the application; hence, it is most important to test the alloy in cyclic conditions. In all cases, oxide scales form and undergo thermal cyclic exposure of temperature, and that causes stress in the oxide layer. Oxide formation takes place when oxygen potential of the medium/ environment is higher than oxygen potential of the oxide [31]. Consider the following reaction:

$$M + O_2 = MO_2 \tag{1.6}$$

Standard free energy of formation (ΔG^o) of metal oxide is given by:

$$\Delta G^o = \frac{-RT \ln a_{MO_2}}{a_M P_{O_2}} \tag{1.7}$$

where a_{MO_2}, a_M are the activity of oxide film and metal; P_{O_2} is the partial pressure of oxygen; T is the temperature and R is universal gas constant. One can predict whether formation of oxide would take place or not based on ΔG^o value, that can be estimated by the Ellingham diagram [32]. From the Ellingham diagram, one can see that stability of oxides of iron, nickel, and cobalt (base metals of the majority of the alloys) are less stable compared to those of the solute elements such as chromium, aluminum, and silicon.

1.5.2 Oxidation Kinetics

The rate of oxidation reaction is very important for analyzing the oxidation resistance behavior of alloys. Oxidation is generally measured by weight gain per unit area versus time. The various empirical rate laws which were observed under various conditions are illustrated below:

1. Linear rate law $W = k_L t$ where W is weight gain per unit area, t is time and k_L is the linear rate constant. Sodium and Potassium oxidize rapidly and follow linear law of oxidation.

2. Parabolic rate law $W^2 = k_c t + C$ where W is weight gain per unit area, t is time and k_p is parabolic rate constant. Elements such as Fe, Cr, Co, Ni, and Cu follow parabolic law.

3. Logarithmic rate law $W = k_e \log(Ct + A)$ where k_e, C, and A are constant. Aluminium, Copper, and other metals oxidize in this manner.

4. Cubic rate law $W^3 = k_c t + C$ where k_c and C are constants. Zirconium and Hafnium follow cubic rate law.

Linear rate law is least desirable while parabolic and logarithmic rate laws are desirable for high temperature oxidizing atmosphere. Depending on the ratio of amount of consumption of metal ion to amount of oxide layer formed, oxide can be protective or nonprotective. When the oxide scale gets thicker, the strain energy stored in the scale surpasses the interface fracture energy, and spallation takes place; sometimes, due to increase in thermal stress, strain energy increases, and results in spalling [30, 31].

Oxygen reaction with a metal surface takes place in different steps, the first step involves adsorption of oxygen molecules at the surface and their dissociation. It is followed by interaction of chemisorbed oxygen with metal and eventual covering of the all surfaces,

there after diffusion of oxygen and metallic ions takes place through the formed oxide layer. Diffusion can occur through the grain boundary, defects, lattice, or other short circuit diffusion paths. This leads to formation of voids and vacancies in the grown oxide layer and metallic substrate. Since oxide growth depends on the diffusion of oxygen cations and metallic anions, grown oxide generally has nonstoichiometric structure. These oxides can be classified as p and n type oxides, p type oxides are metal excess or holes are majority charge carriers, and n type oxides are metal deficient where electrons are majority charge carriers. Examples of p type oxides are MnO, CoO, etc. and for n type are Al_2O_3, SiO_2, etc. [33].

1.5.3 Oxidation of Fe-Cr-Mn-N Austenitic Stainless Steel
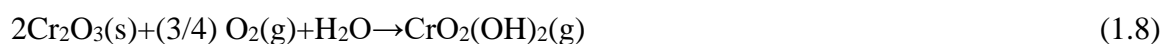
Austenitic stainless steels contain Cr, as discussed earlier formation of uniform chromia layer takes place at high temperature in oxidizing atmosphere. At higher temperatures, this phenomenon becomes more severe due to enhancement in the diffusion of metal ions towards the surface. Few studies on the high temperature properties of Fe-Mn-Cr-N steel have been reported. Karthik et al. reported the effect of high temperature ageing on microstructure and mechanical properties of the steel [13]. It was observed that ageing at 850°C significantly reduced the yield strength and tensile strength of the steel. As discussed earlier, this class of steel is also a candidate material for fusion reactors where it is exposed to higher temperature which results in oxidation of alloy surface. Oxidation study carried out by Douglass et al. on Fe-Cr-Mn-N alloys in the temperature range of 700-1000°C shows a higher oxidation rate than chromia forming alloys. It was also concluded that the high chromium content in nitrogen stabilized nickel free stainless steels lowers the oxidation rate compared with the less chromium content steels [34]. A study on oxidation characteristics of Fe-18Cr-18Mn stainless steel with varying nitrogen concentrations in the temperature range of 525-725°C, shows that the addition of nitrogen does not alter the

oxidation properties. It was also concluded that addition of Si, Mo, and Ni improves the oxidation resistance [35]. A brief literature survey on high temperature oxidation of Fe-Cr-Mn-N austenitic stainless steel is given in Appendix A.

Alloying of elements such as Cr, Al, and Si improves high temperature oxidation and corrosion resistance. These elements form a protective layer on the surface which inhibits the diffusion of oxygen ions. Oxidation depends on steel chemistry, temperature, and the gas atmosphere. The chemistry of steel and temperature of exposure cannot be changed; therefore, gas environment plays a vital role. Oxidation can occur in various environments such as air, moist air, reducing gas, etc.

1.5.4 Oxidation Under Moist Air Environment

Chromium in the stainless-steel forms a protective Cr_2O_3 layer at the surface and that restricts ingression of oxygen ions. This chromia layer becomes unstable in a moist atmosphere in the temperature range of 600-900°C due to formation of volatile compound after reaction with water [36]. Chromium evaporation/ volatilization is a serious problem, faced by Cr containing alloys such as 304L, 310, Fe-15Cr, Ni-Cr, etc. Chromium evaporation occurs by formation of two volatile species CrO_3 (reaction 1.8) and $CrO_2(OH)_2$ (reaction 1.9) [37].

$$2Cr_2O_3(s)+(3/4)\ O_2(g)+H_2O \rightarrow CrO_2(OH)_2(g) \tag{1.8}$$

$$Cr_2O_3(s) + (3/2)O_2(g) \rightarrow 2CrO3(g) \tag{1.9}$$

This problem is most prominent in solid oxy fuel cell interconnecting plates where ferritic stainless steels are used. Austenitic stainless steel also suffers from a similar problem, a study on oxidation of 304L at 600 °C in H_2O containing environment shows evaporation of Cr, leading to outer surface oxide layer rich in Fe [38]. High concentration and high flow rate of air containing water vapor leads to decrease in ability to form protective Cr_2O_3 at

the surface. Various authors have proposed use of Mn-Cr steels to reduce vaporization rate of chromia layer, up to a certain extent by forming $MnCr_2O_4$. Addition of Mn lowers chromia activity and results in lowering of Cr evaporation by forming a uniform spinel layer [39]. A study on oxidation of Mn added Ni-Cr alloys showed reduction in evaporation of Cr from the spinel layer [40]. Study carried out by Rakshith Sachitanand et al. on commercial interconnect material shows that alloys with high content of manganese suffer less Cr evaporation whereas alloys without Mn suffer four times higher chromium evaporation rate [41].

Gas flow rate also influences the high temperature oxidation, increase in flow rate results in severe oxidation, also known as breakaway oxidation. It is essential to know the behavior of an alloy system in flowing air (moist/dry) at high temperatures because in most industrial applications, high pressure gases are used, such as in steam turbines where the air contains water vapor. In most of the industries where high temperature operations are carried out, water vapor present in the surroundings accelerates the corrosion and oxidation process. Since high nitrogen austenitic stainless steels are candidate material for intermediate temperature application and contain high Mn, it is essential to understand the oxidation behavior of these steels. High chromium containing steels suffer from chromium vaporization during oxidation in the temperature range of 600-900°C in humid air with high flow rates. The study carried out on chromium vaporization in high temperature alloys shows that manganese containing steels form a spinel layer of $(Cr, Mn)_2O_4$ which reduces the chromium vaporization rate by 61-75%, compared to pure chromia forming alloys. The effect of gas (wet air) flow rate on the oxidation behavior of 625 alloys in the temperature range of 900-1000°C shows that by increasing flow rate from 0.5 to 6 m/s, chromium loss increased due to formation of volatile species [42]. Chromium vaporization plays a major role during high temperature oxidation in humid air condition. Various studies show that

water content in air increases the chromium vaporization and also increases oxidation resulting in formation of Fe rich oxide scale in Fe-Cr steel. Study carried out on high temperature oxidation behavior of 441 stainless steel grade in air flow and humid atmosphere shows that high flow rate causes increase in the growth rate of oxide scale whereas humid environment (water vapor with air) improves the adherence of oxide scale [43]. Effect of flow rate on oxidation of nickel metal in air with a mixture of nitrogen and oxygen shows that flow rate had no measurable effect on oxidation rate [44]. However, the oxidation rates at higher airflow showed lower values. J. Zurek et al. studied the oxide morphology of 10% Cr ferritic steel in Ar-H_2O and Ar-H_2O-H_2 mixtures, at different flow rates, and showed that at lower flow rates oxide thickness was more than that at the higher flow rate [45]. It can be concluded that there are very limited data available on high temperature oxidation of high manganese nitrogen stabilized austenitic stainless steel at different flow rates.
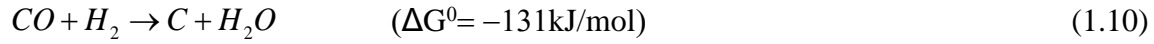
1.6 Metal Dusting

Metal dusting is a severe form of high temperature corrosion that occurs in reducing atmosphere/ low partial pressure of O_2 or where the partial pressure of reducing gases such as CO, CO_2, and H_2 is high compared to oxygen. This type of corrosion occurs in carbonaceous environment such as in gas reforming units, refiners, direct reduction furnaces, etc. In metal dusting, metal disintegrates into metal/metal carbides in high carbon activity gaseous environment ($a_c>1$) in the temperature range of 400-800°C [46, 47].
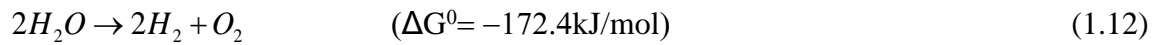
1.6.1 Thermodynamics of Metal dusting

Carbon deposition during metal dusting starts from CO adsorption which requires a surface/ catalyst (Fe, Ni, Cr) in form of C (adsorbed) and O (adsorbed) at surface, hydrogen takes away the oxygen by forming H_2O, leaving carbon at the surface. In the intermediate temperature range of 400-800°C, under reducing environment, both oxidation and
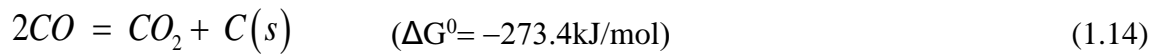
carburization processes can occur simultaneously. This results in formation of oxides along with carbon deposits [46]. Coke deposition at the surface of any component weakens its heat transfer capacity as well degrades the component. High activity of carbon arises at intermediate temperature by the following gas reactions. Activity of carbon (a_c) can be calculated considering these reactions in equilibrium.

$$CO + H_2 \rightarrow C + H_2O \qquad (\Delta G^0 = -131 \text{kJ/mol}) \qquad (1.10)$$

$$a_c = \frac{p_{H_2} \cdot p_{CO}}{p_{H_2O}} \cdot K_1 \qquad (1.11)$$

$$2H_2O \rightarrow 2H_2 + O_2 \qquad (\Delta G^0 = -172.4 \text{kJ/mol}) \qquad (1.12)$$

$$p_{O_2} = \left(\frac{p_{H_2} \cdot K_2}{p_{H_2O}} \right)^2 \qquad (1.13)$$

$$2CO = CO_2 + C(s) \qquad (\Delta G^0 = -273.4 \text{kJ/mol}) \qquad (1.14)$$

$$a_c = K_3 \cdot \frac{(p_{CO})^2}{p_{CO_2}} \qquad (1.15)$$

where p_{H_2}, p_{CO} and p_{H_2O} are the partial pressures of hydrogen, carbon mono oxide, and water respectively. K_1, K_2 and K_3 are equilibrium constants of reactions 1.11, 1.13 and 1.15 respectively.

1.6.2 Mechanism of Metal dusting

Steel (low/ high alloy), nickel base alloys and cobalt base alloys are prone to metal dusting. The mechanism of metal dusting is complex and not well understood, however based on the alloy composition various researchers proposed different mechanisms in past. In Fe base (Type I) alloys, carbon from the gaseous phase diffuses into the matrix, resulting in formation of M_3C, $M_{23}C_6$, M_7C_3 (M:Fe, Cr, Mn, Ni) and matrix eventually gets supersaturated with carbon and gets decomposed into iron particles and coke [47, 48]. Formation of metal carbides leads to volume expansion, that results in generation of compressive stress which leads to detachment of metal particles. This causes to metal loss

and pits formation at the surface. Nickel based alloys and other austenitic stainless steels follow similar mechanism (Type II) but without forming any intermediate carbides. Austenitic matrix alloys have higher carbon solubility compared to ferritic alloys, that leads to supersaturation of carbon in matrix, and causes decomposition of metal surface into fine metal particles [49, 50]. Since in austenitic alloys metastable carbides could not form, an inward graphite formation into the carbon supersaturated matrix leads to small metal fragmentation with graphite flakes. Further, some authors have reported Type III type of mechanism in which disintegration of metals takes place by selective oxidation of carbides [50]. Type III mechanism is crucial for the gas environment containing vapor content and there are some studies that have reported that this mechanism can operate at lower water content. This mechanism is important for chromia forming alloys operating in reducing atmosphere. In this mechanism, initially, carbon dissolution leads to formation of the carbide M_7C_3 at carbon activity of more than one and that of $M_{23}C_6$ at lower carbon activity, of less than one. Here oxygen plays important role, by selectively oxidizing the metal carbides, leaving behind the metal dust containing spinel, oxides or matrix particles.
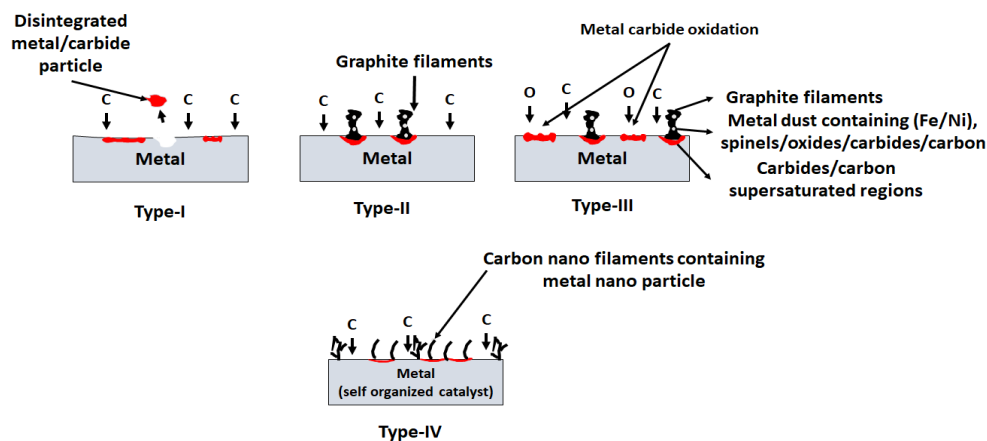
Figure 1.2: Schematic representation of metal dusting mechanisms.

Type II and Type III both occur simultaneously in austenitic stainless steel and Ni-base alloys. P. Szakalos [50] described Type IV mechanism in that degradation continues by forming nano particles of metal from the corrosion product. The end corrosion product

comprises of particles of oxides and spinel, which act as a catalyst site for nanotube formation. Schematic representation of the various mechanisms is shown in **Figure 1.3.** The combined carburization and oxidation processes in a reducing gas atmosphere have been reported by Grabke [47, 48, 51], Szakálos et al. [49, 50], Young et al. [52, 53], and Schmid et al. [54]. Thermal cycling during operation of equipment causes frequent rupture and healing of the protective chromia layer, present on the austenitic stainless-steel surface. Due to rupture of the protective film, carbon and oxygen present in the environment attack the bulk alloy selectively below the surface, and depletion of alloying elements occurs due to carburization and oxidation. This disintegrates metal particles and deposition of carbon containing metal dust takes place [46, 55]. Metal dusting starts from the deposition of unwanted carbon on the alloy surface containing Fe, Cr, Ni or Co. Severity of attack depends on the operating temperature, alloy composition and gas composition.

1.6.3 Metal Dusting of Various High Temperature Alloys

Metal dusting of 304 L austenitic stainless-steel shows that Ni has a detrimental effect because of the graphite stabilizing effect of Ni whereas Ni free chromia forming alloys exhibit lower metal dusting rate [49]. Study on 321 austenitic stainless steel shows that geometry of sample also influences the metal dusting phenomenon, edges and corners were found more prone to metal disintegration [56]. Oxidation and metal dusting of 304 L shows that selective oxidation of metal carbides was the primary mechanism of metal dusting. It was also concluded that activity, calculated from the conventional equilibrium carbon deposition reaction was unhelpful [55]. Metal dusting behavior of 800 HT for 500 h at 570°C at 1 bar shows pitting at the surface because of breakage of the protective oxide layer by selective carbide oxidation and volume expansion. Metal dusting of Ni based alloys showed high resistance towards metal dusting because of high Cr content and formation of chromia layer, whereas resistance to metal dusting of Cu rich FeNiCr model alloys was

lower due lower carbon transfer and graphite nucleation [57]. Fe-Cr alloy with varying Cr content shows that at 80 wt% of Cr there was no graphite, formation due to rapid chromium carbide formation. Effect of metal dusting was studied also on martensitic steel, it showed internal carburization; a new model was proposed for non-steady state carburization in which the rate of carbon diffusion in the matrix was proportional to the difference between equilibrium carbon content and solute carbon content [58]. Metal dusting of Fe-Ni and Fe-Ni-Cr alloys in cyclic conditions shows that cyclic conditions lead to spallation of protective oxide layer and causes internal carbide and spinel formation in both alloys [59]. Buyanov et al. [60] and Vedyagin et al. [61] described that pure metals and bulk metal alloys can be considered as a precursor of self-organized catalysts, consisting of dispersed metal particles, for the synthesis and growth of carbon nanotubes. Various high temperature alloys have been studied for their metal dusting behavior as shown in Appendix B, it shows that metal dusting behavior of austenitic stainless steel with Ni content is well studied.

1.6.4 Role of Oxide Layer

Oxide layer at the surface during metal dusting plays important role, most of the commercial stainless steels are capable of forming chromia, alumina layers. If there is a continuous supply of metal ions to the oxide layer and the oxide layer is uniform and homogenous throughout the surface on an alloy surface then only it can protect the alloy from metal dusting. However, in most cases the growth of uniform and homogenous protective layer and the supply of metals ions at the surface is inhibited after certain interval of time, in these cases metal dusting starts at the defected oxide surface (cracks). At low temperature (<500°C), oxide layer does not completely form at the surface due to low diffusivity of matrix elements [46]. A study carried out by Aurelie Rouaix-Vande Put et al. on various alumina and chromia forming alloys (Ni base and Fe base) shows that even the alloys with very protective oxide layers, undergo metal dusting after long exposure [62].

They also concluded that water content in gas mixture reduces the carbon activity, but this does not hold well with low alloy steels.

Various literature is available on the alloys, forming Cr_2O_3 and $MnCr_2O_4$ layer, on chromium evaporation in humid environment but only limited study is available on the behavior of $MnO/MnCr_2O_4$ forming alloys, in reducing atmosphere. Manganese has very attractive property for metal dusting application, it exhibits anti coking property and also inhibits the diffusion of carbon into the steel matrix. From the literature, it is clear that austenitic stainless-steels containing Ni have been well studied but no studies are available on Ni free austenitic grade high manganese steel.

1.7 Solid Particle Erosion

Solid particle erosion is defined as abrasive wear process in which high velocity particles repeatedly impact against surface, causing volume loss of material. These high velocity particles are entrained through any medium (liquid/ gas). This phenomenon is associated with both constructive processes such as abrasive jet machining, blast cleaning, etc. and destructive processes such as gas transmission pipelines, turbine blades in power generation, heat exchangers, etc. In hydroelectricity generation, underwater parts operating in silt ladens suffer erosion which causes serious problems such as failure of components, plant shut down, heavy loss in power generation, etc. In mining industry, dredging work and waste disposal industry erosion is a serious problem. Gas flow containing particulates causes erosion on the internal surface and valves in gas pipeline industry. Mainly in steam gas reforming where natural gas or solid carbonaceous feedstock such as coal, coke, biomass, etc. is reformed into syngas containing carbon mono oxide and hydrogen with other gases, they also contain sand particles which cause erosion of components [63]. Traditionally alloys having good combination of mechanical properties such as Fe based alloys (martensitic, austenitic stainless steel) and Ni based superalloys are used in such

industries. Cast martensitic stainless steel is preferred in severe erosive environments such as in hydro turbines due to its high hardness and corrosion resistance [64]. However, difficulty in weldability and quantity of martensite cause problems in maintenance, also fully martensitic structure is susceptible to hydrogen embrittlement. On the other hand, austenitic stainless steel has good combination of mechanical properties in a wide range of temperature, corrosion resistance, and weldability. Although their strength is not as high as of martensitic stainless steel, N alloying increases the strength and is gaining much attention because it is a better solid solution strengthener than carbon, and most importantly it reduces the cost by replacing nickel.

1.7.1 Effect of Erosion Parameters

Solid particle erosion depends on the angle of impact, velocity of erodent, erodent property (shape, size, hardness of erodent), flow rate, and surface material property. Based on these parameters researchers have proposed different erosion ratio equations. Erosion rate can be defined as the ratio of mass loss to the mass of the erodent which has unit of g/g. Particle properties such as density, hardness, and size influence the erosion rate, for example Hutching et al. showed that erosion rate varies with angularity of particle, erosion rate with angular particles was four times higher compared to round particles [65].

1.7.1.1 Particle Size

Particle size also influences the erosion rate, larger particle has higher kinetic energy than smaller particles. Past studies show that erosion rate and particle size have linear relationship [66, 67]. This was due to larger size of particle which causes change in impact velocity due to collision. Desale et al. correlated particle size to erosion rate by the following equation where n is constant and can vary between 0.3 and 2.0 and it depends upon the material property, experimental condition, particle velocity [68].

$$Erosion\ Rate \propto (Particle\ size)^n \tag{1.16}$$

In case of sand particle n=1 and erosion rate have linear relationship with sand particle size. In general, larger particle causes more erosion damage because they have higher kinetic energy and impact force. Smaller particle has lower kinetic energy and also, get affected by turbulence. Both linear and power law relations have been suggested by various researchers.

1.7.1.2 Hardness of the Erodent

Another factor that influences erosion rate is erodent property, mainly hardness, erodent having higher hardness cause severe mass loss on the other hand erodent having lower hardness shatter into smaller particles after collision, that results in loss of mass and kinetic energy. Wada and Watanable 1987 et al. proposed the following equation where H_p is the hardness of erodent particle, H_t is the hardness of target material and n is empirical constant [69].

$$Erosion\ Rate\ \propto (\frac{Hp}{Ht})^n \qquad (1.17)$$

1.7.1.3 Density of the Erodent

Density of the erodent also affects the erosion rate, higher the density higher will be the kinetic energy, that results in higher mass loss or high erosion rate. Property of carrier fluid or the medium in which erodent is carried also influences the erosion rate, it has largest influence because it can affect impact angle and velocity of particles. Erodent is carried by fluid to the wall; fluid properties such as viscosity, density can affect the solid particle erosion behavior. It directly affects the local particle concentration and that can affect the particle-particle interactions. The properties of material walls also influence the erosion rate, higher the hardness higher will be the erosion rate and vice versa.

1.7.1.4 Impact Velocity

Impact velocity is the most important parameter that influences the erosion rate, it has direct relation with erosion rate as shown in the equation below, where n is constant and can vary between 0.4-4.5 [70]. Generally, its value is 2, based on work of Finnie [71].

$$Erosion\ Rate\ \propto\ (Velocity)^n \qquad\qquad (1.18)$$

1.7.1.5 Impact Angle

For ductile material at lower impact angle erosion rate is high because the interaction area is more at lower angle also at lower angles formation of platelets and cutting is easier, as angle increases the interaction area decreases and also the erosion rate for a ductile material. For brittle material the behavior is reverse, at normal angle the erosion rate is high and at lower angle erosion rate is lower. This is due to cracking of brittle material at normal angle.

Most of the materials which are used in gas and oil industry pose both ductile and brittle behavior. Temperature also influences the erosion rate, if there is increase in ductility of material on increasing the temperature erosion rate will decrease and if there is decrease in ductility with increase in temperature erosion rate will increase. Depending on the nature of material (ductile /brittle) various mechanisms for erosion are proposed in past studies. In ductile erosive process forging and extrusion are the main material removal process. During the first interaction of impact particle crater and lip formation takes place. These lips are forged and extruded by subsequent particle impact; this whole mechanism is called as platelet mechanism. In this mechanism, material removal takes place due to high rate of plastic deformation causing fracture of material surface. Ductile erosion is characterized by features such as ploughing and cutting, the maximum erosion is at lower angles. On the other hand, in brittle failure material is removed by cracking and chip formation and the maximum erosion at 90° [71].

1.7.2 Erosion of Austenitic Stainless Steel

Stainless steels are widely used in various components operating in high temperature eroding environments. As discussed earlier, due to their higher strength, high temperature stability and corrosion resistance, austenitic stainless steels are widely used in erosive environments. Alan Levy et al. [65] studied erosion behavior of various stainless steels (ferritic and austenitic) at elevated temperature and concluded that austenitic stainless steel was less eroded compared to ferritic stainless steel at elevated temperature. They also observed that as the temperature increases erosion rate diminishes. Problem of erosion corrosion occurs at elevated temperature; various industries where components are subjected to different atmosphere face this problem. For example, in coal combustion power plant where component is subjected to high temperature flowing combustion gas with dust particles in it, causes erosion corrosion. Components such as pipes, nozzle, burner, heat exchanging tube, outlet ducting undergo erosion due to the ash present in the flowing combustion gas. The gas chemistry (reducing) and high temperature also enhance the corrosion.

A study on erosion corrosion of iron and nickel alloys in combustion gas environment shows that conventional austenitic stainless steel 304 and 310 SS perform better as compared to nickel-based alloys [72]. Solid particle erosion is biggest problem in fluidized bed combustion systems where generally austenitic stainless steels are used, a comparative study between austenitic stainless steel (304 and 316L) and martensitic stainless steel 420 shows that martensitic stainless steel performed better at all angles and exhibited ductile behavior at 30^0 while 304 and 316L stainless steels showed brittle characteristics by detachment of large particles and formation of large craters [73]. Alloy chemistry is one of the important factors which influences mechanical properties. For example - ductility affects erosion rate, a comparative study of solid particle erosion of AISI 310S, AISI 316,

AISI 1020, and 6060 aluminum shows that 6060 aluminum alloy shows higher resistance to solid particle erosion due to its lower hardness. High ductility reduces the mass loss and converts the kinetic energy of impinging particles to heat and plastic deformation. All four metals shows ductile erosion behavior with peak erosion at lower angle of 15 and 30^0 [74]. Study carried out by Sundararajan and Shewmon et al. suggested that mass loss due to erosion occurs when a critical fracture strain is reached, which causes fragmentation, cracking and removal of flakes [75]. It has also been proposed that microstructure of material should be such that it does not accumulate strain after impacting particle strikes the surface [76]. As discussed earlier martensitic alloys such as 13/4 having 13wt%Cr and 4wt%Ni are widely used in high erosive medium, but due to problem in maintenance and weldability these alloys are less preferred.

Recently, N alloyed austenitic stainless steels such as Cr-Mn and Cr-Mn-Ni are tested for their erosion resistance as a possible alternative. A study carried out by AK Chauhan et.al. on solid particle erosion of 13/4 martensitic stainless steel and nitrogen alloyed nitronic stainless steel (23 wt%Cr, 4 wt%Ni and 0.38wt%N) shows high resistance towards solid particle erosion of nitronic stainless steel which was attributed to high hardness and ductility. The even distribution of hard carbides stabilizes the austenitic matrix [77]. Another study carried out by Ashish Shelokar et al. on comparison of solid particle erosion behavior of martensitic stainless steel (13/4) with high nitrogen alloyed austenitic stainless steel (28/4N) shows excellent resistance of 28/N austenitic stainless steel towards air jet erosion due to its higher toughness and strain hardening exponent. In both the stainless-steels, material was removed by ploughing at lower angle [78]. Cavitation erosion is one of the problems which is faced by engineering components, in continuous contact with liquid. High nitrogen austenitic stainless steel (CrMnN class) is one of the attractive alternate solutions for this problem. They possess excellent resistance to cavitation erosion

because nitrogen alloying improves corrosion resistance [23]. A brief literature survey on erosion behavior of various austenitic stainless steel is given in Appendix C. From the literature survey, it is clear that nitrogen alloyed nickel free stainless steels could be better alternative to martensitic and ferritic grade due to their combination of properties. It can be seen that there is no reported study on high temperature solid particle erosion behavior of high nitrogen nickel free austenitic stainless steel [79].

1.8 Aqueous Corrosion

Our previous study shows that manganese oxidizes rapidly and forms manganese oxide layer at the surface and that is not protective during higher temperature exposures. At higher temperatures of 400 and 800°C, precipitation of Cr_2N occurs, that causes decrease in mechanical and corrosion properties. Precipitation of nitrides influences directly pitting resistance of these categories of alloy. The shape, amount and type of the chromium nitride precipitate formed, also affect corrosion resistance of these alloys. All these parameters generally depend upon the temperature of exposure. Study carried out by K. Krishna Kumar et al. [80] shows that ageing at 700, 800, and 900°C for 14 h causes formation of chromium nitrides, with increase in temperature, the amount of lamellar nitrides increases. They found that at 900 and 800°C pitting resistance was higher and disk-shaped nitrides resist pitting. Alloying element such as molybdenum with increased nitrogen content improves the corrosion resistance. K.L. Chao et al. showed that Mo addition improved corrosion resistance by forming effective barrier of MoO_2 and that inhibits diffusion of corroding species. They also showed that with increase in Mn content corrosion resistance decreases. On the other hand, compared to conventional nickel containing austenitic stainless steel high nitrogen nickel free stainless-steel possesses better pitting resistance [81]. Study carried by Xinqiang Wu et al. shows that compared to 316L high nitrogen nickel free stainless steel shows greater resistance towards pitting. Sensitization treatment to high

nitrogen stainless steel causes rapid increase in corrosion rate [15]. Another study by Norman Kauss et al. shows that Fe-Cr-Mn-N austenitic stainless steel performed better in terms of mechanical properties and pitting potential resistance. They also concluded that if the possibility of sensitization during use is ruled out then this class of alloys can be considered better than conventional austenitic stainless steel [82]. Passive film and its composition play important role in providing corrosion protection from any environment. In high nitrogen nickel free stainless steel passive film is generally composed of oxides and hydroxides of Mn, Fe, and Cr. Manganese dissolution in aqueous solution causes decrease in corrosion resistance, while higher Cr content could delay the process. In case of sensitization, chromium gets combined with nitrogen to form chromium nitride along the grain boundaries which leaves chromium depleted region leading to corrosion attack.

Our studies show that these classes of alloys are susceptible to precipitation at temperatures above 500°C. Our study showed that mechanical properties such as tensile strength and ductility of present grade of austenitic stainless steel do not get affected due to ageing up to 100 h below 500°C, it opens a new realm for application of these alloys at intermediate temperature. Some of the applications could be in metal dusting environment, since Mn in the steel forms manganese oxide, that inhibits the deposition of carbon, and in an erosive environment where these alloys performed better than conventional nickel containing stainless steel. However, to the best of our knowledge, there are no studies that have focused on the effect of pre-exposure at intermediate temperature range from 400-700°C for 100 h on potentiodynamic corrosion. The literature survey (Appendix D) shows that the most of studies are focused on sensitization behavior, normally occurring above 800°C. In the present study, an attempt has been made to explore full potential of the material for creating more possible applications of these alloys.

1.9 Motivation

Nickel free high nitrogen and manganese stabilized austenitic stainless steel is extensively used in biomedical, transport, aerospace, defence, oil, and gas pipelines field. These steels are extensively studied for their room temperature and cryogenic properties. Nitrogen containing stainless steels are subjected to variable temperatures of exposure during their fabrication. This temperature may vary from 400 to 700°C depending upon the processes used. The material is also considered as a possible replacement of existing 316L stainless steel due to its excellent mechanical and corrosion properties. Most of the work available in the literature is mainly concentrated on the precipitation of harmful phases (sensitization) above 800°C. Appendix A to D show that there is no study available on the oxidation, metal dusting, erosion, and corrosion behavior of Fe-18Cr-21Mn-0.65N stainless steel. Being a cost-effective replacement of various grades of commercially available austenitic stainless steels, high manganese nitrogen stabilized steel can be used under various environments. The results obtained are quite encouraging and open a new field of applications of nickel free grades in the intermediate temperature range.

1.10 Scope of Work

In the present investigation, a nickel free (low nickel) nitrogen and manganese stabilized austenitic stainless steel (Fe-18Cr-21Mn-0.65N) was exposed between 400 to 700°C and subjected to oxidizing, reducing, erosive and corrosive environments. The exposed samples were extensively examined using advanced characterization tools like Electron Probe Micro Analyzer (EPMA), X-ray photoelectron spectroscopy (XPS), Raman Spectroscopy, X-Ray Diffraction, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), etc. The mechanism of deterioration under various conditions are stabilized and compared with the available literature.

1.11 Objective of Work.

The objective of the present work is to study the behavior of Fe-18Cr-21Mn-0.65N austenitic stainless steel in the temperature range of 400-700°C, as recorded below:

1. Effect of moist air environment on oxidation behavior for100 h at different flow rates;

2. Effect of metal dusting in 25%CO+75%H_2 up to 300 h;

3. Solid particle erosion of samples exposed at different temperatures for100 h;

4. Potentiodynamic corrosion behavior of pre-exposed samples in aqueous chloride medium (0.5 M NaCl solution).