Preface

Nickel free or low nickel nitrogen and manganese stabilized austenitic stainless steels based on Fe-Cr-Mn-N alloy system are an important class of engineering material that exhibit a wide range of properties such as strength, toughness, high pitting corrosion resistance, and creep properties. Nitrogen and manganese alloying enhances the austenitic stability and work hardenability of this class of steel. The 200 series of austenitic stainless steel exhibit acceptable strength in the temperature range from cryogenic to higher temperature. Applications of conventional austenitic stainless steels such as 316L, S304, S310, etc. are restricted mainly due to the high cost of nickel. Fe-Cr-Mn-N class of alloys are well studied and documented for biocompatibility and other applications such as retainers' rings in power generators, drill collars of oil rigs, vessels of fusion bed reactors, and armor materials in the defence sector. In the nuclear industry, it is highly undesirable to use high nickel containing stainless steel because nickel in the steel undergoes activation by neutron radiation. This reduces ductility of the material in service and creates problems in the disposal of a component after decommissioning. In such applications, the Fe-Cr-Mn-N steel is cyclically exposed between 300-700°C. In several applications, this grade of stainless steel is welded with other low alloy steels and C-Mn steels, undergoes intermediate temperature exposure (400-700°C for 10-40 h) during stress relieving heat treatment. Austenitic stainless steel is widely used in heat exchangers and gas reforming units where it is exposed to intermediate temperature range from 300-500°C. Low temperature (400-500°C) stress relieving treatment of 8-10 h, is needed to remove peak stress and maintain dimensional stability during machining of stainless steel, which causes cyclic oxidation. Components such as transporting pipes which are used to transport a reducing gas mixture of CO and H_2 suffer from carbon corrosion. These components get eroded with time due to the impingement of sand particles inside the gas on the interior of the pipes. Cl ions are inevitable in various industries such as fossil, food, paper, and chemical. Stainless steel components have been widely used in such industries and are exposed to sea water environment in the coastal region.

In the present work, high temperature oxidation, metal dusting, erosion, and corrosion behavior of Fe-18Cr-21Mn-0.65N austenitic stainless steel, with a negligible amount of nickel (present as impurity, derived from the raw materials used in steel making) has been studied in the temperature range of 400-700°C. This thesis is divided into seven chapters and the details of each chapter are given below:

Chapter-1 presents a brief introduction of high manganese nitrogen stabilized austenitic stainless steels. This chapter describes the role of alloying elements and the physical metallurgy of nitrogen and manganese alloyed austenitic stainless steel. An extensive literature survey has been made on the oxidation, metal dusting, erosion, and corrosion behavior of high manganese nitrogen stabilized austenitic stainless steel. The gaps were identified from the literature. The scope and objectives of the present research work are described.

Chapter-2 deals with material and methods of oxidation, metal dusting, erosion, and corrosion tests. The initial characterization of the material, such as optical microscopy and mechanical properties are included in this chapter. This chapter also comprises the details of the experimental setup used in different experimental work and characterization techniques used in the present study.

Chapter-3- deals with the cyclic oxidation behavior of nitrogen and manganese stabilized austenitic stainless steel (Fe-18Cr-21Mn-0.65N) from 400-700°C up to 100 h. The effect of moist airflow on oxidation behavior from 400-700°C was systematically studied gravimetrically and the oxidized surfaces were characterized using SEM-EDS and XRD.

During oxidation, Mn diffused out from the matrix to surface and reacted with the oxygen associated with the passive chromia layer and formed nonprotective Mn_2O_3 and spinel of the oxides of Fe, Cr, and Mn. At 700°C, there was rapid vaporization of Cr and consequent reduction in weight gain in dynamic air (DA) as compared with that in static air (SA). Precipitation of Cr_2N of different morphology was established through TEM analysis. The rate of oxidation increased with a rise in temperature in both the conditions. The high diffusion coefficient of Mn through the chromia layer was the key factor in lowering the oxidation resistance of this steel. Oxidation from 500-700°C resulted in the formation of a duplex oxide layer with Mn oxide at the top and spinel $CrFeMnO_4$, Fe_2MnO_4, $FeMn_2O_4$, at the bottom. Evaporation of Cr due to the formation of volatile $CrO_2(OH)_2$ at 700°C, decreased the weight gain in humid dynamic air condition as compared to that in static air. TEM study showed cellular precipitation of HCP chromium nitride (Cr_2N) at 600 and 700°C while at 500°C faceted globular morphology was observed. Precipitation of the detrimental σ phase was not observed in this study.

Chapter-4 presents the features of metal dusting of Fe-18Cr-21Mn-0.65N in syngas environment (75% H_2 and 25 %CO) at 400-700°C, under cyclic exposure for 300 h. Study reveals carbon corrosion at 400-500°C, however, at 600-700°C, oxidation of Mn and formation of Mn-Cr-O spinel significantly reduced the carbon attack. The surface and cross section of the exposed coupons were examined by XRD, SEM-EDS, and EPMA. Metal dusting resulted in formation of very few corrosion pits of the size 2-7μm and epitaxial growth of carbon nanotubes on the surface exposed at 400-500°C. Extensive growth of carbon filaments was found from 400-500°C due to the high activity of carbon. The limited metal dusting (carbon erosion) of metal particles showed formation of a few shallow pits. Metal dust comprising of graphite, Mn, and Fe along with fragmented metal carbide particles formed from low temperature exposure. At high temperature of 600-700°C rapid diffusion of Mn resulted in the formation of a thick porous layer of Mn oxide and that inhibited the growth of carbon filaments. This was followed by an intermediate layer of spinel of Mn, Cr, and O. The presence of a few metal carbides/oxides showed that initially the process started with carburization reaction but later oxidation of these carbides took place. In short, the alloy exhibited Type III mechanism of metal dusting where initially formed metastable carbides were selectively oxidized, depending upon the activity of carbon.

Chapter 5 presents high temperature erosion behavior of high manganese nitrogen stabilized austenitic stainless steel, exposed at 400-700℃ for 100h, at three different impingement angles of 60°, 75° and 90°. Acicular alumina was used as an erodent with a discharge rate of 4.6±0.5 gm/min. Optical microscopy, Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD) were used to characterize the eroded surface. Tensile testing and microhardness evaluation was also carried out for better understanding of the erosion behavior. Erosion rate increased with rise in temperature of exposure and was found to be associated with decrease in tensile strength and hardness of the steel. Oxidation at high temperature during pre-exposure, played an important role in accelerating the erosion rate, particularly at 600 and 700℃.

Oxidation of the alloy, during exposure, produced brittle oxide scale, composed of spinel of Mn, Cr, and O. Pre-exposure at higher temperature caused precipitation of Cr_2N, that reduced tensile strength and hardness of the alloy. High velocity impact of alumina particles caused breakage of brittle oxide layer and directly eroded the base material. Rise in temperature caused increase in erosion rate at all impingement angles. As the angle of impingement increased from 60° to 90°, erosion rate decreased at 600 and 700℃ due to the formation of soft ferrite at the surface, below the oxide layer. The changes in hardness were highest at 90° of impingement angle at all temperatures and the erosion rate was lowest. It is attributed to higher plastic deformation and reduced velocity of the incoming particle by rebounding interaction. The mechanism of erosion was ploughing/cutting, lip formation at a lower angle of impingement, delamination and crater/pit formation at normal angle, at all temperatures.

Chapter 6 deals with corrosion behavior of Fe-18Cr-21Mn-0.65N austenitic stainless steel, pre-exposed at intermediate temperature from 400-700°C, for different time intervals, up to 100 h. Potentiodynamic polarization test was performed at room temperature in seawater environment (0.5M NaCl) to evaluate corrosion behavior of the steel samples pre-exposed at different temperatures. Polarization test shows that an increase in the temperature of exposure, reduced the corrosion resistance of the steel. EIS study of the passive layer formed also showed a decreasing trend in corrosion resistance of the passive film. The corroded surface of the sample was characterized by X-ray photoelectron spectroscopy (XPS) and Scanning electron microscopy (SEM-EDS). XPS analysis revealed oxides and hydroxide of Cr^{+3}, Mn^{+3}, and Fe^{+3}. Higher temperatures of exposure favored formation of manganese hydroxide. Pitting mechanism was prominent in the specimens exposed from room temperature to 500°C, whereas there was a mixed mode of corrosion (intergranular combined with accelerated pitting) in the specimens exposed at higher temperatures of 600 and 700°C. Precipitation of Cr_2N along grain boundaries and within the matrix was found to be the main cause of the accelerated corrosion attack.

Chapter 7 presents the overall summary of the present investigation, including important conclusions and scope of the future work.