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## PREFACE

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Super austenitic stainless steel (SASS) grades possess outstanding mechanical properties, oxidation as well as corrosion resistance over a wide range of temperature. These highly alloyed grades are also known as Fe-Ni-Cr alloy, which are specifically alloyed with additional stabilizing elements like Mn, Si, Cu, Mo, N and to some extent Boron to enhance their working under service conditions. Oxidation resistance of Fe-Ni-Cr alloys depends on the formation of chromia ( $\text{Cr}_2\text{O}_3$ ) which exhibits slow growth rate and there is minimum porosity in the region of scale interface.

Various SASS grades have been used in extreme service environments, such as seawater handling systems and heat exchanger tubes, chemical processing equipments waste incinerators etc,. The high content of Mo, up to  $\approx 7$  wt% increases the susceptibility to formation of intermetallic phases. These steels face serious problem of oxidation when exposed to higher temperatures due to formation of volatile oxides such as  $\text{MoO}_3$ . These volatile oxides are formed from the anionic diffusion of oxygen through the porous scale, which further leads to depletion of the base elements through cationic diffusion.

Numerous studies have been carried out on oxidation behavior of such SASS grades at nominal service temperature from 500-900 °C. It was found that under flowing air condition the attack was not severe, whereas under stagnant air condition the attack was severe due to which catastrophic attack could not be prevented. Volatile species in Fe-Ni-Cr alloys, such as  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , become highly unstable above 600 °C. In contrast, Ni hinders the formation of oxidizing species namely Fe, due to which outward depletion of

the base metal is obstructed and the oxidation resistance is improved. However, no systematic study has been reported on 904L for its oxidation resistance.

Biomass fired plants are more environment friendly than fossil fuels fired ones and cause almost zero CO<sub>2</sub> emission. Biomass and waste are renewable fuels and good substitutes of fossil fuels for power generation, for a sustainable society. However, burning of biomass fuel results in deposition of ash, which contains inorganic alkali chlorides and sulphates and reduce thermal efficiency of the heat exchangers and cause severe corrosion at working temperature. The usage of waste products in energy production is known as WTE (Waste to Energy). The presence of both alkali chlorides and sulphates results in lowering of melting temperature of the deposits and accelerates the rate of corrosion. The main problematic element in biomass ash environment is potassium which combines with passivation layer of Cr<sub>2</sub>O<sub>3</sub> and forms K<sub>2</sub>CrO<sub>4</sub> rather than sodium, at lower temperatures up to 400 °C. Although, protective oxides are stable in air, they become less stable in contact of KCl at high temperature.

The present investigation deals with systematic study of oxidation behavior of the 904L steel by cyclic and isothermal exposures at 500-650 °C for 100 h. During cyclic exposures, 15 cycles were carried out, for maximum up to by 100 h whereas, during Isothermal exposure, the samples were subjected to 25, 50, 75 and up to 100 h at 500, 550, 600 and at 650 °C in stagnant air atmosphere. The isothermal and cyclic hot corrosion behavior of the 904L steel was carried out in synthetic biomass ash environment, using two different mixtures of NaCl+KCl+Na<sub>2</sub>SO<sub>4</sub>+K<sub>2</sub>SO<sub>4</sub> salts, SM1 and SM2, with Cl:S ratio of 40:60 and 60:40 respectively, at 500-650 °C up to 100 h. It has been observed that cyclic exposure of the SASS 904L at elevated temperature is more detrimental than isothermal

exposure. The severity of damage was highest from hot corrosion due to SM2 salt mixtures having more Cl ions. The oxide scale and corrosion products were characterized using XRD, SEM (EDS) and EPMA techniques.

**Chapter 1.** Presents a brief introduction along with literature review on properties and applications of the 904L SASS. The motivation behind the current work and objectives are also described.

**Chapter 2.** Presents the details of materials used and experimental methods in the present work. The details of various characterization techniques used are also provided.

**Chapter 3.** Deals with the cyclic oxidation tests, which were carried out on the super austenitic stainless steel 904L up to 100 h over the temperature range of 500–650 °C in a stagnant air atmosphere. The oxidized surfaces and cross sections of the samples were examined by scanning electron microscope (SEM-EDS), X-ray diffractometer and Electron Probe Micro Analyzer (EPMA). The weight change was found to follow nearly parabolic rate law, up to the initial 5-20 h. From 500-550 °C there was maximum weight gain after 5 h of exposure, whereas from 600-650 °C, maximum weight gain was after 10-25 h of exposure. XRD analysis showed that the strongest diffraction peak was mainly of the austenite ( $\gamma$ )-matrix, both in the unexposed as well as in the sample exposed even at 650 °C. Oxidation products were mainly oxides of Cr, Fe and Ni, of increasing thickness with temperature of oxidation. Also, the sample exposed at 650 °C showed spinels of  $\text{FeCr}_2\text{O}_4$ ,  $\text{NiCr}_2\text{O}_4$  and  $\text{FeNi}_2\text{O}_4$  along with these oxides.

**Chapter 4.** Presents isothermal oxidation behavior of the 904L stainless steel from 500-650 °C for 100 h. Individual sample/s were heated from room temperature to four different temperatures, from 500-650 °C at 5 °C/min, for 25, 50, 75 and 100 h. After the exposure, samples were cooled outside the furnace to room temperature and their weight was measured. The oxidation kinetics showed nearly parabolic behavior. The oxide scales formed, were characterized by SEM-EDS, XRD and EPMA. Oxide scale formed at lower temperatures were thinner than those formed at higher temperatures. Irregular growth, as well as grain boundary cationic diffusion from the fine porous layer of the base metal was revealed from the cross section analysis. No spallation was observed over the entire experiments. It was found that thin scale and the slow kinetics was good for the 904L steel to be used at 500 and 550 °C or even up to 600 °C, however above 600 °C, Fe-Cr rich nodules were found to form at higher temperature and from long exposures.

**Chapter 5.** Describes cyclic hot corrosion behavior of the super austenitic stainless steel 904L in the temperature range 500–650°C, in synthetic biomass ash environment of alkali salts of NaCl, KCl, Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>, up to 100 h. Samples were mechanically polished and spray coated with alkali chlorides and sulphates with two different ratios of chlorine and sulphur, Cl:S=40:60 (SM1) and Cl:S=60:40 (SM2), to 3-4 mg/cm<sup>2</sup>. The hot corrosion kinetics was studied by weight change of the salt coated samples and the corroded samples were characterized by SEM/EDS, XRD and EPMA. The hot corrosion rate of the samples coated with SM1 and SM2 at 500 °C was comparable and lowest. However, at higher temperatures from 550-650 °C the rate of corrosion from SM2 was significantly higher than that from the SM1. The higher content of sulphur in SM1 reduced

the severity of corrosion resulting from chlorine. There was significant difference in surface morphology of the samples corroded with SM1 and SM2 salt mixtures. The higher rate of hot corrosion from SM2, with higher ratio of Cl:S (60:40) was found to be associated with porosity, developed in the protective oxide layer by volatile chlorides and consequent active oxidation of the material.

**Chapter 6.** Presents isothermal hot corrosion behavior at four different temperatures of 500, 550, 600 and 650 °C for 25, 50, 75 and 100 h. Each sample was weighed prior to and after hot corrosion. The surface of the samples were coated by two different compositions of salt mixtures SM1 and SM2 as described in the earlier chapter 5. The hot corroded samples were characterized by both SEM-EDS and XRD analysis. From the surface morphology, it was evident that NaCl and KCl were equally corrosive at higher temperatures (600-650°C). The cross section analysis, showed that at 650 °C the thickness of the scale formed by SM1 was thinner and consisted of dual layer, while SM2 coated sample showed thicker and multi layer structure. The isothermal hot corrosion of SASS 904L was found to be less severe as compared to cyclic hot corrosion described in the previous chapter 5.

**Chapter 7.** Compares the cyclic and isothermal oxidation as well as hot corrosion behavior of the SASS 904L.

**Chapter 8.** Presents the major conclusions drawn from this study and the suggestions for future work.