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Hot Corrosion behaviour of Metals and Alloys in the Molten Salt of Na_2SO_4-NaCl Environment

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ABSTRACT: The degradation of metal and alloys caused by corrosion at higher temperatures when their surfaces are covered with a thin film of fused salt in an oxidizing atmosphere is known hot corrosion. The hot corrosion is unpredictably rapid rate of oxidation. The hot corrosion phenomena is defined as the accelerated oxidation of materials covered with a thin film of fused salt exposed to an oxidizing gas atmosphere at elevated temperatures. Hot corrosion is a phenomenon, when a non protective porous oxide scale is produced at the surface of material in the presence of salt contaminants like Na_2SO_4, NaCl, and V_2O_5. As a result, the load bearing-ability of the materials diminishes rapidly, leading to catastrophic failure. In the present study behavior metal and alloy in molten salt of Na_2SO_4-NaCl have been discussed under the light of present literature.

I. INTRODUCTION

The hot corrosion resistance of metals/alloys mainly governed by the type of oxides developed on the surface and their adherence to the surface of metal/alloy. For good corrosion resistance the oxide scale formed must be dense, continuous, nonporous and stable. In general chromium and aluminum forms most protective oxides at high temperature [1] and these oxides particularly are protective in sulfidizing environment [2-3]. The hot corrosion of heat-resistant alloys forming protective oxide was accelerated in the presence of molten salts such as NaC1, SO_2, and Na_2SO_4 [4].

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Zahs *et al* (2000) [5] had conducted the thermogravimetric studies of Fe, Cr, Ni and their alloys at 400°C, 500°C, 600°C and 700°C in chloridizing and oxidizing atmospheres. They observed that the corrosion mechanism, particularly for temperatures > 500°C, is active oxidation, i.e. penetration of chlorine through metal oxides, chloride formation at the metal, diffusion of the chlorides and their oxidation and formation of non-protective oxide scale. The corrosion behavior mainly depends on the Gibbs free energy during chloride development. Since Iron and chromium has high negative Gibbs free energy, hence these elements have great affinity for the formation of $FeCl_2$and $CrCl_2$ respectively through active oxidation. Comparatively Nickel has less negative Gibbs free energy for the formation of $NiCl_2$hence it is less prone to be attacked by active oxidation.

Anuwar *et al* (2007) [6] in their hot corrosion study of alloy Ti–6Al–4V (Ti-31) in Na_2SO_4–60% V_2O_5 and Na_2SO_4–50% NaCl at 750 °C reported that the corrosion rate of Ti-31 is comparatively more in molten salt environment than in airenvironment. The severity of corrosion of Ti-31alloy is more in Na_2SO_4–60%V_2O_5 environment followed by Na_2SO_4–50% NaCl and air environment. The degradation of Ti-31 happens because of the reactions in between titanium and chloride ions, sulphur and vanadium.

Wang and Zhou (2013) [7] studied high temperature degradation behavior of Nb–16Si–24Ti–6Cr–6Al–2Hf in the blend of Na_2SO_4 and NaCl molten salt at 900°C. They showed that the corrosion kinetics of the given material followed parabolic law. The oxide scalemade-up of two layer one outer which is slack and spongy and other an internal oxidation inner layer. Outer oxide scale is primarily consisted of TiO_2, $TiNb_2O_7$, Nb_2O_5, $CrNbO_4$ and SiO_2 whereas inner layer of TiO_2. Based upon this they discussed the mechanism of hot corrosion of the given materials in molten salt of Na_2SO_4 and NaCl.

Liu *et al* (2008) [8] investigated the hot corrosion behavior of Ni based M38G superalloy in the blend of 75wt. %Na_2SO_4-25wt. %NaClmolten salt at 800°C and 850°C. They found that M38G superalloyexperiencedhigh rate of hot corrosion. Authors reported that at 800°C temperature, cumulative weight change was 12mg/cm^2 after 102 hoursof exposure. Whereas at temperature of 850°C there is drastic change in weight as compared to 800°C temperature, which is21mg/cm^2 after 37 hrs of corrosion test. Authors also reported the effect of pre-oxidation treatment. They observed that the pre-oxidation treatment improved the hot corrosion resistance of superalloy to some extent in the blend of Na_2SO_4-NaCl molten salt at both 800°C and 850°C. Though, with increasing the temperature,protective behavior of the oxide layer decreases. They reported that the pre-oxidation treatment did not affect the hot corrosion behavior of superalloy at 875°C.

Gurappa (2003) [9] did hot corrosion study of titanium alloy, IMI 834 (Ti-5.8Al-4.06Sn-3.61Zr-0.7Nb-/0.54 Mo) at 600°C in various environments of Na_2SO_4,90% Na_2SO_4-10%NaCl and 90% Na_2SO_4-5%NaCl-5%V_2O_5. He reported that the materialfollowed the parabolic law for kinetics indifferent molten salts. The corrosion rate is approximately6 times in the molten salt of chloride and around7 times with the addition of 5% of vanadium in the molten saltas compared to corrosion rate in 100%Na_2SO_4molten salt. This shows that the rate of corrosion is maximum in the presence of chloride and vanadium molten saltsfollowed by chloridemolten salts and least in pure Na_2SO_4molten salt at given temperature. The alloy was cracked at 600°C in chloride-containing environment, whereas no cracks were found in the scale when samples were subjected to Na_2SO_4molten salt. Author suggested that the chloride ions are responsible for the oxide scale to crack whichprovide the passage to corrosive species to penetrate and react with underlying substratematerial and enhance the rate of corrosion. He further reported that depth of oxygen dissolved region depends upon the temperature and the environment. The depth of oxygen dissolved region is minimum in Na_2SO_4molten salt and maximum in 90% Na_2SO_4-5% NaCl-5% V_2O_5environment. The total depth of the titanium alloy affected in 65 hours is around hundred times as compared to the oxidation in air for 100 h at the same temperature.

The hot corrosion behavior of Inconel 740 alloy , coated with 5% Na_2SO_4 + 5% K_2SO_4 + 90% $Fe_2O_3/Al_2O_3/SiO_2$ in 1:1:1 ratio, and in gas mixture of N_2 + 15% CO_2 + 3.5% O_2 + 0.25% SO_2 was investigated by Zhao (2006) [10]. He found that the average metal losses at 700°C for 1984 hours and 5008 hours are 8.89 and 19.37 µm respectively in the given environment. He found that with the progress of study the quantity of sulfides under the scale and scale thickness increases. After exposure for 1984 hrs the oxide layers formed are continuous, compact and adherent to the surface of the specimen. However, after exposure of 5008 hours in the given environment, they have revealed the formation of a layered structure with outer layer slack and spongy whereas the inner layer was dense and strongly adherent to the surface.

Tsaur *et al* (2005) [11] studied the hot corrosion performance of 310 stainless steel at 750°C in mixtures of various NaCl/Na_2SO_4 ratios (100/0 wt.%, 75/25 wt.%, 50/50 wt.%, 25/75 wt.% and 0/100 wt.%). Authors suggested that sodium chloride plays the major role to accelerate the corrosion rate at high temperature in the molten salt of NaCl/Na_2SO_4. The NaCl in molten salt depositslowers down the development of shielding oxide scale during the starting stage which results in the propagation of hot corrosion in steel. The mixtures with 75% NaCl showed the most severe corrosion due to molten eutectic salt and capillary transport.

Deb et al. (1996) studied [12] the hot corrosion performance of a cast nickel-based superalloy coated with 60% Na_2SO_4-30% $NaVO_3$-10% NaCl. They found that the corroded specimens indicates a thin band of nickel oxide, followed by a thick band of $Ni_3(VO_4)_2$ and a inner porous duplex band of oxides of nickel and chromium. The degradation rate decreased with course of study, which might be due to the formation of refractory Ni-vanadate bandpresent on the surface.They found the presence of sulphates caused internal sulphidation of the substrate materialunder the external oxide band in 100% Na_2SO_4 and 75%Na_2SO_4 + 25%NaCl malts.Authors suggested that the volatile species of chlorides results in the development of cracks and pits, which provide easy path for the species to penetrate into the alloys. They observed that the vanadate in combination with sulphate and chloride leads to extra fluxing of the scale, which damage the integrity and dilutethe mechanical propertiesof material.

Gurrappa (1999) [13] investigated the high temperature corrosion behavior of Ni-base superalloy CM 247 LC in Na_2SO_4 and Na_2SO_4+NaCl melt at 900°C. The author reported that the superalloy CM247LC got harshly degraded in only 4 hours and completely damaged in 70 hrs in 90%Na_2SO_4 + 10%NaCl environment at 900°C. The life of the superalloy is reported only 2 hours in 90%Na_2SO_4 + 5%NaCl + 5%V_2O_5 environment at 900°C.

Peters et at (1976), Pettit and Meier (1985), and Fryburg *et al* (1984) [14-16] discuss the effect of Mo on the high temperature corrosion of superalloys.

They suggested that the alloy containing Mo suffers catastrophic oxidation as MoO_2 react with Na_2SO_4 to form an acid (SO_2-rich) salt, resulting in acidic fluxing. The MoO_3 reacts with Na_2SO_4 form Na_2MoO_4, $Na_2MoO_4.MoO_3$ and $Na_2MoO_4.2MoO_4$. All these phases are liquid and reported to have high solubility for Al_2O_3 and Cr_2O_3.

Hiramatsu *et al* (1989) [17] studied the nine kinds of stainless steels to investigate the effects of alloying elements on the high temperature corrosion behavior in NaCl molten salt at different temperatures 450^{o}C, 550^{o}C, 650^{o}C and 750^{o}C. They observed that the corrosion rate rises with rise in surrounding temperature. Austenitic stainless steels showed better hot corrosion resistance than ferritic stainless steels. Aluminum, oxygen and chlorine were observed concentrated along grain boundaries after hot corrosion in NaC1. Austenitic stainless steels showed the condensation of nickel at grain boundaries. Aluminum was found to be useful for enhancing the high temperature corrosion resistance of ferritic stainless steel. Both silicon and nickel improved the hot corrosion resistance of austenitic stainless steel. Authors proposed that hot corrosion rate enlarged while Cr_2O_3 reacts with NaCI to generate Na_2CrO_4rather than a protective oxides at the surface. The austenitic stainless steel with high percentage of silicon exhibit good hot corrosion resistance as it produces SiO_2 which did not chemically react with NaCl.

Yan *et al* (2013) [18] compared the hot corrosion behavior of alumina-forming austenitic (AFA) stainless steel, nickel-base super-alloy K438, K417 and 316L stainless steel in molten salt of sodium sulphate at 900^{o}C. Authors reported that the AFA alloy showed greater hot corrosion resistance in the molten sodium sulphate, as compared to super-alloy K417, K438 and 316L stainless steel. Better performance of AFA steel against hot corrosion is because of the formation of a thin and dense Al_2O_3 scale in the early stage of hot corrosion which further facilitated formation of a compact Cr_2O_3 scale on itself, and act as barrier against sulphur penetration.

Lortrakul (2014) [19] proposed bi-layer Type-II hot corrosion mechanism for single crystal Ni-based superalloy (CMSX-4) coated with 0.3 mg/cm^2 of Na_2SO_4 at 700^{o}C in an O_2-SO_2-SO_3 atmosphere for times ranging from3 min to 50 h. The hot corrosion consists of two stages: In Stage I rapid dissolution of CMSX-4 by a molten eutectic of the type Na_2SO_4-$NiSO_4$ or Na_2SO_4-$CoSO_4$ and formation of these molten eutectics discontinued after consumption of the applied Na_2SO_4. The corrosion scale developed during stage I consisted of two layers.

In the Stage II which starts after 30 min, the nickel sulfate was not observed which was observed in stage I. In stage II the scale mostly makes of oxides and sulfides of Ni, Co, Cr and Al. The external surface of the outer layer has more concentration of cobalt.

II. CONCLUSIONS

Hot corrosion is an accelerated kind of oxidation at elevated temperature in the presence of molten salts. Many engineering systems working at elevated temperature such as power plants, gas turbines and incinerators fail due to hot corrosion. Every metal or alloy oxidizes to form oxides at elevated temperature in the presence of oxygen. The oxides formed on the surface act as a protective layer. This protective layer of oxides does not allow oxygen to penetrate and prevent further oxidation. But, if contaminants such as sulfates, chlorides, or vanadates are present in the environment, they form a low melting point eutectic mixture and cover the surface with thin film of fused salt. It results in formation of porous non-protective oxide scale which allows the aggressive species to penetrate into the base metal and causes accelerated degradation of materials.

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