Study of cyclic oxidation and hot corrosion of 310 SS under the environmental impurities of Na$_2$SO$_4$+V$_2$O$_5$ at different temperatures.

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Abstract. The high temperature behaviour of 310 stainless steel has been studied at 750, 900, 950 ºC in air and 2 mg per cm$^2$ mixtures of molten salt (NA$_2$SO$_4$ 60%+V$_2$O$_5$) environment. The corrosion behaviour and morphological development were investigated by weight change kinetics, characterization techniques, depths of attack, metal losses, and elemental analysis. The results of 310SS deposited with salt mixtures show that weight change kinetics in simple oxidation reveals a steady-state parabolic rate law after initial cyclic heating, while the kinetics with salt and vanadium oxide display multi-stage loss of material. The characterization results show that there is formation of oxides on the surface of oxidized sample and then the hot corroded samples show formation of respective metal sulphides which is the reason for spallation of material so that again internal layer is exposed to environment.

1. Introduction

The 310SS material contains the following elements, in which vanadium oxide forms carbides at sensitization temperature, and other elements like Cr (chromium), Ni (Nickel), Ti (Titanium), Mn (Manganese) and Fe (Iron) forms respective metal oxides (1). The iron-base austenitic alloy, 310SS (stainless steel), is one of the most utilized high-temperature alloy components in industrial engineering plants. Low-grade fuels with high concentrations of sulfur, vanadium, and sodium are often used for firing industrial processes, such as oil- and coal-fired power generation. Vanadium present in the fuel as vanadium paraphyrene transforms into the V$_2$O$_5$ while combustion going on, then these Na$_2$SO$_4$ and V$_2$O$_5$ form low melting point inorganic compounds initiated to eutectic reaction below 600ºC (2) and (3).

During combustion, the products, alkali metal sulfates and V$_2$ O$_5$ vapors combine with other ash constituents and deposit onto cooler component surfaces, resulting in severe corrosion attack by oxidation, sulphidation, chlorination and even hot corrosion. Aircraft engines and the boilers of off-shore industrial rigs undergo hot corrosion when the sodium chloride from the ocean breeze mixes with Na$_2$ SO$_4$ from the fuel and deposits on hot-section components, leading to accelerated attack of the alloy substrate (1). The hot corrosion often increases the corrosion loss of heat-resisting alloys by over a hundred times.
Table 1. Composition of 310SS.

|   | C   | Mn | V   | Si  | Ni  | Cr  | S   | P   |
|---|-----|----|-----|-----|-----|-----|-----|-----|
|   | 0.067 | 1.50 | 0.181 | 0.41 | 19.39 | 24.16 | 0.004 | 0.038 |

In 310SS material pitting resistance is very low due to the absence of Mo, in this condition precipitation of vanadium oxide on the material causes accelerated corrosion (3). Since salt of Na$_2$SO$_4$ with the vanadium oxide the corrosion effect on the material will be very high which compared with oxidation process of 310SS.

2. Experimental Programme

Experimental setup for this experiment is tubular furnace 1200 °C which internally insulated by alumina tubes. To keep the sample for oxidation and hot corrosion alumina boats are used, these boats can withstand at high temperature as alumina melting temperature is 2000 °C.

2.1. Specimen preparation

There is 200x200 mm square plate of 310SS sheet available, which is then cut into the small pieces of 10mmx10mm as specimen. These specimens given mirror finish by polishing belt grinder, then emery papers of grade 1/0,2/0,3/0,4/0, alumina and diamond. Polishing is very essential so that surface should be exposed equally and there shouldn’t be crack, scratch, sharp corner as corrosion will firstly attack on these parts (5). The specimen dimensions and weight is measured for comparing its changes in dimension and weight for further experimental calculations. Every specimen’s weight and dimension note down for future reference.

The experiment started with keeping samples in alumina boat then that boat kept in furnace at temperature 750°C, 900°C and 950°C for 2 h per cycle and before weighing sample allowed to cool in furnace and continued these cycle up to 50h. So the temperature exposed to these samples is exact as like real condition. The cycle of exposure to high temperature is 5 hours then the weight of sample been checked on the weighing machine. Average of four reading is taken, and then weight gain calculated from the previous reading. These cycles continued for 50 hours for oxidation and hot corrosion.

2.2. Oxidation

First oxidation process carried out, where five separate samples of 310 SS of dimension 10x10mm square taken kept in furnaces having temperature 750°C (2 samples, numbered 6&7 ); 900°C (2 samples numbered 8&9) ; 950°C (1 sample, numbered 10) respectively. After every cycle specimen is taken out from furnace after reaching to room temperature which is then weighed and weight gain calculated. By visual observation these samples become brown in colour after first cycle due to oxidation and then every other cycle the dark brown colour of sample becomes uniform.

After each cycle the weight change of specimen is calculated and note down. In case of oxidation, specimen is gaining weight after each cycle, and it was slowed down after 25-40 hours of heating. The weight gain is very low as compared to initial readings and slowly it is going to be constant as observed up-to 50 hours of heating. Characterization of specimen is done, by observing microstructure of sample, SEM and EDX images taken for morphological and elemental analysis.

2.3. Hot corrosion

Same procedure of heat treatment is applied for the hot corrosion only the specimen is coated mixture of vanadium oxide and sodium sulfate having temperature 750°C (2 samples, numbered 1&2); 900°C (2 samples numbered 3 & 4) ; 950°C (1 sample, numbered 5) respectively. In hot corrosion the sample is dip into the vanadium oxide with sodium sulphide, where 2 mg per cm$^2$ of surface area with 40%
vanadium oxide and 60% sodium sulphide taken into the silica crucible. The wet mixture of vanadium oxide and sodium sulphate salt is coated with brush and allowed to get dry and coated until the coating come to 2 mg per cm² area of each sample. Let the cyclic heat treatment continued for 50 hours, after every cycle the sample is weighed, then again kept for Heat treatment as per ASTM GT54.

2.4. SEM Images and Elemental analysis
SEM is scanning electron microscopy which is used to surface morphological study of sample, by which surface observed to see uniformity of scale and its degradation. EDX is used to get elemental analysis.

3. Results and Discussion

3.1. Visual inspection
Samples show discoloration, where the samples became dark grey and completely lost metallic reflectivity. For oxidation samples, there is only colour change and boats are clean but for hot corrosion samples there is spallation of material in boat and also outside boat in furnace seen, which implicates that severe loss of material. Yellow colour of salt deposited permanent marks on surface of samples with alumina boat. Corroded samples internal layer of material is exposed to environment.

3.2. Corrosion kinetics
From Figure 1 we can see samples no. 6 to 10, every sample gains weight due to metal oxide formed on the surface which satisfies parabolic curve for oxidation. From the figure 1, it is shown that weight gain of the sample is high in initial 2-3 hours almost like linearly high reaction rate. But after some hours of heat treatment weight gain is reduced which means the oxidation rate of sample is going to be reduced. And some hours of heating the weight gain is showing almost parabolic structure. Initially 25-30 h was found to be more aggressive due to continuous supply of metal ions to the substrate however, after 25h the oxidation rate becomes constant for all the cases studied.

Also on other side for hot corrosion samples the weight gain is too high but the metal compound formed during heat treatment is get separated from material and fall into boat shown in figure 2. For sample no. 5 it is observed weight gain is higher initially upto 10 hrs later on sudden loss in weight due to spallation of metal compound outside the boat, as aggressive salt reaction and cyclic ‘heating and cooling’ makes material weaker. Except sample 5, all other samples showing parabolic behaviour for certain period but when threshold level is crossed, means the reaction is accelerated then outer layer get broken, which leads to expose the internal surface of metal. After that metal sulfidation is initiated soon leads to degradation of material. The weight gain square (mg²/cm⁴) versus time (h) plots were used to establish law for the hot corrosion. Although the data showed small deviations from the parabolic rate law, the hot corrosion process could process could still be approximated by a parabolic rate law in all the cases investigated. The parabolic rate constant Kp was calculated using Pilling and Bedworth equation (8):

\[
\left( \frac{\text{delta } W}{A} \right)^2 = K_p \cdot t + C
\]

Where delta W/A is the weight gain per unit surface area (mg/cm²), "t" is the time of exposure, and C is a constant. As seen from the weight gain plots the curves can be best fitted by linear least square method (5).

Corrosion kinetics is slow for hot corrosion compared to the oxidation, it might be possible that oxidation protective layer is stronger and still continues to grow also there is no such effect like spallation since as per the graphs Kp is higher.
3.3. Microstructure examination

Figure 3 in which sample 6a and 6b SEM images shows that there is uniformity of protective layer formed. Since also there are no gaps or deepness so that new surface is going to expose. Same 7a and 7b; 8a & 8b, 9a & 9b, 10a and 10b will give you the strong idea of material weight gain is higher but there is no chance of spallation of material. No new surface of 310SS is exposed to the environment. By the weight gain graph it might be confusion that material gain is more in oxidation but images will confirm that surface is still protected. Surface of oxidation samples uniformly covered with oxides of metal which is finely distributed and strongly bonded not allowing the new surface to get expose and the metal ions are transfused to oxygen ions via protective layer only since weight gain is higher in oxidation.

Also from figure 4 shows that salt effects on 310SS at various temperatures makes material prone to reaction mechanism develops deepness cavity observed images since it is possible weight change is more in case of hot corrosion but after every cycle layer is depleted since again inner layer is exposed which first protects and then again depleted shows weight gain is less compared to oxidation, but if these cycles has been continued above 50 hrs, then it might be possible the depleted layers get spilled out of boat and the same result will be seen as like sample 5 that weight is reduced as discussed in corrosion kinetics.

From hot corrosion 1a image shows that inner exposed layer of material idea about the attack of salt which makes material to lose its protective layer after forming sulfidation and also vanadates. The images of hot corrosion 2a, 2b, 3a, 3b, 4a, 4b sample where corals of chromium compounds and ferrous compounds formed. Sample 5a and 5b image showing powdered layer of Cr and Fe formed due to very aggressive reaction mechanism of salt deteriorating the material.
Figure 3. SEM images of oxidation samples from No. 6-10 respectively.
3.4. Elemental analysis

Elemental analysis is shown in the figure 5, hot corroded samples forming powdered compounds of chromium but due to salt attack is internal layers are exposed and Ferrous compounds formed. Here at 750°C both samples 1 and 2 will give 16% Cr which is reacted less than that present in 310SS constituent which should be present to protect material from corrosion but at high temperature salt becomes more catastrophic to attack inner Fe forming Fe compounds. It observable that as temperature increases the Cr compounds are separated from the surface of 310SS reducing the weight percentage content of Cr and internal Fe get exposed.

From Figure Oxidation sample 6, 7, 8, 9 and 10 will show that \( \text{Cr}_2\text{O}_3 \), \( \text{MnO} \) is the protective layer contents where \( \text{Cr}_2\text{O}_3 \) is the corrosion resistant compound. EDX will show that as temperature increases, the \( \text{Cr}_2\text{O}_3 \) decreasing and \( \text{MnO} \) increasing means more of the manganese transforming into metal oxide acting as one of the gap filler for protective scale. Also there are metal oxides of Nickel and Iron formed observed from EDAX make aware of thick scale of protection is present for 310SS during oxidation. The scale formed was adherent, impervious and there was no spalling of scale. Following is the reaction mechanism (5) and (9):

**Triggering Reactions:**
\[
2\text{Cr} + 3/2\text{O}_2 = \text{Cr}_2\text{O}_3 \\
\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5 + 2\text{Cr} = 2\text{NaVO}_3 + \text{SO}_3 + 2\text{Cr} = 2\text{NaVO}_3 + \text{Cr}_2\text{O}_3 + \text{S}.
\]

**Fe** + **S** = **Fe**_2**S** or **Fe**_3**S** (Iron has two valences due to isotropic nature.)

**Autocatalytic reaction:**
\[
\text{Na}_2\text{SO}_4 + \text{Fe}_2\text{S} = \text{S} + \text{Fe}_2\text{O}_3 + \text{Na}_2\text{O} \\
\text{Na}_2\text{O} + \text{V}_2\text{O}_5 = 2\text{NaVO}_3 \\
4\text{Fe}_2 + 4\text{S} = 4\text{Fe}_2\text{S} \text{ or } 4\text{Fe}_3 + 4\text{S} = 4\text{Fe}_3\text{S}
\]

**Enhanced Oxidation phase:**
\[
\text{Fe}_2 + \text{Fe}_2\text{S} = \text{Fe}_2\text{Fe}_2\text{S} \\
\text{Fe}_2\text{Fe}_2\text{S} + \text{O}_2 + 2\text{Cr}_2\text{O}_3 = 2\text{FeCr}_2\text{O}_4 + \text{Fe}_2\text{S} \text{......... (4) & (10)}
\]

The reaction equations shown into the mechanism provides the path by which vanadates and metal sulfidation become the reason to destruction of 310SS. The salt melts at 880°C and vanadium oxide accelerates the melting of salt as it acts as catalytic agent, so the sample is advanced to sulphidation.
4. Conclusions
1. As per the method of weight change there is always weight gain in oxidation which parabolic rate law proved by Wagner theory and during hot corrosion the specimens is reducing weight which is shown as linear rate law.
2. During oxidation of specimens the surface is oxidized as per seen in the SEM images. But during hot corrosion the sample reduces weight means the protective oxide scales spalled out and the inner layer is ready for reaction which again fall down due to sulphidation.
3. By SEM analysis oxidized samples are covered with metal oxide layer while the hot corroded sample shows like debris structure as outer layer which keep degrading due to sulphidation but still 310SS stubborn resistant upto 750˚C to some extent but after protective layer broken it will degrade.
4. EDX results obtained shows that in oxidation Chromium is the most observed metal oxide and acting as a protective scale, but in oxidation metal sulphides are formed.
5. Chromium is the lowest deficient energy metal since it forms maximum diffusion barrier chromium oxide layer in 310SS material where Fe₂O₃, NiO are other metal oxides also present on the surface of oxidized specimen.
6. During hot corrosion sodium sulphate is a catastrophic agent initiates to eutectic reaction called sulfidation, which is accompanied by V₂O₅, which again auto catalytic phase converted and finally enhanced oxidation phase reached and metal sulfides form like Ni₃S₂, FeS, Cr₂S, Fe₃S₄.
7. As temperature plays very great role during oxidation and hot corrosion, as heat treatment changes from type 1 to type 2, degradation of material increases.
8. At low temperature during oxidation thick scale of Cr₂O₃ is formed and as temperature increases there is possibility of old scale is cracked.
9. When there is exposure to salt and the temperature increases from 750 °C to 950 °C for 310SS, it is clearly seen Metal Oxide scale broken and every time internal surface is ready to react, deteriorate the metal. With increasing temperature degradation increases exponentially.

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