THE EFFECT OF NICKEL INCREASING AND ALUMINUM ADDITION ON SULFIDATION RESISTANCE OF Fe-Ni-Cr ALLOYS

E. Kordzadeh* and M. Bozorgmehr

Department of Material Science and Engineering, Shahid Bahonar University of Kerman
P.O. Box 76175-133, Kerman, Iran
el_kordzadeh@yahoo.com – mohsen.bozorgmehr@gmail.com

*Corresponding Author

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Abstract In this research the effects of; increasing the amount of nickel and adding aluminum to create and prolong sulfidation resistance of Fe-Ni-Cr alloys have been investigated. Sulfidation tests were carried out at 1100°C in S/O bearing atmosphere. Prior to the tests, the specimens were annealed in argon at 1250°C for 8 hrs. Weight changes were measured and corroded deposits were analyzed by scanning electron microscope, X-ray diffraction, energy dispersive spectrometry and optical microscope. The results showed that, sulfidation resistance decreases as nickel content increase. Aluminum addition has good sulfidation resistance effect for these alloys, since alumina layer is more protective than chromia.

Keywords Heat Resistant Steel, Alumina, Sulfidation, Chromia, Intermetallic Phase

1. INTRODUCTION

Fe-Ni-Cr and other austenitic heat resisting alloys are widely used at high temperatures since they form a protective oxide layer of Cr2O3 on the surface of the alloy. This film is stable up to 1000°C. At higher temperatures Cr2O3 volatilizes and transforms to CrO3, which decreases the corrosion resistance of the alloys [1-3].

It has also been shown in McGurty’s works that aluminum is a suitable substitute for chromium, it forms Al2O3 layer on the surface. Fe-Ni-Cr-Al alloys have various applications in many industries particularly; heat treatment furnaces, oil refinery furnaces, gas turbines, petrochemical furnaces, glass manufacturing, synthetic rubber and conversion of fuel fissile [4,5]. These alloys are relatively a new class of alloys containing aluminum, typically in the range of 4-5 wt % and containing high concentration of superior oxidation resistance, with much higher strength than single phase austenitic stainless steel [5].

Aluminum oxide is a nonspalling layer and is more protective than chromium oxide film. Sensitization of commercially available austenitic stainless steel is related to the formation of chromium carbide. The formation of this carbide results in the depletion of chromium at grain
boundaries, to the extent that the properties such as corrosion resistance which depends on the chromium oxide content of the protective film, is decreased [6,7].

The value and usefulness of the Fe-Ni-Cr-Al alloys relate primarily to Al content of the alloy and aluminum oxide content of protective film. Sensitization does not play a major role in high aluminum Fe-Ni-Cr-Al alloys [6,7]. Transport through α-Al2O3 scales is extremely slow, relative to chromia. These characteristics make these alloys one of the most suitable one at temperatures higher than 950°C [8,9]. However, the scales which are developed near the surface also contain less stable oxides such as NiO, FeO and spinels. The proportion of the latter is determined by their relative growth rate, compared to the rate of nucleation of more stable phases, including Cr2O3 and Al2O3 [5]. These alloys containing 20 percent or more nickel are more stable than 300 series stainless steel. The high nickel content enables the alloy to acquire super alloy properties [10].

Some researches have been conducted on the corrosion resistance of these alloys in different atmospheres. For example Loudjani has investigated the corrosion of Fe-Ni-Cr, Fe-Cr-Al and Fe-Ni-Cr-Al alloys in H2/H2O/H2S mixtures and Lions on the sulfidation and sulfidation/oxidation of Fe-Cr, Fe-Cr-Al and Fe-Ni-Cr-Al alloys at high temperature. Their finding show that aluminum is an effective factor in improving sulfidation resistance of alloys, but neither of them have worked on changing the nickel content to compare its effect on sulfidation resistance of Fe-Ni-Cr-Al alloys nor have they worked on SO2 bearing atmosphere [4,11]. In this research, the effect of increasing nickel and adding aluminum for the high temperature sulfidation resistance of high aluminum Fe-Ni-Cr-Al alloys in SO2 bearing atmosphere has been investigated.

### TABLE 1. Chemical Composition of Fe-Al-Cr-Ni Alloys (wt %).

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Al</th>
<th>Si</th>
<th>Mn</th>
<th>Mo</th>
<th>eF</th>
<th>Bal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.08</td>
<td>20.3</td>
<td>17.6</td>
<td>6.0</td>
<td>0.59</td>
<td>0.68</td>
<td>0.24</td>
<td>Bal.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>20.5</td>
<td>21.8</td>
<td>6.1</td>
<td>0.45</td>
<td>0.69</td>
<td>0.30</td>
<td>Bal.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.07</td>
<td>20.2</td>
<td>25.0</td>
<td>6.0</td>
<td>0.49</td>
<td>0.68</td>
<td>0.28</td>
<td>Bal.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.07</td>
<td>20.0</td>
<td>30.5</td>
<td>6.0</td>
<td>0.52</td>
<td>0.62</td>
<td>0.28</td>
<td>Bal.</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.08</td>
<td>20.0</td>
<td>18</td>
<td>---</td>
<td>0.5</td>
<td>0.65</td>
<td>0.38</td>
<td>Bal.</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.07</td>
<td>20.4</td>
<td>37.6</td>
<td>6.5</td>
<td>0.5</td>
<td>0.68</td>
<td>0.28</td>
<td>Bal.</td>
<td></td>
</tr>
</tbody>
</table>

Bal. = Balance
tests were done at SO₂ bearing atmosphere up to 100 hours. To characterize the structure and composition of the corrosion products, a series of analytical techniques, including X-ray diffraction (XRD) model JDX 8030, scanning electron microscope (SEM) model S-4500, energy dispersive spectrometry (EDS) and optical microscope model Olympus CKX was used.

3. RESULTS AND DISCUSSION

In Fe-Ni-Cr-Al alloys β-NiAl is stable up to 1200°C but the precipitation kinetic in this range is slower than the rate of the formation of oxide layer [12]. The relationship between weight changes and exposure time is shown in Figure 1.

All alloys exhibit first a rapid and then a slow weight gain rates using sulfidation processes. After a transient rapid rate, the growth rate of the scales follows a parabolic law, with a lower rate. In all curves, weight gains could be separated in two regions. The first region corresponds to the growth of protective layer. Sulfidation test results have shown that heat resistant steels with lower nickel content have higher resistance in sulfur bearing atmospheres. Aluminum addition increases sulfidation resistance of the alloys. During the first step, the reaction follows a linear rate law. The
linear rate law observes, if the reaction rate is controlled by gas phase transport, or phase boundary reaction [13]. By increasing time, the thickness of the scale is increased and diffusion through corrosion products becomes a rate determining factor. During this stage, parabolic rate law is predominated (Figure 1).

Although the alloys had different nickel content, but nickel and chromium equivalents for casting alloys were determined by Hull equations [4]. The volume percentage of ferritic phase can be calculated from Schoaffer diagram [4]. The nickel and chromium equivalents for different alloys and the volume percentage of ferritic phase are shown in Table 2.

In Fe based alloys, unsuitable balance between ferrite producing elements (alphagen) to austenite producing elements (gammagen) may cause considerable ferrite in the structure. The difference in the behavior between ferritic and austenitic grades of similar chromium and aluminum content can most probably be attributed to higher diffusivity of bcc structure [14].

XRD patterns of two different Fe-Ni-Cr-Al alloys are shown in Figure 2. In Fe-Cr-21Ni-Al with lower nickel content (Figure 2a), Al2O3 and Fe1-XS phases are observed in X-ray diffraction pattern. These layer forms more rapidly on the ferritic substrate. A survey of thermodynamic stabilities diagrams between sulfur and oxygen and some common metals shows that the oxides are stable under high sulfur and low oxygen pressure. The reaction between sulfur and oxygen forms SO2, and in this situation only some oxides such as Al2O3, TiO2 and SiO2 are stable [11]. The great stability of these oxides and high stoichiometry caused an effective protection in sulfur containing environments. By increasing the amount of nickel, the presence of Fe1-XS, (Ni,Fe)9S8 and NiAl becomes obvious in XRD pattern (Figure 2b).

As the quantity of iron and nickel increases on the surface, the extent of corrosion reaction increases. On the other hand, in the alloy with higher nickel content, β-NiAl participants lowered the aluminum content of substrate and consequently effected the formation of a continuous layer. Nickel also has another deleterious effect on sulfidation resistance of Fe-Ni-Cr-Al alloys. The precipitated formation of β-NiAl caused the formation of a continuous layer of pyrrhotite. Fe-Ni participates in Fe-30Ni-Cr-Al alloy after 25 hours in SO2 bearing atmosphere showed in Figure 3.

In SO2 bearing atmosphere, compact and adherent oxide is needed to provide a barrier between substrate and atmosphere and to protect the alloy for long time. In the severe sulfidation condition, scale could easily fail. Elements such as magnesium, iron and nickel diffused through the oxides and react with environment to form external sulfides such as MnS, Cr2O3, Cr2S4 and Fe1-XS. On the other hand, iron and nickel sulfides which probably were formed inside the oxide layer would cover it completely after a long time. In S/O bearing atmosphere, fractures occur in Fe-Ni-Cr alloys. XRD pattern of alloy no. 5 shows in Figure 4.

According to this pattern, Fe1-XS, FeCr2S4 and (Fe,Ni)9S8 form. Sulfur diffuses through the cracks, surface layer and pores which will form high chromium sulfides in the alloy, depletes the chromium of the underlayer (Figure 5). In this case, the chromium content becomes less than needed for reformation of new protective layer and sulfidation increases. It was noticed that alumina layer is more protective and adherent than chromia layer.

Sulfides are generally FeS, Cr2S3 or combinations of these two which is called P-type [15]. Since the growth rate of these sulfides is rapid, concentration of cationic vacancies increases at the interface of alloy/scale and forms pores in the region hence spallation occurs. The presence of pores is obvious in the surface layer. SO2 molecules are diffused through those pores and will go toward the substrate, at scale/substrate interface, SO2 molecules will decompose and react with substrate. In alloys with higher nickel content, Fe-20Cr-37Ni-6Al, the thickness of sulfide layer and cracks in the cross section are observed (Figure 6).

As the thickness of the surface layer reaches the critical values, spalling is initiated. The formation of eutectics such as NiS and FeS caused a rapid corrosion of materials. The first effect of surface sulfides is to facilitate the diffusion of sulfur through protective layer. The sulfides are non-stoichiometry and transportation of anions and cations carried out through them.
TABLE 2. Chromium to Nickel Equivalent and Volume Percent of Ferrite Phase for Different Alloys.

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr_{eq}/Ni_{eq}</td>
<td>1.493</td>
<td>1.342</td>
<td>1.248</td>
<td>1.127</td>
<td>1.222</td>
<td>1.042</td>
</tr>
<tr>
<td>% Vol. of Ferrite</td>
<td>29</td>
<td>16</td>
<td>12</td>
<td>5</td>
<td>11</td>
<td>4</td>
</tr>
</tbody>
</table>

Eq. = Equivalent

Figure 2. XRD patterns of Fe-Ni-Cr-Al alloys after 100 hrs (a) Fe-21Ni-Cr-Al (b) Fe-37Ni-Cr-Al.
This is due to high defect concentrations in sulfides structure and high diffusivities of cations in sulfides. The diffusion of sulfur compound in grain boundaries and expansion due to reactions in this region caused the formation of cracks in the scale layer. By increasing the thickness of the oxide layer, the internal stresses exceeded the stress allowance of the cover layer and after that, cracking and spalling is observed.

4. CONCLUSIONS

- By comparing alloys no. 1 with no. 6 (except no. 5 without Al) it could be seen that nickel decreases sulfidation resistance of Fe-Ni-Cr-Al alloys for three reasons:
  - The formation of NiAl decreases the aluminum needed for the formation of protective layer of alumina.
Figure 5. SEM micrograph and line scanning of alloy no. 5 after 100 hrs.

Figure 6. Cross section of Fe-37Ni-Cr-Al alloy after 75 hrs (X 500).
The formation of eutectic sulfides with low melting points facilitates the diffusion of sulfur through protective layer. These sulfides are non-stoichiometry and transportation of anions and cations are carried out through them. It causes a rapid sulfidation of the alloys.

Austenitic structure has fewer adherences to alumina layer than ferritic structure and it can be seen by comparing the adherence of protective layer of alloys no. 1 to 6 (except no. 5).

- Aluminum addition increases the sulfidation resistance of the alloys. It can be seen by comparing alloy no. 5 and no. 1. All alloys exhibit lower weight gain rates than alloy no. 5.
- Comparing alloy no. 5 with no. 1 shows that alumina layer is more protective than chromia layer. Aluminum oxide is a non spalling layer and is more protective than chromium oxide film. Alloys no. 5 showed spallation after sulfidation tests.

5. REFERENCES