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HOT CORROSION OF Co-Cr, Co-Cr-Al, AND Ni-Cr ALLOYS IN THE
TEMPERATURE RANGE OF 700 - 750°C

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1.0 Introduction

Coatings based on the Co-Cr-Al system are now widely used in marine aircraft turbines. They are known to have excellent hot corrosion resistance at normal turbine operation temperatures (900-1000°C). However, they are subject to severe degradation at lower temperatures (700-800°C) which can occur when the turbines are operating at low power or at particular locations on turbine components which normally fall into this temperature range.

Considerable uncertainty still exists regarding the mechanisms of this form of corrosion despite several careful investigations. The corrosion morphology corresponding to low temperature hot corrosion has been well characterized on components removed from marine services (1,2). The attack is primarily of a pitting type with the oxide in the pits enriched in Cr and Al in alternating layers and depleted in Co. A Co-rich oxide covers the pits. There is little or no sulfidation in the alloy and generally no depletion of 6-CoAl below the oxide pit. A thin zone at the base of the pit is found to contain S, Al, and O in a phase (or phases) which are apparently not water soluble. Small amounts of water soluble Co have also been observed on corroded coatings and the oxide pits are permeated by Na₂SO₄ which is also water soluble. Barkalow and Pettit were able to reproduce this morphology at 700°C by exposing CoCrAlY coatings with Na₂SO₄ deposits to oxygen containing SO₃ at pressures greater than 10⁻⁶ atm. The rate of degradation was found to be proportional to the SO₃ pressure and negligible in the absence of SO₃. These observations have been incorporated into the following mechanism by Pettit and co-workers (1,3).

The reaction of CoO and SO₃ forms CoSO₄ which forms a low melting point solution with Na₂SO₄. The liquid salt then penetrates the
Al$_2$O$_3$ scale at cracks. Alternating layers of Al and Cr are formed by selective removal of Al from the alloy presumably by Al-sulfite formation at the liquid/alloy interface where the $p_{O_2}$ is low and then reprecipitation as oxide where the $p_{O_2}$ is higher. The Al-depleted alloy is converted to Cr$_2$O$_3$ to form the Cr-rich region and Co which diffuses to the liquid/gas interface forming Co-oxide or sulfate. It is suggested$^{(1,3)}$ that this mode of attack is not operative at high temperatures because much higher SO$_3$ pressures are required to form sulfates and sulfites.

Smeggil$^{(2)}$, on the other hand, suggests that the corrosion morphology may be reproduced in the absence of SO$_3$ in the gas phase if the coatings are exposed to brief thermal excursion and transient reducing conditions and proposes this an an alternate mechanism. Laboratory hot corrosion experiments in which specimens were periodically cycled to 1300°C for 30 seconds in carbonaceous material produced corrosion morphologies similar to those observed in marine turbines and have produced changes in coating microstructure similar to those observed by Smeggil in marine turbine components. Smeggil does not offer a mechanism for the degradation produced by the high temperature excursions.

Luthra and Shores$^{(4)}$ have studied the low temperature hot corrosion of Co-30Cr and Co-10Al alloys between 600 and 750°C. They find that Co-30Cr undergoes a pitting type of attack in the presence of SO$_3$. The pit contains Cr$_2$O$_3$ and Na$_2$SO$_4$ with a sulfur-rich band at the alloy(scale) interface and an external scale of Co$_3$O$_4$ or CoSO$_4$, depending on the SO$_3$ pressure. The Co-10Al alloy showed uniform attack rather than pitting but its corrosion morphology was otherwise analogous to that for Co-30Cr. The mechanism proposed by Luthra and Shores includes the formation of a liquid Na$_2$SO$_4$-CoSO$_4$ phase as a
result of reaction between transient CoO and SO₃. The rapid dissolution of Co into this salt is proposed to prevent the formation of a continuous Cr₂O₃ or Al₂O₃ film.

Studies at the University of Pittsburgh⁵ have shown that the introduction of SO₃ into gas phase results in pitting-type hot corrosion of both Co-27Cr and Co-18Cr-6Al alloys giving corrosion morphologies similar to those described above. Higher SO₃ pressures were required to form pits on the Co-Cr alloy and thermal cycling resulted in pitting of both alloys at lower SO₃ pressures. The presence of NaCl in the gas also produces a pitting type of attack in Na₂SO₄-coated Co-Cr-Al which is somewhat similar to that produced by SO₃. However, a major difference was a porous microstructure produced below the pit by the formation of volatile chlorides of Al and Cr which were transported outward through the pores and converted to oxide in regions of higher pO₂.

The objective of the research described in this report was to more clearly define the effects of SO₃, alloy composition, and alloy microstructure in the early stages of the Na₂SO₄-induced hot corrosion of Co- and Ni-based alloys in the temperature range 700-750°C.

2.0 Experimental

The alloys studied were Co-27Cr, Ni-20Cr, and Co-18Cr-6Al*. The alloys were tungsten arc melted under an argon atmosphere. Specimen coupons were cut from the alloys, polished through 600 grit silicon carbide and cleaned ultrasonically. Sodium sulfate coatings were applied by spraying with aqueous solutions while the coupons were heated using a hot plate and a heat lamp. Coating weights were usually 1 mg/cm².

*All concentrations expressed in weight percent.
although some thinner coatings were also used.

The specimens were exposed in tube furnaces to oxygen at 1 atm. The SO$_3$ pressure in the gas was controlled by using O$_2$-SO$_2$ mixtures or by passing O$_2$ through a permeation tube apparatus to introduce small amounts of SO$_2$ and passing the gas over a Pt catalyst to establish the SO$_2$/SO$_3$ equilibrium.

The specimens' weight changes were determined by weighing them before and after exposure. The oxidized specimens were studied using optical and scanning electron metallography, EDAX, and X-ray diffraction. The salt was washed from selected specimens and analyzed by atomic absorption spectroscopy at NASA Lewis Research Center.

3.0 Experimental Results and Discussion

3.1 Co - Cr and Ni - Cr Alloys

Figure 1 shows a cross-section through a pit typical of those observed on binary Co-Cr alloys. This specimen was exposed with a 1 mg/cm$^2$ coating of Na$_2$SO$_4$ for 48 hours at 750°C in oxygen in which the PSO$_3$ was 5.8 x 10$^{-3}$ atm. Table 1 indicates the presence of SO$_3$ caused a 40-fold layer weight change for the alloy compared with O$_2$. The micrograph and X-ray maps indicate a thick external scale of cobalt oxide covering a pit containing Cr$_2$O$_3$ with a sulfur-rich region at the pit base. Some penetration of fingerlike corrosion product is also evident below the scale/alloy interface. Figure 2 shows more detail of these protrusions below a similar pit. The sulfur map, Figure 2d, indicates a significant concentration of sulfur in the protrusions. Point count EDAX analysis indicates the matrix between the protrusions is partially depleted of Cr. It, therefore, appears this region is depleted of Cr by the formation of Cr$_2$O$_3$ in the pit and the formation of the protrusions which are sulfides (and, perhaps, oxides) of Cr. (It must be pointed
The above results suggest a sulfidation/oxidation mechanism to be a major contributor to the pit formation in Co-Cr alloys. The corrosion process is envisaged as follows. The high $SO_3$ pressure in the gas phase results in the formation of a liquid $Na_2SO_4-CoSO_4$ solution which locally dissolves the protective external $Cr_2O_3$ scale. (The higher $SO_3$ pressure required to induce this mode of attack in $Cr_2O_3$-forming as compared with $Al_2O_3$-forming alloys is indicative of the lower solubility of $Cr_2O_3$ in acid melts.) The molten salt penetrates below the scale. The conditions of low $pO_2$ and high $pS_2$ established at this location result in the dissolution of Co which is transported outward until it precipitates as Co oxide where the $pO_2$ is higher and the formation of Cr sulfides. The combination of disruption produced by the rapid dissolution of Co and localization of Cr in sulfides prevents a continuous $Cr_2O_3$ scale from reforming.

Figure 3 shows severe corrosion at the corner of a Ni-20Cr specimen exposed under the same conditions as the Co-Cr alloy in Figures 1 and 2. The specimen has gained about ten times more weight than that exposed in the absence of $SO_3$, Table 1. In this case considerable quantities of Cr sulfide are present at the scale-alloy interface. Figure 4 shows a micrograph and X-ray images of the corrosion product on the same specimen. Nickel may transport through a liquid $Na_2SO_4-NiSO_4$ melt. (There is an eutectic between the extended solid solution of NiSO$_4$ in $Na_2SO_4$ and NiSO$_4$·$Na_2SO_4$ at about 670°C, 35% NiO/NiSO$_4$.) and precipitate as NiO or NiSO$_4$ near the gas interface. Chromium remains essentially below the initial alloy/salt interface and is oxidized in-situ. The EDAX spectrum of Figure 3d verifies that the outer regions of the pit are rich in Cr, Ni, and S. The result coupled with the micrograph,
Figure 3c, suggest this region consists of $\text{Cr}_2\text{O}_3$ and Ni-sulfide, e.g. point A on the stability diagrams for the Cr-S-O and Ni-S-O systems, Figures 5 and 6. These results suggest the sulfidation and subsequent oxidation of Cr prevents a $\text{Cr}_2\text{O}_3$ scale from forming in the attacked region of this alloy also.

3.2 Co - Cr - Al Alloys

Figure 7 shows the morphology of a pit formed in Co-18Cr-6Al exposed to $\text{O}_2$ with $p_{\text{SO}_3} = 2 \times 10^{-3}$ atm. for 48 hours at 750°C with a Na$_2$SO$_4$ coating. The pit is rich in Al and Cr with a Co-rich external layer and S-enrichment at the pit base. Water-soluble Co was found on the surface of similar alloys, particularly after longer times under thermal cycling conditions. An additional feature of this figure is preferential attack of the $\delta$-CoAl phase. Figure 8 shows this feature for an earlier stage of the pit formation. The $\delta$ is preferentially attacked and appears to provide a path for more rapid propagation of the corrosion product into the alloy than is available through the solid solution phase. It should be pointed out that the round shape of the pit in this figure may be the result of a sectioning effect through a pit propagating in three dimensions. The more rapid attack along the Al-rich, Cr-free phase may be consistent with the greater solubility of Al$_2$O$_3$ in acid melts as compared with Cr$_2$O$_3$.

The observations of the corrosion morphologies for the Co-Cr-Al alloys do not lead to a clear mechanism. The sulfite mechanism proposed by Pettit and co-workers$^{(1,3)}$ can explain the observed behavior. However, thermochemical calculations for Na-sulfite indicate this compound never appears as a stable compound at unit activity in the temperature range under consideration$^{(7)}$. Data are not available for Al-sulfite and this compound has not been found in the literature. However, the
possibility of forming Al-sulfite at less than unit activity in Na₂SO₄ is a possibility and could allow the observed corrosion behavior to be explained. More work is needed in clarifying this mechanism.

The sulfidation/oxidation mechanism proposed in the previous section for Co-Cr and Ni-Cr could also explain the behavior. However, sulfides have not been observed at the pit base in the present investigation. This mechanism may be responsible for the pitting behavior observed by Smegil (2) when specimens were exposed under transient reducing conditions in the absence of SO₂. These conditions will cause the sulfur potential in the salt to become very high and may well initiate pitting corrosion via the sulfidation/oxidation mechanism observed for binary Co-Cr alloys.

Finally, it must be remarked that similar pitting morphologies may be generated by a number of mechanisms. As noted earlier (5), the presence of NaCl vapor can produce pitting of Na₂SO₄-coated Co-Cr-Al although additional features in the form of porosity arise in this case. A sulfidation/oxidation mechanism is observed to operate in binary Co-Cr alloys and pits may be produced in Co-Cr-Al both by high SO₃ pressures and by transient reducing conditions. Also, as seen in Figure 9 a Co-Cr-Al alloy may undergo pitting-type corrosion in the absence of a salt deposit (8). This specimen is a Co-18Cr-6Al-1Hf alloy exposed at 1000°C for 94 hours to a simulated coal gas in which p₀₂ \( \approx 10^{-15} \) atm. and p₅₂ \( \approx 2 \times 10^{-6} \) atm. (p₅₀₃ \( \approx 10^{-15} \) atm.). The major factor determining whether or not pits form is the ability of the environment to continually prevent the formation of a protective scale at localized sites. However, the detailed features of the pits will generally be different for the different mechanism (e.g. the thick Co-oxide outer scale did not occur in Figure 9) and must be carefully evaluated before a mechanism can be prepared with confidence.
SUMMARY

The effect of SO$_3$ pressure in the gas phase on the Na$_2$SO$_4$-induced hot corrosion of Co-Cr, Ni-Cr, and Co-Cr-Al alloys has been studied in the temperature range 700 - 750°C. The degradation of the Co-Cr and Ni-Cr alloys was found to be associated with the formation of liquid mixed sulfates (CoSO$_4$-Na$_2$SO$_4$ or NiSO$_4$-Na$_2$SO$_4$) which provided a selective dissolution of the Co or Ni and a subsequent sulfidation/oxidation mode of attack which prevented the maintenance of a protective Cr$_2$O$_3$ film. A clear mechanism was not developed for the degradation of Co-Cr-Al alloys. The sulfite model proposed by Pettit and coworkers or a modification of the above sulfidation/oxidation mechanism are both capable of explaining the experimental results. Additional work is needed in this area. Finally it was illustrated that a pitting - corrosion morphology can be induced by a number of different mechanisms.

REFERENCES


8. C. M. Packer, Lockheed Palo Alto Research Laboratory, unpublished research.

ACKNOWLEDGEMENT

The authors are grateful to Prof. F. S. Pettit for many useful discussions during the course of this study.
TABLE 2: Weight Changes (mg/cm\(^2\)) After 48 Hrs. at 750°C

<table>
<thead>
<tr>
<th>Gas Composition</th>
<th>(O_2)</th>
<th>(O_2 + 1000 \text{ ppm } SO_2)</th>
<th>(O_2 + 1% SO_2)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>(P_{SO_3} = 6 \times 10^{-4} \text{ atm})</td>
<td>(P_{SO_3} = 6 \times 10^{-3} \text{ atm})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 mg/cm(^2) Na(_2)SO(_4)</td>
<td>1 mg/cm(^2) Na(_2)SO(_4)</td>
<td>1 mg/cm(^2) Na(_2)SO(_4)</td>
</tr>
<tr>
<td>Alloy</td>
<td>No Salt</td>
<td>1 mg/cm(^2)</td>
<td>No Salt</td>
</tr>
<tr>
<td>Co-20Cr</td>
<td>1.5</td>
<td>0.4</td>
<td>0.43</td>
</tr>
<tr>
<td>Co-27Cr</td>
<td>0.09</td>
<td>0.05</td>
<td>0</td>
</tr>
<tr>
<td>Co-18Cr-6Al</td>
<td>0.05</td>
<td>-0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Co-18Cr-6Al-11f</td>
<td>0.1</td>
<td>0</td>
<td>0.13</td>
</tr>
<tr>
<td>Ni-20Cr</td>
<td>0.14</td>
<td>0.14</td>
<td>0.24</td>
</tr>
</tbody>
</table>

(S): Scale spalled off during cooling to room temperature
Figure 1. Corrosion morphology for Na$_2$SO$_4$-coated Co-27Cr exposed to O$_2$ + SO$_3$ ($p_{SO_3} = 5.8 \times 10^{-3}$ atm) for 48 hrs. at 750°C.

Figure 2. Scanning Electron Micrographs of the specimen in Fig. 1 showing more detail of the corrosion front morphology; a, b, c, and S distribution d.
Figure 3. Corrosion morphology for Na$_2$SO$_4$-coated Ni-20Cr exposed to $\text{O}_2 + \text{SO}_3$ ($\text{pSO}_3 = 5.8 \times 10^{-3}$ atm) for 48 hours at 750°C. a, b, c. SEM micrographs. d, e, f. EIM spectra from the locations indicated in c.
Figure 3. (Cont'd.)
Figure 5. Stability diagram for the Ni-S-O system at 1000°C.

- NIS\(_2\)(s)
- NIS\(_1\times\)\(\frac{1}{2}\)(s)
- Ni\(_3\)S\(_2\)\(\times\)10
- NiS\(_2\)(s)
- NiO(s)
- N\(_2\)(g)

Log \(P_{O_2}\) [atm] vs. \(P_{S_2}\) [atm]
Figure 6. Stability diagram for the Cr-S-O system at 1000°K.
Figure 7. Corrosion morphology for Na₂SO₄-coated Co-18Cr-6Al exposed to O₂ + SO₃ (p_SO₃ = 2 × 10⁻³ atm) for 48 hours at 750°C.

a, b. Scanning electron micrographs.
c, d, e, and f. Co-, Cr-, Al-, and S X-ray maps of a.
Figure 7. (Cont'd.)
Figure 8. Corrosion morphology for Na$_2$SO$_4$-coated Co-18Cr-6Al exposed to O$_2$ + SO$_3$ ($p_{SO_3} = 2 \times 10^{-3}$ atm) for 4 hours at 750°C.
  a, b. Scanning electron micrographs.
  c, d, e, and f. Co, Cr, S, and Al X-ray maps of b.
Figure 4. Scanning electron micrograph of specimen in Fig. 3(a) and Ni (b), Cr (c), and S (d), X-ray maps.
Figure 9. Pitting of Co-18Cr-6Al-1Hf produced in the absence of Na₂SO₄ by a high p₃₂, low p₂O gas.