The Effect of Sulfur and Zirconium Co-doping on the Oxidation of NiCrAl

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ABSTRACT

The adhesion behavior of Al₂O₃ scales formed on NiCrAl+Zr alloys was examined as a function of both sulfur and zirconium doping levels. In general, very high levels of zirconium were required to counteract the detrimental effects of sulfur. A sulfur-zirconium adherence map was constructed, as determined from the oxidation and spallation behavior in 1100°C cyclic tests. For low sulfur alloys (< 500 ppma), the amount of zirconium required for adherence at any given sulfur level can be described by Zr > 600 S⁰.² (in ppma). These results underscore the importance of sulfur to adhesion mechanisms and suggest that sulfur gettering is a first order effect of reactive element additions to MCrAl alloys.

INTRODUCTION

The viewpoint that reactive element additions produce scale adhesion through a chemical bonding mechanism is based on two fundamental possibilities. One is that interfacial segregation of these elements serves to strengthen the oxide-metal bond. The other is that the dopants are highly sulfur-active and getter sulfur impurities in the bulk, thus preventing surface segregation of sulfur and "poisoning" of the interfacial bond. To determine which mechanism controls adhesion, it is necessary to conduct experiments where sulfur or dopant segregation is controlled independently of one another. For example, achieving adhesion by removing sulfur from an undoped alloy would show that sulfur control is a sufficient condition for adhesion. Preventing adhesion by sulfur additions to a doped alloy would show that sulfur control is a necessary condition for adhesion. Similar statements and critical experiments are difficult to conceive for dopant additions or deletions because they would simultaneously affect sulfur segregation. Furthermore, the effects of varying dopant levels are subject to the
complication that prior theories (growth stress, scale plasticity, vacancy sink, or pegging) cannot be immediately ruled out.

Some success in achieving adhesion by removing sulfur has already been reported. High purity starting materials were used to produce a NiCrAl casting with a sulfur impurity level of 1-2 ppmw compared to 20-30 ppmw for commercially pure alloys (1). This high purity alloy had a weight change of -0.1 mg/cm² in an 1180°C, 90 hr cyclic test compared to -26 mg/cm² for the commercially pure NiCrAl and +0.4 mg/cm² for NiCrAlY. Similarly, the nonadherent behavior of a 9.8 ppmw sulfur NiCrAl was changed to adherent by approximately 13 purging cycles by which sulfur was continuously reduced to below 3 ppmw (2,3). Subsequent 1100°C, 25 hr cyclic tests for specimens purged to various sulfur levels indicated a weight change of +0.1 mg/cm² for "0.0" sulfur (extrapolated), compared to -3.5 mg/cm² for 9.8 ppmw sulfur and +0.5 mg/cm² for NiCrAlY NiCrAlY. It can be argued that the additional effect of bond strengthening due to the dopants may be greater than that caused by sulfur removal. However a crude evaluation of the data from these two studies indicates that sulfur elimination can account for 98% and 90%, respectively, of the reduction in weight loss caused by Y-doping. Thus it appears that within the limitations of these experiments, sulfur removal is a sufficient condition for adhesion.

The purpose of the present study is to determine whether sulfur control is necessary for adhesion, i.e., do dopants always produce adhesion irrespective of the sulfur content. Thus various levels of elemental sulfur were added to a NiCrAl+0.2%Zr alloy known to have good scale adhesion properties and examined in cyclic oxidation. A secondary goal was to determine what zirconium levels are required for adhesion at various sulfur levels, i.e., an adhesion map was constructed for various S||Zr contents.

**EXPERIMENTAL PROCEDURE**

Button melts of Ni-15Cr-13Al were tungsten electrode arc melted with various additions of sulfur (0-2000 ppm) and zirconium (0-10,000 ppm). The buttons were homogenized in air at 1250°C for 24 hr. Coupons 0.1 x 1 x 1 cm were finished to 600 grit emery and cyclicly oxidized in air at 1100°C for 200 1-hr cycles. X-ray diffraction of the scale phases and SEM/EDS of the scale microstructures were performed at 10 and 200 hr.
glow discharge mass spectroscopy were used to measure sulfur contents. X-ray fluorescence was used to measure both sulfur and zirconium contents. Chemical analysis remains a problem in that large variations (2x) exist within one alloy grouping (fixed S or Zr). The average values of any one group did vary systematically with (and approached) the intended addition level. The results are therefore discussed in terms of the intended doping level for the sake of simplicity.

RESULTS AND DISCUSSION

Gravimetric curves showing the effect of sulfur on NiCrAl+1000 ppma Zr and the effect of zirconium on NiCrAl+1000 ppma S are shown in figures 1a and 1b. Clearly 100 ppma sulfur was sufficient to cause considerable weight loss due to spalling. 500 ppma S caused the greatest weight loss, but was not as severe as the undoped NiCrAl. Adding zirconium produced successive benefits in the cyclic behavior of sulfur-doped NiCrAl, figure 1b. However 3000 ppma Zr was insufficient to counteract the effects of 1000 ppma S. Many of the curves in figure 1 show minima where spalling to bare metal has produced sufficient aluminum depletion to change the scale from Al-rich to Ni,Cr-rich phases. At these minima, >40 hrs., the metallic appearance of the coupons changed to a dark grey-green. Subsequent increases in weight were thus caused by these faster growing oxides which did not spall to bare metal.

The relative effects of various zirconium and sulfur levels can best be compared in the region before this transition occurs, i.e., where the weight change is primarily an indication of spalling degree. This is done by plotting weight change as a function of S and Zr content in 3-D at specific times less than 60 hr, figure 2. Again the basic conclusions are that low sulfur can produce spalling for NiCrAl+Zr, while high zirconium is insufficient to restore adhesion for NiCrAl+S. An adhesion map could not be constructed because only one alloy exhibited fully adherent behavior. Therefore more alloys were obtained at low S (<100 ppma) and at very high Zr (3000 and 10,000 ppma).

The correlation of scale phases with weight change is shown in figures 3a and 3b for NiCrAl+1000 ppma Zr and NiCrAl+100 ppma S. XRD was performed at the end of the test (200 hr). However the weights are shown for the well-behaved portion of the gravimetric curve (60 hr) since
they are more significant than those at 200 hr. The trend with increasing sulfur content is:

\[ \text{Al}_2\text{O}_3 \rightarrow \text{NiAl}_2\text{O}_4 \rightarrow \text{Cr}_2\text{O}_3 \rightarrow \text{NiCr}_2\text{O}_4 \rightarrow \text{NiO}. \]

Also note that adherence was significantly affected well below 100 ppmma S. In figure 3b the reverse trend with increasing zirconium is loosely categorized as:

\[ \text{NiO} + \text{NiCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3 \rightarrow \text{NiAl}_2\text{O}_4 + \text{Al}_2\text{O}_3. \]

Here adherence was conferred between 1000-3000 ppmma Zr for 100 ppmma S alloys, coincident with alumina being maintained as the major phase.

Visual differentiation of all the alloys was most prominent at very early times, before severe spallation and massive, fast growing scales developed. Therefore to help characterize the means by which sulfur additions affected weight changes, SEM/EDS and XRD were performed on a separate set of alloys oxidized for only 10 cycles. A summary matrix is shown in figure 4. Here no NiO or NiCr2O4 has formed yet, but it is clear that the more adherent alloys (high Zr, low S) are more exclusively Al2O3 + NiAl2O4.

The microstructure of selected alloys is shown in figure 5. The use of atomic-number-sensitive backscatter electron imaging was extremely useful in discerning regions of spalling to bare metal as well as in identifying scales high in Ni or Cr. Basically the 0-S||1000-Zr adherent alloy showed minimal areas of spalling to bare metal, while the other alloys showed spalled areas increasing with sulfur content and decreasing with zirconium content. For these other alloys, the scale structure was basically one of an aluminum-rich, dark base oxide with bright overgrowths or nodules of Ni,Cr-rich oxides. Examples of this multilevel structure and crystallographic nodules are shown in figures 6 and 7 for 1000-S||1000-Zr and 1000-S||0-Zr alloys, respectively.

Normalized EDS Ni,Cr,Al peak intensities for these features are shown in figure 4. Note that the alloys without zirconium have dark-appearing base scales with an Al level of about 50 compared to 70-75 for zirconium containing alloys. Thus enough spalling has occurred at very early times to effect a transition to Al-poor scales. Also note that the bright overgrowth oxides are rich in Cr and Ni and not apparent for the adherent 0-S||1000-Zr alloy.

In order to construct an adherence map, weight changes in the well-behaved initial portion of the gravimetric curves (40 hr) were plotted as function of sulfur and zirconium contents for all 28 alloys, figures 8a and 8b.
This allowed a rather precise interpolation of composition for a fixed value of weight change chosen to be the criterion of adherent behavior, i.e., 0.0 mg/cm². Such a value is not a strict definition of total adherence, since obviously some spalling occurred to offset the normal weight gains. However since $k_p$ increases strongly with Zr content (4), a more meaningful criterion is not readily available.

Credibility for the technique is strengthened by noting that all the alloys showing adherent scales visually (solid points) were also those with positive 40 hr weight changes. Interpolated critical S or Zr values are indicated by the arrows. These values are shown in figure 9 (diamonds) along with all the alloys tested (circles). The adhesion boundary at the lower sulfur contents can be approximated by $Zr_C = 600 S_0^{0.2}$ (in ppma). Thus it is predicted that 600 ppma of zirconium is required to produce adhesion for an alloy having 1 ppma sulfur. (This prediction is high in light of the adherent scales produced at 2-3 ppma sulfur in undoped NiCrAl alloys (1-3)). The critical $Zr/S$ ratio varied from a low of 6-to-1 at 500 ppma S to 100-to-1 at 10 ppma S, which is well in excess of the amount dictated by ZrS or ZrS$_2$ stoichiometry.

This adherence envelope is believed to be a reflection of sulfur segregation behavior in S|Zr codoped alloys. It is hypothesized that a critical sulfur level (or activity) can be tolerated at the oxide-metal interface and that the compositions defined by the adherence envelope produce this level. Segregation theory predicts that an increase in bulk sulfur content does indeed result in a corresponding increase in the surface content of sulfur on nickel: $X_{surf}/X_{sat.} = X_{bulk} \cdot \exp(135 \text{ kJ/RT})$, (5). Here the basic driving force is the low solubility and low surface energy of sulfur with respect to nickel. Zirconium additions will offset this driving force by the free energy of formation of stable sulfides (6,7). A more exacting theoretical interpretation of the curve in figure 9 is not possible without knowledge of $Zr$ and $S$ solubility levels and activities in equilibrium with various sulfides and Zr-Ni intermetallics over the wide composition range studied.

The overall observation that a stoichiometric amount of zirconium is insufficient to produce adhesion at a given sulfur level is consistent with the original study by Smeggil, et al (8). They found that 0.15 and 0.45 wt.% $Y_2S_3$ was insufficient to produce adhesion for NiCrAl unless further additions of 0.1 and 0.3 wt.% $Y$ were made. However, it is difficult to explain the similar behavior of
NiCrAl+0.3Y and NiCrAl+0.3Y+0.03S (500 ppma S) reported by Luthra and Briant, especially since sulfur (and yttrium) were indeed found to segregate (9). NiCrAl+0.3Y+0.2S (3000 ppma S) did show extensive spalling, which is consistent with the present study. A possible explanation of the above discrepancy is that yttrium, at a given bulk and interface level, is more effective than zirconium in preventing non-adherent behavior.

**SUMMARY AND CONCLUSIONS**

The most important conclusion from this study is that low-level sulfur doping (<100 ppma) quite seriously compromised the otherwise adherent behavior of NiCrAl+1000 ppma Zr. Therefore sulfur doping is sufficient to cause spalling, presumably by interfacial segregation, even when the zirconium level exceeds the amount required to getter all the sulfur in the form of sulfides. Increases in sulfur content caused a progression toward more spalling to bare metal, faster aluminum depletion, and formation of less protective Ni, Cr-oxides. Higher sulfur levels required more zirconium to restore adherent behavior.

An S||Zr adherence map, constructed from the gravimetric data and the added dopant levels, produced an adherence envelope described by \( Zr_c = 600 S_c^{0.2} \) in ppma. The segregation thermodynamics of these alloys is not sufficiently known to account for this envelope. Yet it is hypothesized that this curve defines a locus of constant interfacial sulfur content (or activity) as can be tolerated without massive scale spallation. In conjunction with the prior works on sulfur removal, it can now be claimed that sulfur control is both a necessary and sufficient condition for adhesion. We therefore maintain, in agreement with one of the original studies of the sulfur effect (8), that the interaction between reactive-elements and sulfur must be a first order effect of these dopants in \( \text{Al}_2\text{O}_3-\text{NiCrAl} \) adherence mechanisms.

**REFERENCES**


Figure 1. - Cyclic oxidation curves for Si/Zr co-doped NiCrAl.
(1100°C, 1-HR CYCLES).
FIGURE 3. - CORRELATION OF SCALE PHASES AFTER 200 CYCLES WITH WEIGHT CHANGE AFTER 60 CYCLES.
<table>
<thead>
<tr>
<th>3000 PPM Zr</th>
<th>1000/1000 = S/Zr</th>
<th>1000/3000 = S/Zr</th>
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<tbody>
<tr>
<td>0/1000 = S/Zr</td>
<td>500/1000 = S/Zr</td>
<td>1000/1000 = S/Zr</td>
</tr>
<tr>
<td>0 ppm Zr</td>
<td>1000 ppm Zr</td>
<td>3000 ppm Zr</td>
</tr>
<tr>
<td>0/0 = S/Zr</td>
<td>500 ppm S</td>
<td>1000 ppm S</td>
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- **XRD PHASES**
  - EDS Ni/Cr/Al
  - DARK SCALE
  - CRYSTALS

- **Y/Y'** = 55/37/8
- **β** = 66/16/18
- **Ni/Cr/Al**
- **∆M/A SIGN**

**FIGURE 4. - SUMMARY OF SCALE PHASES AND NORMALIZED Ni, Cr, Al SEM/EDS RATIOS AT INITIAL DEGRADATION (10 CYCLES).**
Figure 5. - Backscatter Electron Images showing increases in spalled areas (bright) with increases in S and decreases in Zr for the 10 hr samples.
**Figure 6.** Region of extensive overgrowths of Cr-rich crystals for 10-hr oxidation of 1000-500-20 NiCrAl.

**Figure 7.** Secondary electron/backscatter electron images showing multilevel structure: spalling to metal, dark Al-rich base oxide, and bright Ni, Cr-rich crystals for 10-hr oxidation of 1000-500-20 NiCrAl.
FIGURE 8. - FAMILIES OF WEIGHT LOSS VERSUS COMPOSITION CURVES (AT 40-HR) FOR ALL SI/Zr CO-DOPED ALLOYS, (BASELINE INTERSECTIONS DEFINE ADHERENCE CRITERION).
FIGURE 9. - SIZR ADHERENCE MAP CONSTRUCTED FROM 1100 °C/40 HR DATA IN
FIGURE 8. (DIAMONDS ARE INTERPOLATED CRITICAL VALUES, SOLID CIRCLES
FOR ADHERENT ALLOYS, OPEN CIRCLES FOR NONADHERENT).
The adhesion behavior of A12O3 scales formed on NiCrAl+Zr alloys was examined as a function of both sulfur and zirconium doping levels. In general, very high levels of zirconium were required to counteract the detrimental effects of sulfur. A sulfur-zirconium adherence map was constructed, as determined from the oxidation and spalling behavior in 1100 °C cyclic tests. For low sulfur alloys (<500 ppma), the amount of zirconium required for adherence at any given sulfur level can be described by \( Zr > 600 S0.2 \) (in ppma). These results underscore the importance of sulfur to adhesion mechanisms and suggest that sulfur gettering is a first order effect of reactive element additions to MCrAl alloys.