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

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ABSTRACT

The adhesion behavior of Al_2O_3 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 $Zr > 600\ S^{0.2}$ (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 possibilites. 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/cm^2 in an 1180°C, 90 hr cyclic test compared to -25 mg/cm^2 for the commercially pure NiCrAl and +0.4 mg/cm^2 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/cm^2 for "0.0" sulfur (extrapolated), compared to -3.5 mg/cm^2 for 9.8 ppmw sulfur and +0.5 mg/cm^2 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 ppma) and zirconium (0-10,000 ppma). 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. Oxygen combustion and

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 systemmatically 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

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they are more significant than those at 200 hr. The trend
with increasing sulfur content is:

$$Al_2O_3 \rightarrow NiAl_2O_4 \rightarrow Cr_2O_3 \rightarrow NiCr_2O_4 \rightarrow NiO.$$
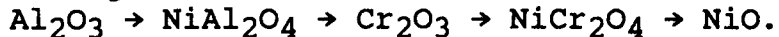
Also note that adherence was significantly affected well
below 100 ppma S. In figure 3b the reverse trend with
increasing zirconium is loosely categorized as:

$$NiO + NiCr_2O_4 + Cr_2O_3 \rightarrow NiAl_2O_4 + Al_2O_3.$$
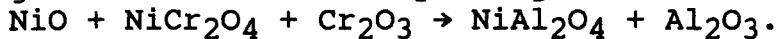
Here adherence was conferred between 1000-3000 ppma Zr for
100 ppma S alloys, coincident with alumina being maintained
as the major phase.

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
$NiCr_2O_4$ has formed yet, but it is clear that the more
adherent alloys (high Zr, low S) are more exclusively Al_2O_3
+ $NiAl_2O_4$.

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 crystallograghic 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.

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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/cm^2. 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 $Zr_c = 600 \ S_c^{0.2}$ (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: $X_{surf.}/X_{sat.} = X_{bulk} \cdot \exp(135 \ kJ/RT)$, (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 Al_2O_3-NiCrAl adherence mechanisms.

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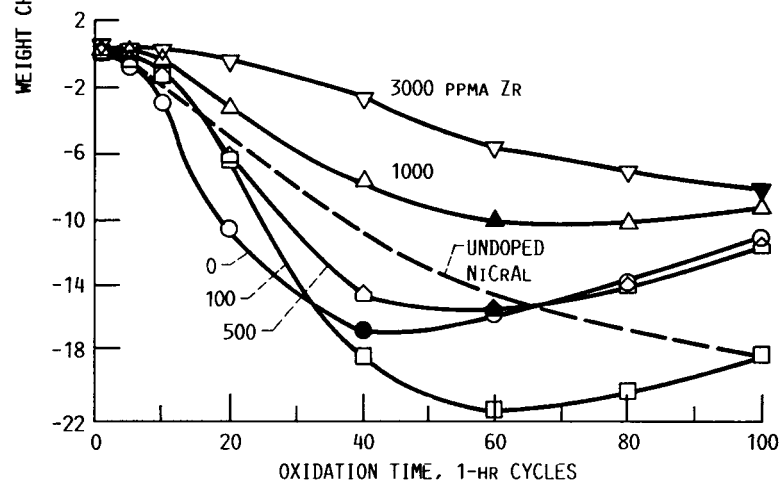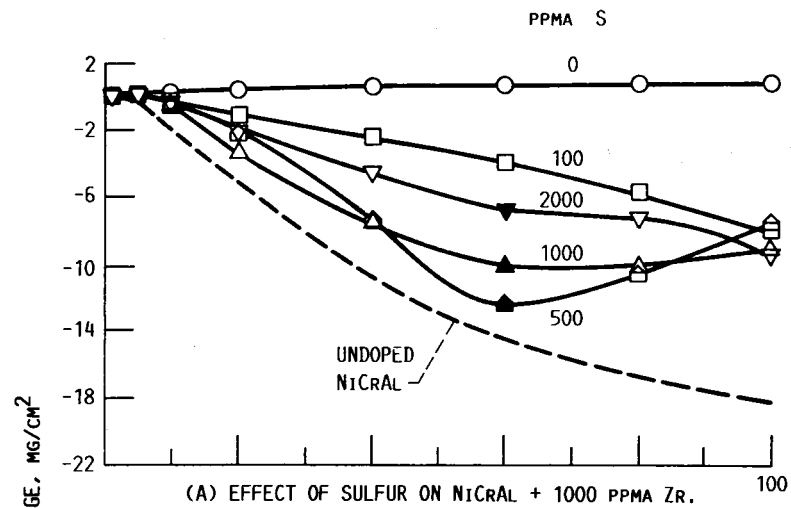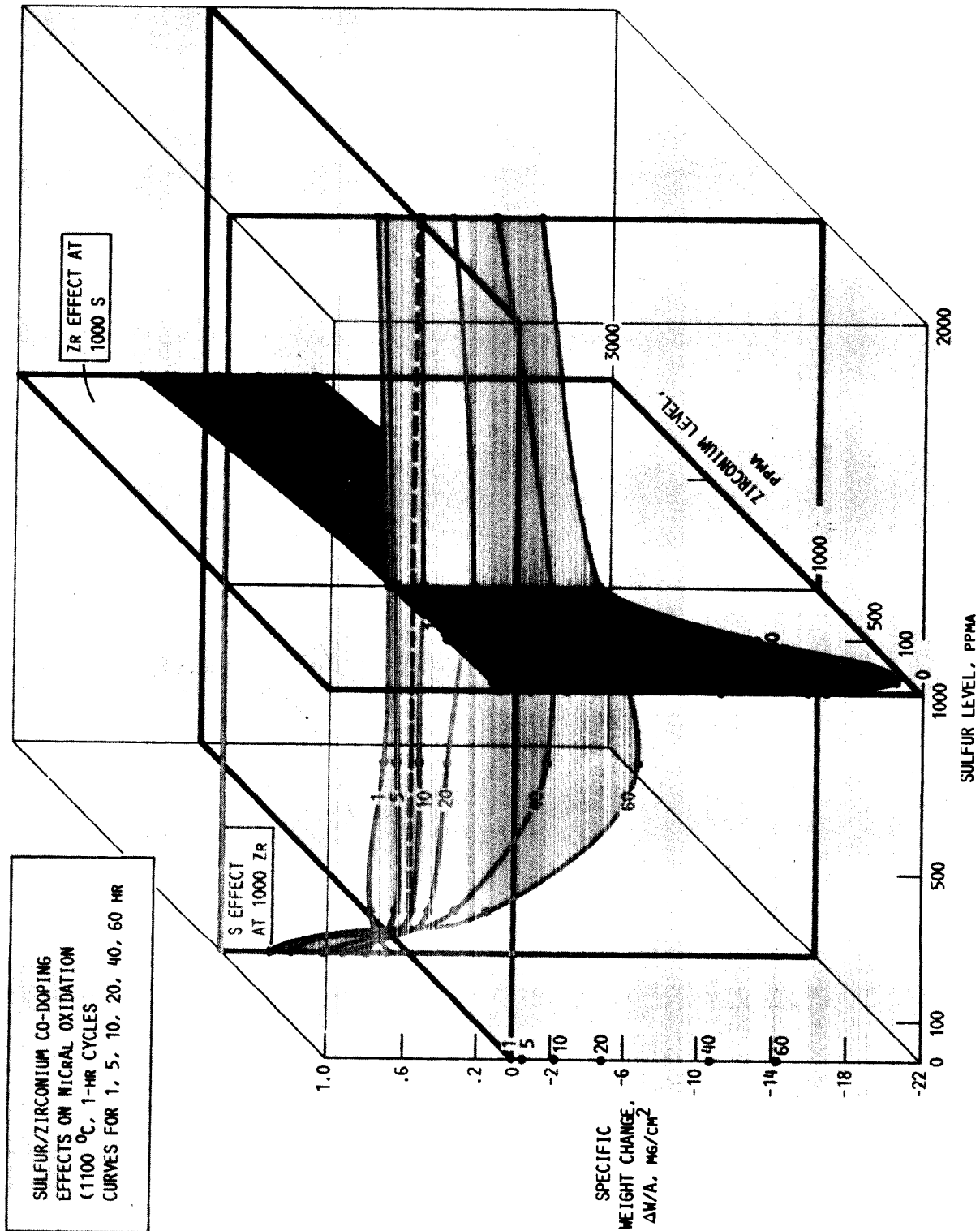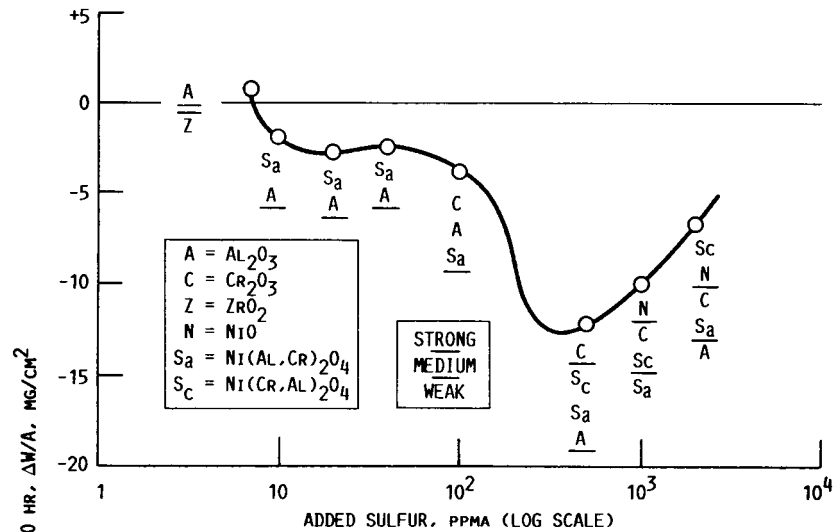
FIGURE 1. - CYCLIC OXIDATION CURVES FOR S||Zr CO-DOPED NiCrAl.
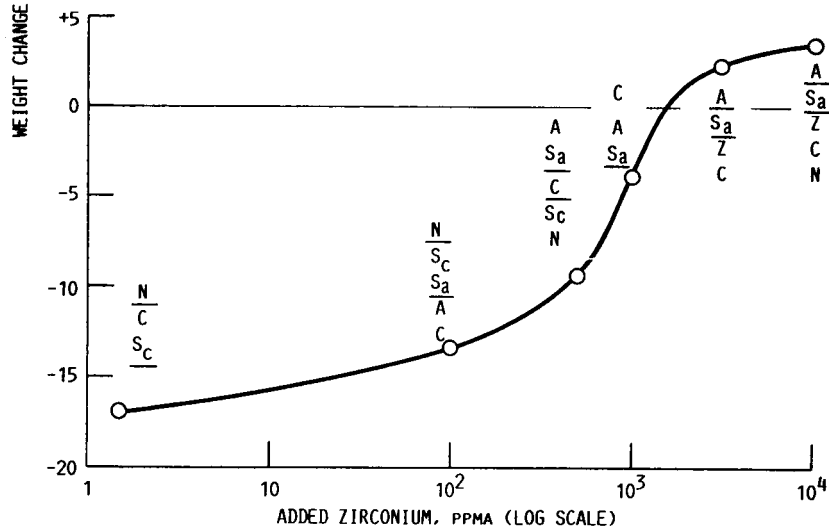(1100 C, 1-HR CYCLES).

FIGURE 2. - THREE-DIMENSIONAL REPRESENTATION OF S/Zr COMPOSITIONAL EFFECTS ON CYCLIC OXIDATION WEIGHT CHANGE.

CD-87-27634

SULFUR/ZIRCONIUM CO-DOPING
EFFECTS ON NiCrAl OXIDATION
(1100 °C, 1-HR CYCLES
CURVES FOR 1, 5, 10, 20, 40, 60 HR

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WEIGHT CHANGE AT 60 HR. $\Delta W/A$, MG/CM^2

$+5$

0

$\dfrac{A}{Z}$

S_a
$\underline{A}$

S_a
$\underline{A}$

S_a
$\underline{A}$

-5

C
A
$\underline{S_a}$

S_c
$\dfrac{N}{C}$
$\dfrac{S_a}{A}$

A = AL$_2$O$_3$
C = CR$_2$O$_3$
Z = ZRO$_2$
N = NIO
S$_a$ = NI(AL,CR)$_2$O$_4$
S$_c$ = NI(CR,AL)$_2$O$_4$

STRONG
MEDIUM
WEAK

-10

$\dfrac{N}{C}$
$\dfrac{S_c}{S_a}$

-15

$\dfrac{C}{S_c}$
S_a
$\underline{A}$

-20

1   10 10^2 10^3 10^4

ADDED SULFUR, PPMA (LOG SCALE)

(A) EFFECT OF SULFUR ON NICRAL + 1000 PPMA ZR.

$+5$

0

C
A
$\underline{S_a}$

$\dfrac{A}{S_a}$
$\dfrac{}{Z}$
C

$\dfrac{A}{S_a}$
$\dfrac{}{Z}$
C
N

A
$\dfrac{S_a}{C}$
$\dfrac{}{S_c}$
N

-5

$\dfrac{N}{S_c}$
$\dfrac{S_a}{A}$

$\dfrac{N}{C}$
$\dfrac{}{S_c}$

-10

C

-15

-20

1   10 10^2 10^3 10^4

ADDED ZIRCONIUM, PPMA (LOG SCALE)

(B) EFFECT OF ZIRCONIUM ON NICRAL + 100 PPMA S.

FIGURE 3. - CORRELATION OF SCALE PHASES AFTER 200 CYCLES WITH WEIGHT
CHANGE AFTER 60 CYCLES.

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|		1000/3000 = S/Zr
3000 PPM Zr		⊕ Al_2O_3 $Ni(Al,Cr)_2O_4$ 13/15/71 45/37/14
	0/1000 = S/Zr	500/1000 = S/Zr	1000/1000 = S/Zr
1000 PPM Zr	⊕ Al_2O_3 14/10/76 ----	◎ $Ni(Al,Cr)_2O_4$ Al_2O_3 8/13/76 23/60/12	⊖ $Ni(Al,Cr)_2O_4$ Al_2O_3 Cr_2O_3 9/22/69 25/69/5
	0/0 = S/Zr		1000/0 = S/Zr
0 PPM Zr	⊖ $Ni(Al,Cr)_2O_4$ Al_2O_3 (Cr_2O_3) 16/35/49 31/68/1		⊖ $Ni(Al,Cr)_2O_4$ (Cr_2O_3) 14/37/48 23/76/1

0 PPM S   500 PPM S   1000 PPM S

XRD PHASES
EDS Ni/Cr/Al
● DARK SCALE
● CRYSTALS

γ/γ' = 55/37/8
β = 66/16/18
Ni/Cr/Al

⊕ ΔW/A SIGN

FIGURE 4. - SUMMARY OF SCALE PHASES AND NORMALIZED Ni, Cr, Al SEM/EDS RATIOS AT INITIAL DE-GRADATION (10 CYCLES).

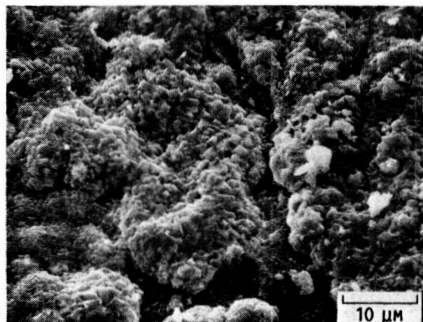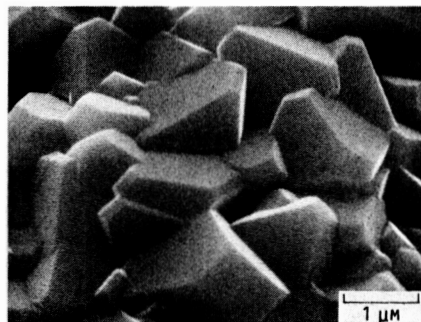(1100 °C, 10 1-HR CYCLES)
500X BACKSCATTER ELECTRON IMAGE
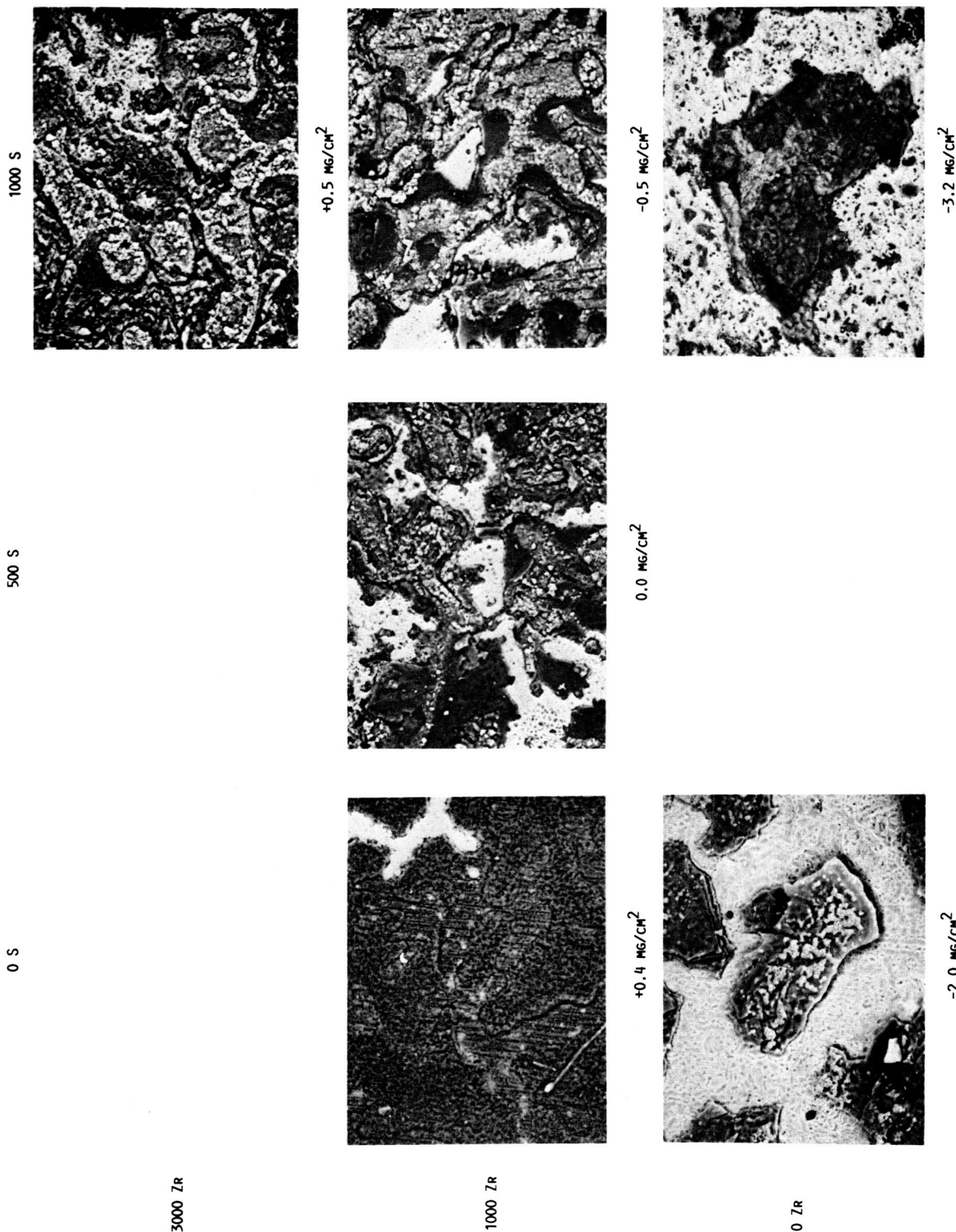
CD-87-27635

FIGURE 5. – BACKSCATTER ELECTON IMAGES SHOWING INCREASES IN SPALLED AREAS (BRIGHT) WITH INCREASES IN S AND DECREASES IN ZR FOR THE 10 HR SAMPLES.
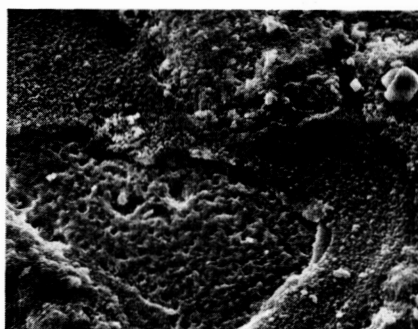
12

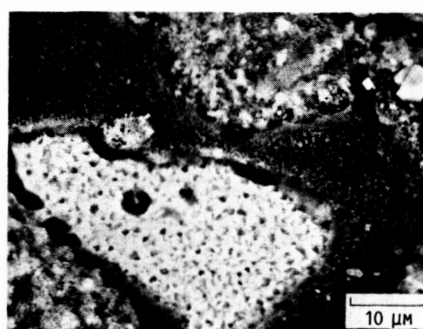2000X   20 000X

FIGURE 6. - REGION OF EXTENSIVE OVERGROWTHS OF CR-RICH CRYSTALS FOR 10-HR OXIDATION OF
1000-S||0-ZR NICRAL.

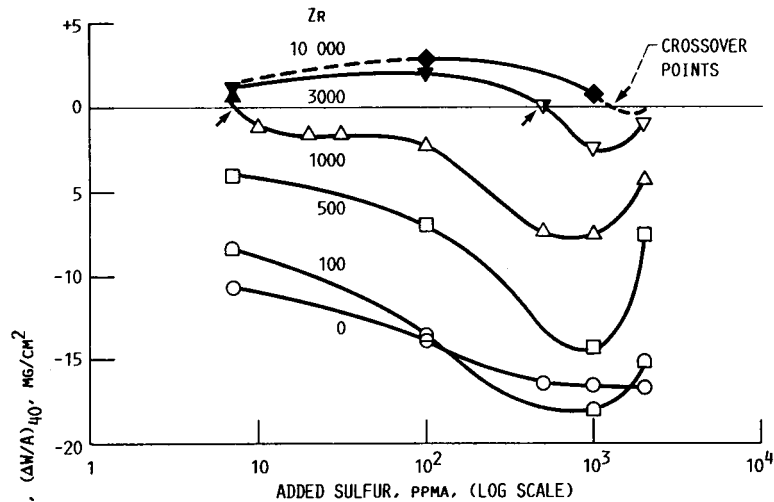2000X   SECONDARY ELECTRON   2000X   BACKSCATTER ELECTRON
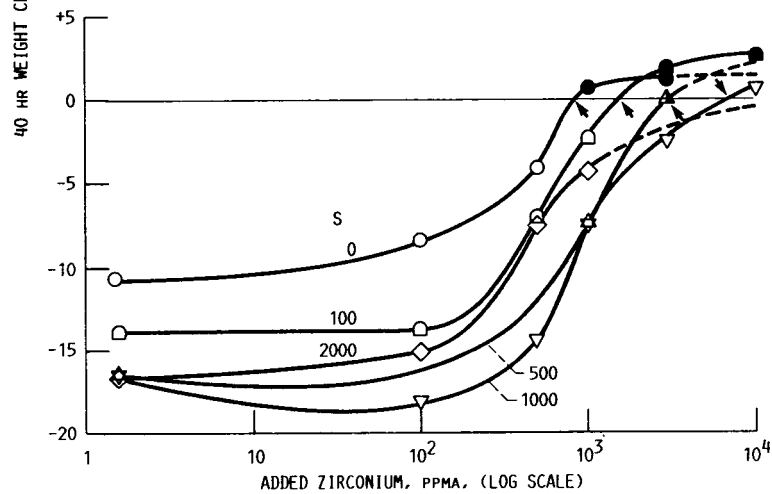   IMAGE   IMAGE

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-S||1000-ZR NICRAL.

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(A) EFFECT OF SULFUR CONTENT AT 5 LEVELS OF ZIRCONIUM.

(B) EFFECT OF ZIRCONIUM CONTENT AT 5 LEVELS OF SULFUR.

FIGURE 8. - FAMILIES OF WEIGHT LOSS VERSUS COMPOSITION CURVES (AT 40-HR) FOR ALL S||Zr CO-DOPED ALLOYS, (BASELINE INTERSECTIONS DEFINE ADHERENCE CRITERION).

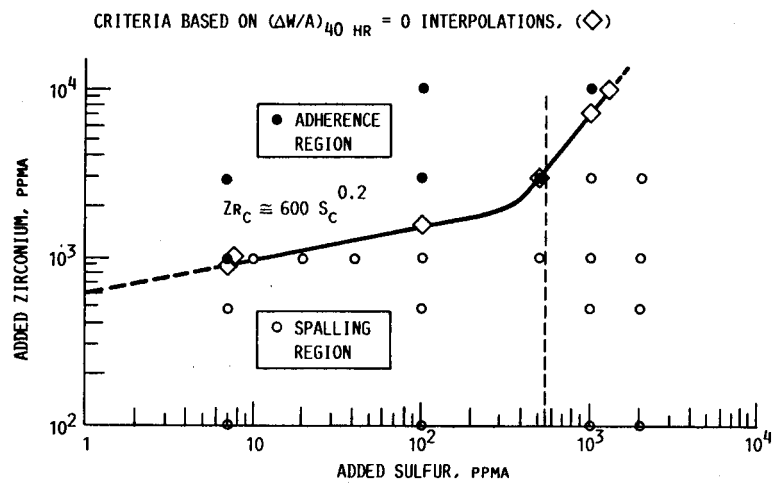CRITERIA BASED ON $(\Delta W/A)_{40\ HR} = 0$ INTERPOLATIONS, ($\Diamond$)

FIGURE 9. - SI/ZR 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).

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16. Abstract

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