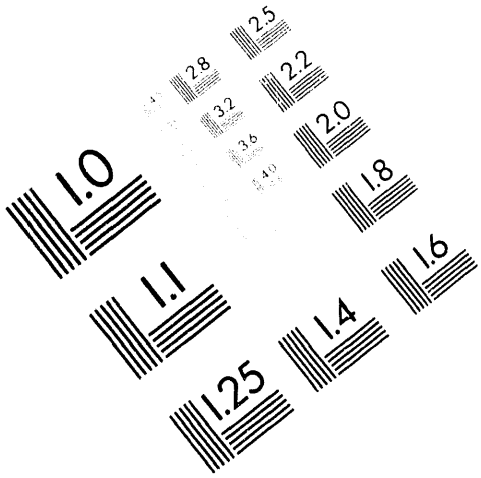
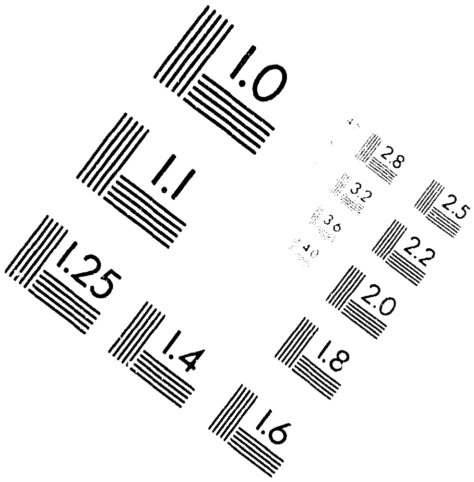
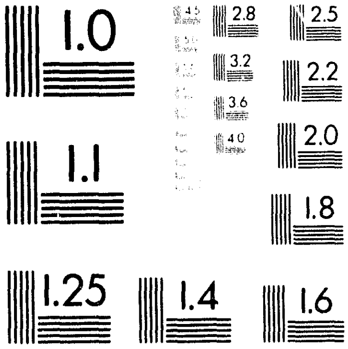


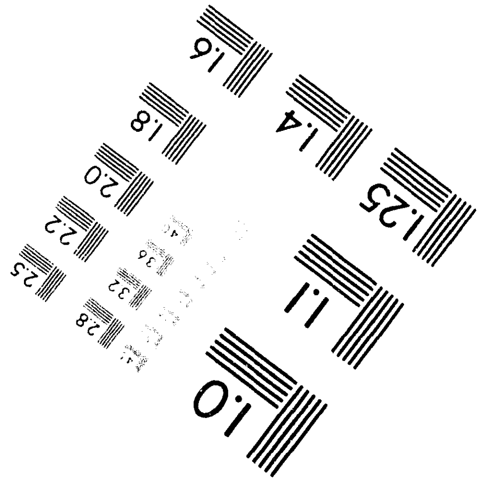
AIIM

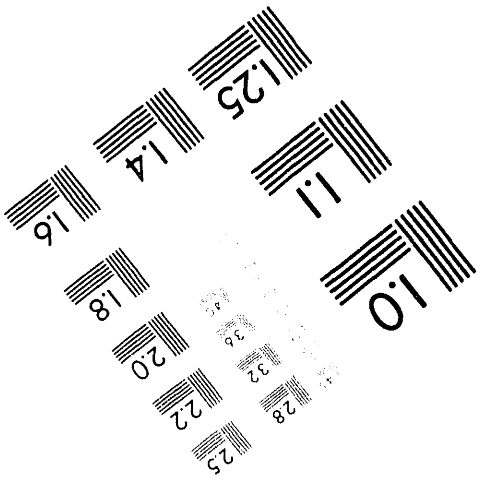
Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202









MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

CONF-940753--10

THE EFFECT OF REACTIVE ELEMENTS ON THE SEGREGATION BEHAVIOR AND MICROSTRUCTURE OF α–Al_2O_3 SCALES ON β–NiAl

K. B. Alexander and B. A. Pint

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6376

In order to improve oxidation resistance, small quantities of certain oxygen-active or "reactive" elements (RE) such as Y, Zr, Hf, or Ce are added to chromia- and alumina-forming high temperature alloys. Many theories have been proposed to explain the effects of RE additions, with a number of these theories including some aspect of the observed segregation of RE ions to oxide scale grain boundaries and the metal-scale interface.[1-8] The RE-ion segregation to the scale grain boundaries has been proposed to affect the oxidation behavior by suppressing cation transport along grain boundaries. It has been demonstrated that the quantity of RE segregation at α–Al_2O_3 scale grain boundaries varies with oxidation time and temperature[7] and is greatly affected by the formation of RE-rich oxide particles in the scale (particularly at the gas interface).[9-10] A previous study of scale formation on Y-implanted β-NiAl found that the Y implant had only a short-term (<1 h) effect at high temperatures.[8] After 50 h, no boundary segregation was detected and all the Y in the scale was contained in YAl_xO_y particles. These observations were attributed to the limited supply of yttrium available. A model has been developed wherein the RE boundary segregation level is not static, but is influenced by the outward transport of RE ions.[10] As a result, RE-rich oxides form at the gas interface, with an associated decrease in the local RE grain boundary segregation.[12]

As an alternative to a system where the RE-ion supply is self-limiting (Y-implant), it was desired to investigate the effect of RE source-removal on microstructure and grain boundary segregation levels. To accomplish this, β-NiAl doped with 0.23 wt % Zr was oxidized in 1 atm O_2 at 1500°C for 50 h. Upon cooling, the ≈30-µm-thick scale spalled into mm^2 pieces. These spalled α–Al_2O_3 scales were subsequently annealed in air at 1500°C for 1 h and 50 h. During annealing, the Zr source (alloy) is absent and there is no oxygen potential gradient to drive Zr diffusion towards the gas interface. Under these annealing conditions, it is expected that steady-state Zr boundary segregation levels should be achieved.

Specimens were fabricated parallel to the metal/scale interface, and grain boundary chemistries were determined with the use of x-ray energy dispersive spectrometry (XEDS). A standardless Cliff-Lorimer method was used to determine the weight percentages of Zr and Al when the probe was positioned on the grain boundary. For this analysis, the grain boundary width and the probe size (and associated probe profile) were assumed to be constant and beam-spreading was ignored. Under these conditions, the ratio of the grain boundary volume to the grain volume is constant, independent of local specimen thickness. A specimen oxidized for 50 h at 1500°C had been previously characterized with a field emission gun scanning transmission electron microscope (FEG/STEM, VG Microscopes Ltd. HB5) with a nominal 2.0 nm probe.[7,10] In the present work, a FEG TEM/STEM (Philips EM400T/FEG), operating in STEM mode with a nominal < 2.0 nm probe is being used. The Zr/Al ratios obtained on the same specimen with the use of the two instruments are shown in Table I. In both cases, there are significant variations in segregation from boundary to boundary. However, the range of observed segregation levels and the average Zr/Al levels are comparable.

A cross-section of a spalled scale is shown in Figure 1. The gas interface microstructure as a function of oxidation time is shown in Figs 2a and 2b. The scale of both the microstructure and the zirconia particles increase with oxidation time. The effect of annealing the spalled scale for 50 h is shown in Fig. 2c. No qualitative change in microstructural scale or zirconia particle size/density occurs after annealing. These results are consistent with the current model in which the gas-interface microstructure development depends on a continuous supply of zirconia diffusing from the metal interface towards the gas interface. These observations also imply that the rate-limiting step in the evolution of the gas interface microstructure is the diffusion of Zr ions to the gas interface. Further work to quantify the zirconia formation and the grain boundary segregation in the annealed scales is under way.[11]

References

1. T. A. Ramanarayanan, et al., *J. Electrochem. Soc.* 131(1984)923.
2. K. Przybylski and G. J. Yurek, *Materials Science Forum* 43(1989)1.
3. C. M. Cotell, et al., *Oxid. Met.* 34(1990)173 .
4. B. A. Pint, et al., *Electrochem. Soc. Extended Abstracts* 91-2(1991)913.
5. H. M. Tawancy and N. Sridhar, *Oxid. Met.* 37(1992)143.
6. B. A. Pint, et al., Proc. *2nd Int. Conf. on the Microscopy of Oxidation*, S. B. Newcomb and M. J. Bennett eds., Institute of Materials, Cambridge, U.K. (1993)463.
7. B. A. Pint, et al., *Proc. Ann. MSA Meeting* 51(1993)950.
8. B. A. Pint and L. W. Hobbs, *Oxid. Met.* 41(1994)205 .
9. B. A. Pint and L. W. Hobbs, *Electrochem. Soc. Extended Abstracts* 93-1(1993)1707.
10. B. A. Pint et al., *Electrochem. Soc. Extended Abstracts* 93-2(1993)676 & 678.
11. The authors would like to thank Dr. J. Doychak at NASA Lewis for providing materials and Dr. A. J. Garratt-Reed for assistance with the FEG/STEM results. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. and by the DOE Distinguished Postdoctoral Research Program, Office of Science Education and Technical Information.

Table I. Apparent XEDS weight percentage ratios from α-Al_2O_3 grain boundaries near gas interface in scales grown on β–NiAl (+ 0.23 wt % Zr) at 1500°C for 50 h. No Zr was detected in matrix.

Instrument	Average Zr/Al	Range of Zr/Al
Dedicated FEG/STEM	0.026	0.011 - 0.043
FEG TEM/STEM	0.022	0.000 - 0.055

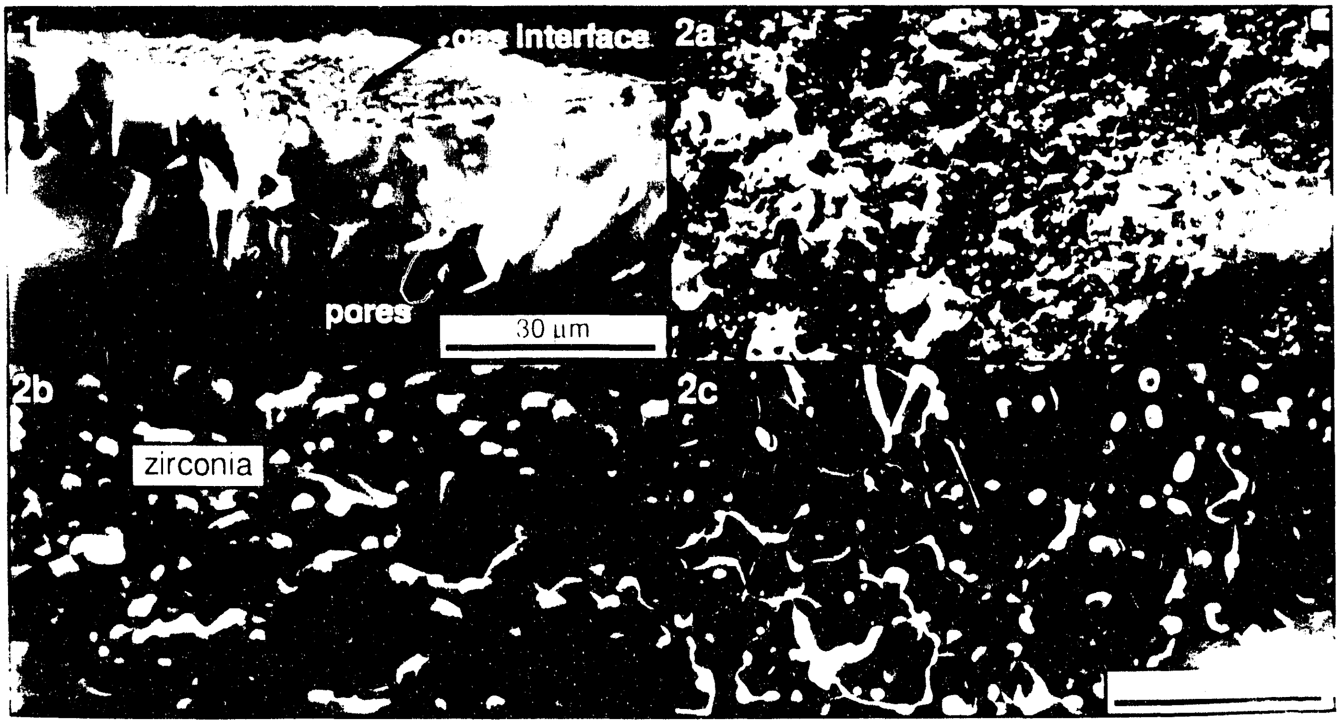


FIG. 1-Scanning electron microscopy (SEM) image of cross-section of α-Al_2O_3 scale on β-NiAl (+ 0.23 wt % Zr) after 50h oxidation at 1500°C. The scale is slightly tilted to show gas interface.

FIG. 2- SEM images of gas interface of α-Al_2O_3 scale on β-NiAl (+ 0.23 wt % Zr) after (a) 0.2h oxidation, (b) 50h oxidation, and (c) 50h oxidation plus 50h anneal (scale only) at 1500°C.

DATE

FILMED

6/28/94

END