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Study of Ionic Grain Boundary Segregation in Thermally Grown Alumina on Single-crystal Superalloys

Kinga A. Unocic and Bruce A. Pint

Materials Science & Technology Div., Oak Ridge National Laboratory, Oak Ridge, TN 37831

The formation of a continuous, thermally grown oxide scale on the surface of alloys inhibits high-temperature oxidation. For high-temperature superalloys, an α-Al_2O_3 scale is preferred because it is more stable and grows at a much slower rate. To improve scale adhesion and reduce the alumina scale growth rate, a well-documented strategy used is the addition of reactive elements (RE), e.g. Hf, Y, Ti, Zr, La, to the alloy [1,2]. One reported strategy to improve the oxidation performance of current generation Ni-base superalloys is to add ppm levels of Y and La; however, there is little mechanistic understanding the benefits from such RE additions, especially when the superalloy is coated with a NiCoCrAlY-type coating.

Two versions of superalloy CMSX4 were used in this study: one with Y and one with both Y and La additions. The surfaces of the specimens (16mm diameter x 1.5mm thick) were polished before oxidation to a 0.3µm finish, then ultrasonically cleaned in acetone and ethanol, and inserted into a hot furnace for a 100h isothermal exposure at 1100°C in dry, flowing O_2. After exposure, the specimens were characterized by a variety of electron microscopy methods and analytical techniques.

The characterization results for both alloys were very similar. Fig. 1a shows a backscattered electron image of a cross-section of the exposed CMSX4. An oxide scale (~5µm thick) formed on the surface of the bare metal, with an evident depletion region beneath the scale due to Al consumption due to scale formation. An electron microprobe elemental map of Hf, Al, and Ti shows segregation of these elements in the specimen (Fig. 1b). Due to the limited map resolution, the segregation of doped elements within the scale and to the surface of the scale could not be readily distinguished. Thus, TEM analysis was included to study segregation of the RE elements to the oxide scale grain boundaries and to the metal/oxide interface. High-angle annular dark-field (HAADF) STEM imaging provided higher Z-contrast imaging resolution; Fig. 2 demonstrates a cross-section of the oxide scale that exhibits a bilayer structure. The outer spinel layer was enriched in large precipitates close to the inner/outer layer interface, while the inner corundum layer was precipitate-free and contained columnar Al_2O_3 grains aligned perpendicular to the metal/oxide interface. Fig. 3a-c shows the region used for energy-dispersive spectroscopy (EDS) mapping, with a selected-area diffraction pattern acquired from the $[\bar{1}11]$ zone axis confirming the presence of the spinel phase ($NiAl_2O_4$). A bright-field STEM image and FFT confirmed the inner layer was α-Al_2O_3. EDS elemental maps of the grain boundary and metal/oxide interface (Fig. 3d) showed only Hf enrichment at the grain boundaries. Segregation of other REs to the metal/oxide interface was not observed, although the La may have been present at the boundary at concentrations below the detection limit of EDS [3].

References

[1] T.J. Nijdam et al., *Acta Mater.* 55 (2007) p. 5980.

[2] G.J.Tatlock et al., *Mater. Corros.* 56, No 12 (2005) p. 867.

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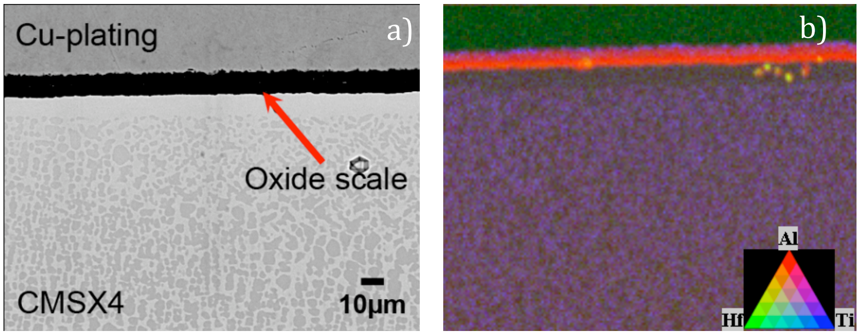

FIG. 1. a) A cross-section of CMSX4 after exposure at 1100°C for 100h. b) EPMA map of a cross-section for Al, Ti and Hf elements.

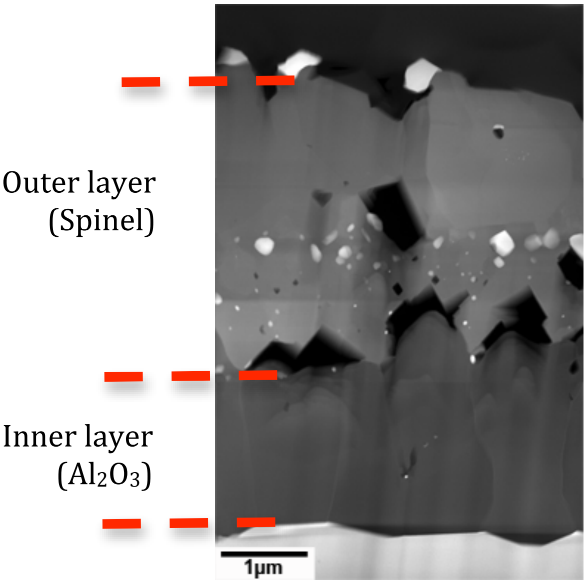

FIG. 2. High-angle annular dark-field (HAADF) STEM image showing the oxide scale formed on CMSX4 superalloy after 100h at 1100°C.

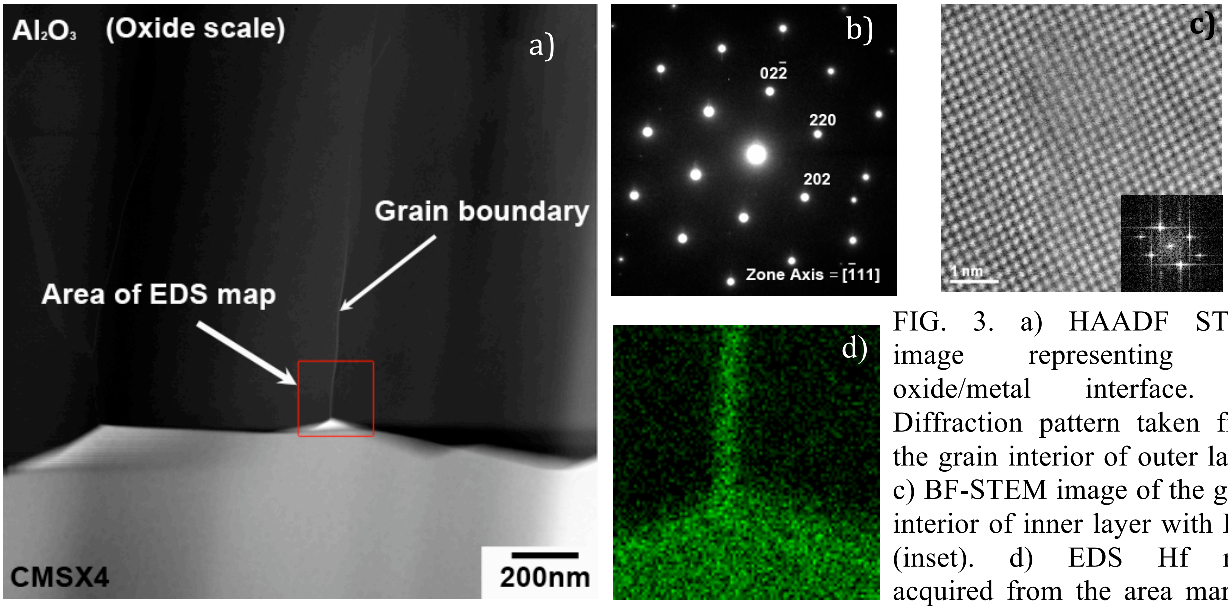

FIG. 3. a) HAADF STEM image representing the oxide/metal interface. b) Diffraction pattern taken from the grain interior of outer layer. c) BF-STEM image of the grain interior of inner layer with FFT (inset). d) EDS Hf map acquired from the area marked on the HAADF image.