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Correlative Atom-Probe Tomography and Transmission Electron Microscope Study of Thermally Grown Oxide on a Commercial Nickel-Based Superalloy, René N'5 Y+®

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The increasing demands for higher fuel efficiency and durability at high temperatures have brought more attention to the thermal barrier coatings (TBCs) that reduce the surface temperature of bare alloys in commercial gas turbine blades for power generation, and in jet engines utilized for aircraft [1]. The native thermally grown oxide (TGO) scale on Ni-based superalloys plays a crucial role as a passivating thermal barrier coating (TBC), preventing further oxidation. To increase the oxidation resistance and solid-solution strengthening in the high-temperature regime of a Ni-based superalloy, refractory metal (RM) elements, such as, Hf, Ta, W, Re, are added to the Ni-Al-Cr base alloy. The oxidation characteristics of Ni-based superalloys have been investigated utilizing X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS), but detailed studies of the chemical distributions of different elements at the subnanoscale in metal oxides are difficult to obtain. Atom-probe tomography (APT), which is a spectrometric technique, is a unique instrument for obtaining sub-nanometer scale composition information with similar detection efficiency for all elements in the periodic table [2]. The recent implementation of femtosecond green or picosecond ultraviolet lasers has made it possible to analyze poorly conducting metal oxides more readily utilizing APT.

Herein we present results on the formation of a TGO layer on a commercial superalloy by utilizing EDS and APT techniques. The material studied is René N'5 $Y^{+®}$ (23.1Co -13.1Cr -17.7Al -4.5Ta -3.0W -2.9Re -0.8Hf -4.0Ru -0.4Zr -1.4Mo -2.8Ti -0.7Nb -0.6C -0.06B -0.08Y -Balance Ni, at.%). The René N′5 Y^+ sample was oxidized at 1100 °C for 100 h and it developed a 3-5 µm thick oxide layer.

Figure 1 is a scanning transmission electron microscopy (STEM) Z-contrast image of a TGO layer and its EDS elemental mapping. The STEM Z-contrast image, Figure 1(a), displays the oxide layer, which exhibits different contrast effects that are due to the different elemental atomic numbers. The bright dot in the oxide layer is associated with the heavy RMs found between the Cr - and Al - oxide regions. EDS mapping shows the elemental distribution in the TGO. Three major elements of oxide layers, Ni, Cr, and Al, are divided from top to bottom and RMs (Ta, W, Ta, and Re) are distributed between Cr- and Al-oxides. Mixtures of Ni, Cr, and Al are also detected between Cr- and Al-oxides, which have the spinel structure [3]. Cobalt is mainly present at the bottom of the NiO but is mixed with Ni in the spinel region. Each oxide region was extracted utilizing a focused ion-beam (FIB) microscope lift-out technique and fabricated into APT microtips for detailed chemical analyses.

Figure 2 displays the APT 3-D reconstructed images of the different oxides in the TGO layer of the Ni-based superalloy. The observed regions are from three samples: (i) NiO layer in the top region of the TGO, figure 2(a); (ii) the middle region is a mixture of five different oxides, figure 2 (b); and (iii) the bottom region is alumina (Al_2O_3) and the superalloy matrix, Figure 2 (c). The elements in the figures are represented by different colors: Ni (green spots), Cr (red spots); Al (cyan spots); Co (blue spots); and the refractory metals (Hf, Ta, W, Re) are brown spots in the 3-D APT reconstruction of the TGO: the size of a spot is not scaled to the atomic size. The middle region in figure 2 (b) contains five different oxides with the main elemental oxides changing from Cr_2O_3 to Al_2O_3 and the refractory metal oxides are imbedded between the above two oxide phases. Figure 2 (c) is the elemental contribution at the interface between Al_2O_3 and the superalloy's matrix. The observed order of oxide formation is $NiO \rightarrow Cr_2O_3 \rightarrow Ta_2O_5 \rightarrow NiTaO_4,\ NiTa_2O_6 \rightarrow Ni(Cr,Al)_2O_4 \rightarrow Al_2O_3$, utilizing correlative APT and TEM analyses. The site-specific FIB microscopy technique for specimen preparation was utilized and the APT results are compared with our TEM observations. And in this manner the complex growth of a TGO on a single-crystal Ni-based superalloy has been successfully analyzed and elucidated.

References

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[3] S. Baik, X. Yin, D. N. Seidman, to appear in Scripta Materialia (2013)
[4] The atom-probe tomography measurements were performed at the Northwestern University Center for Atom-Probe Tomography (NUCAPT). The LEAP 4000X-Si tomograph was purchased and upgraded with funding from NSF-MRI (DMR-0420532) and ONR-DURIP (N00014-0400798, N00014- 0610539, N00014-0910781) grants. We also kindly thank Dr. Ben Nagaraj, GE Aviation, Cincinnati, Ohio, for specimens and discussions.

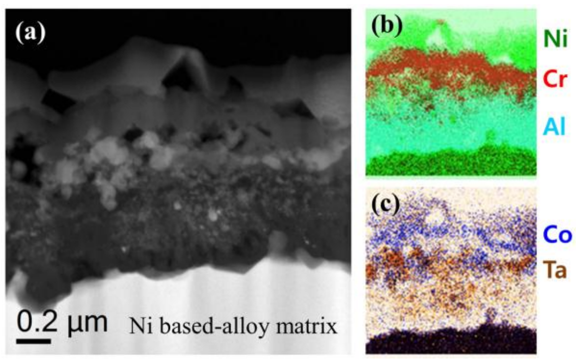

Figure 1. Structure and chemical analyses of a thermally grown oxide (TGO) on a commercial Ni-based superalloy. (a) STEM Z-contrast image; (b) EDS image mapping of Ni (green spots), Cr (red spots), Al (cyan spots), (c) Co (blue spots), and refractory metals (Ta, W, Ta, and Re, brown spots).

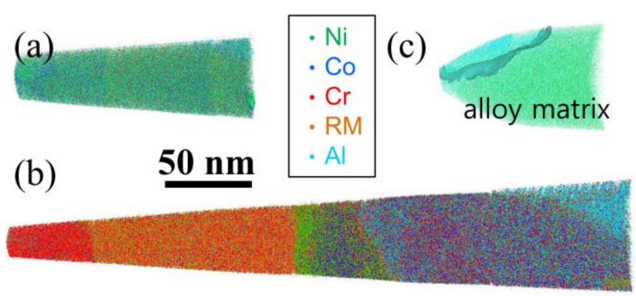

Figure 2. APT 3-D reconstructions of three different oxides in the TGO layer. (a) NiO layer in the top region of the TGO oxide layer; (b) middle region with a mixture of five different oxides; and (c) alumina (Al_2O_3) and the Ni-based superalloy matrix.

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