In-situ Observations on Early Stage Oxidation of NiCr and NiCrMo Alloys

Xiao-xiang Yu[1], Ahmet Gulec[1], Christopher Andolina[2], Evan Zeitchick[3], Kateryna Gusieva[4], Judith Yang[2] John Scully[4], John Perepezko[3] and Laurence Marks[1]

[1.] Department of Materials Science and Engineering, Northwestern University, Evanston, IL, USA.
[2.] Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA, USA.
[3.] Department of Materials Science and Engineering, University of Wisconsin, Madison, WI, USA.
[4.] Department of Materials Science and Engineering, The University of Virginia, Charlottesville, VA, USA

Nickel-based superalloys are widely used structural materials due to their excellent combination of strength, ductility and corrosion resistance at elevated temperature.[1] The addition of minor alloying elements, such as molybdenum (Mo) to the alloys may improve the oxidation and corrosion resistance.[2-4] However, the details of how and why Mo changes the oxidation behavior are still unclear and the synergetic mechanism of Mo and Cr in corrosion resistance is under active debate. The typical postmortem analysis of oxidized samples does not provide a complete picture of oxide nucleation, growth and coarsening. In contrast, in-situ environmental transmission electron microscopy (ETEM) can provide a unique way to monitor the development process.

In this paper, we report the results of in-situ TEM experiments on the early stage oxidation of NiCr and NiCrMo alloys. Ni22%Cr and Ni22%Cr6%Mo (wt.%) sample bars were prepared in an arc furnace and the alloys were homogenized in a tube furnace at 1000 °C for 5 hours followed by a water quench. 3 mm regular TEM disks were cut from the bulk sample, mechanically thinned, dimpled and ion milled until a small hole in the sample center appeared. The in-situ oxidation experiments were performed in a dedicated LaB_6 environmental TEM (ETEM, Hitachi H9500) operated at 300 kV and equipped with a double tilt heating holder. The samples were first reduced under hydrogen gas at 1.1×10^{-2} Pa and 700 °C to remove native oxides and other contaminants. The O_2 gas was then delivered and the oxygen pressure stabilized at $1.3\text{x}10^{-2}$ Pa and 700 °C. Analysis on the postmortem samples after the in-situ experiments was performed by scanning transmission electron microscope, an aberration-corrected JEOL JEM-ARM200CF with collections angles 90 mrad $\leq \beta \leq$ 220 mrad for high angle annular dark field (HAADF) imaging. Compositional analysis was performed with a Gatan Enfina EELS attached to the JEM-ARM200CF.

For both alloys, the epitaxial rock-salt $Ni_{1-x}Cr_xO_{1+y}$ oxide initiated immediately after the introduction of oxygen gas, progressing by a layer-by-layer mode. Kirkendall voids initiated in the rock-salt oxide in NiCr alloys and then diffused to the metal-oxide interface, driven by the metal/oxide misfit stresses. A sequential oxide initiation and phase separation has been observed in NiCr alloys: rock-salt→spinel→corundum. For NiCrMo alloys, Kirkendall voids were not seen and the metastable $Ni_{2-x}Cr_xO_3$ (corundum structure) phase formed shortly after the growth of the rock-salt phase. Chemical analysis shows that solute atoms were captured in the initial oxide before diffusing and transforming to more thermodynamically stable phases. The results indicate that Mo doping may stabilize the cation vacancies and inhibit the Kirkendall voids formation by promoting the nucleation of corundum structure. Density functional theory calculations confirm that the thermodynamic driving force of phase transformation from rock-salt to corundum structure is increased by 0.6 eV per Mo atom.

References:

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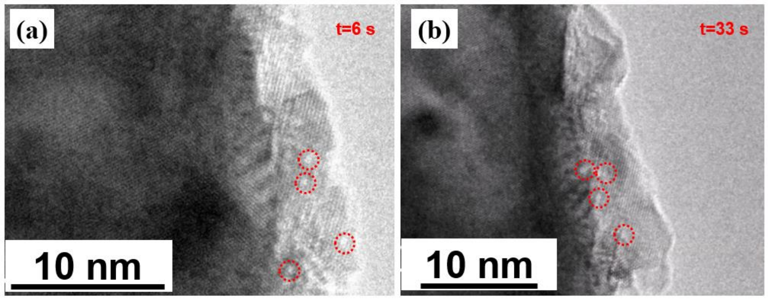

Figure 1. In-situ TEM images showing Kirkendall voids (dotted circles) formed (a) in the rock-salt film and (b) near the oxide-metal interface of the NiCr alloy.

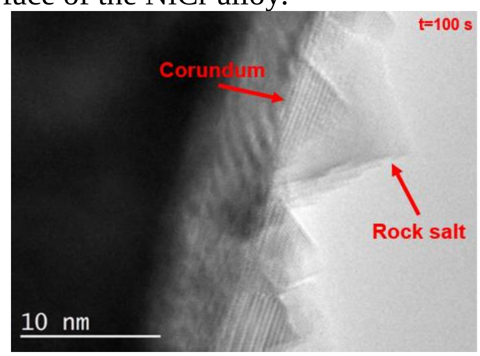

Figure 2. TEM image showing the corundum structure quickly formed after a couple of layers of rock-salt formation in NiCrMo alloy.

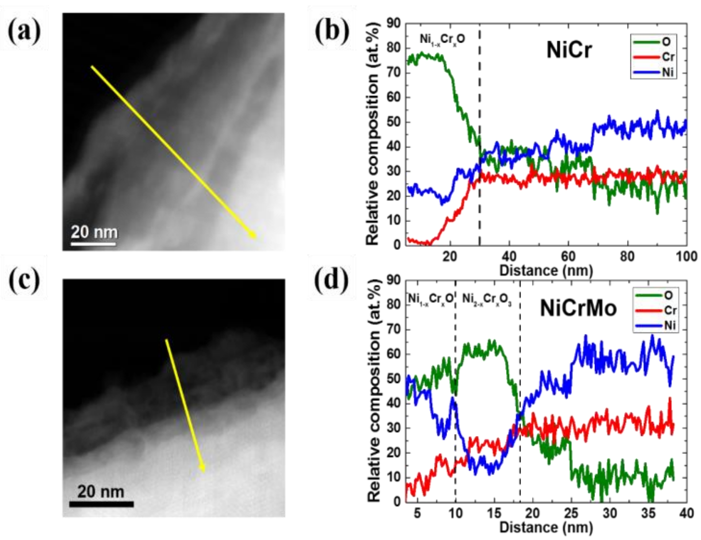

Figure 3. HAADF images of the oxidized samples after in-situ experiments for (a) NiCr and (c) NiCrMo samples, the yellow arrows indicate the EELS line-scanning direction. (b) and (d) are EELS relative composition profiles for Ni-Cr and Ni-Cr-Mo respectively.