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INTERFACIAL SEGREGATION IN OXIDE SCALES ON NiCrAl-BASED ALLOYS

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Previous studies addressing the segregation of reactive elements in protective oxide scales and their beneficial effect on scale adhesion have primarily concentrated on primary alumina-formers (e.g. β-NiAl and FeCrAl).[1] In our study the isothermal oxidation behaviour of three NiCrAl alloys, which form complex oxide scales[2,3] was studied in air at 1473 K for 100 hrs.. The composition (in at.-%) of these alloys is the following: General Electric alloy **René N5** (64.9 Ni, 7.8 Cr, 13.9 Al, 0.1 Fe, 2.1 Ta, 0.05 Hf, 1.6 W, 1.0 Re, 0.15 Si, 7.3 Co, 0.9 Mo, 0.003 Y, 0.003 Zr, 4 ppm S, 0.25 C), **Ni-7Cr-6.5Al+Y** (80.1 Ni, 7.2 Cr, 12.5 Al, 0.01 Fe, 0.14 Si, 0.012 Y, 18 ppm S, 0.05 C) and **Ni-10Cr-10Al+Y** (71.2 Ni, 9.9 Cr, 18.8 Al, 0.01 Fe, 0.02 Si, 0.041 Y, 16 ppm S, 0.04 C).

The resulting oxide scales were characterized by scanning electron microscopy (SEM) and cross-sectional transmission electron microscopy (TEM) techniques. Segregation at internal interfaces was analyzed in the STEM mode on a Philips CM200 FEG-TEM, operated at 200 kV and equipped with a Link ultrathin-window EDS detector. The probe size of the electron beam was about 1.5 nm. Spectra were recorded with grain boundaries oriented parallel to the electron beam.

The oxide scale on René N5 (~5 μm) consists of columnar α-Al_2O_3 at the bottom (~4 μm) and a mixed layer of spinel (Ni, Co, Ta) $(Al,Cr)_2O_4$ and α-Al_2O_3 (~1 μm) at the top (Fig. 1a, 2a). The mixed spinel/alumina layer contains numerous precipitates of Ta,Y,Cr(Hf,Re)-oxides. These are concentrated at the interface between the columnar alumina and the mixed layer. This mixed layer of the scale is prone to spallation. Similar oxide particles can also be found on the scale surface. Spallation of the complete scale exposing the bare alloy occurs only around particles in the alloy, which consist of Ta,Y,Cr(Hf,Re)-oxide in the center, surrounded by spinel (Ni, Co, Ta) $(Al,Cr)_2O_4$ and α-Al_2O_3. Segregation of Ta and Y at oxide grain boundaries, both in the alumina and in the spinel, was found (Fig. 3a). Some oxide grain boundaries also exhibited segregation of Hf and Re.

On Ni-7Cr-6.5Al+Y, the scale (~9 μm) consists mainly of columnar Cr-doped α-Al_2O_3 (Fig. 1b, 2b). On top of it is a thin, porous mixed layer of equiaxed spinel ($NiAl_2O_4$) and α-Al_2O_3, as well as some NiO. Over time NiO transforms to $NiAl_2O_4$ and $NiAl_2O_4$ eventually to α-Al_2O_3; both transformations are pseudomorphic. Spallation of the scale occured only in a few areas associated with the formation of Y_2O_3, $Y_3Al_5O_{12}$ (garnet) and α-Al_2O_3 at Y-rich alloy grain boundaries. Y-rich oxide particles can be found on the scale surface. Yttrium was also found to be segregated at oxide grain boundaries (Fig. 3b) and at the scale/metal interface.

Ni-10Cr-10Al+Y forms an oxide scale (~8 μm) that consists mainly of columnar Cr-doped α-Al_2O_3 (Fig. 1c). Y-rich oxide particles can be found on the scale surface. The higher level of Y in this alloy results in the formation of Y-rich precipitates at all alloy grain boundaries. Preferential internal oxidation ultimately leads to the formation of Y_2O_3, $Y_3Al_5O_{12}$ (garnet) and α-Al_2O_3 at these grain boundaries. Due to the volume change associated with the formation of these phases, almost complete spallation of the oxide scale is initiated from here.

The results are consistent with previous results on primary alumina-formers. Reactive elements present in the alloy diffuse into the oxide scale and segregate to grain boundaries where they change the diffusion processes resulting in a columnar grain structure of the alumina scale.[4]

References:

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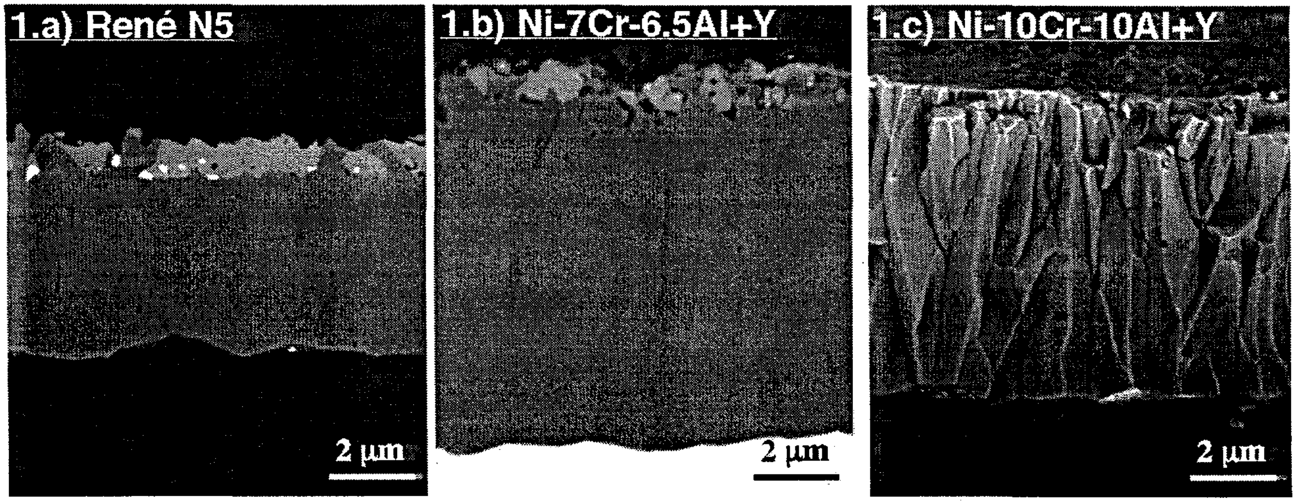
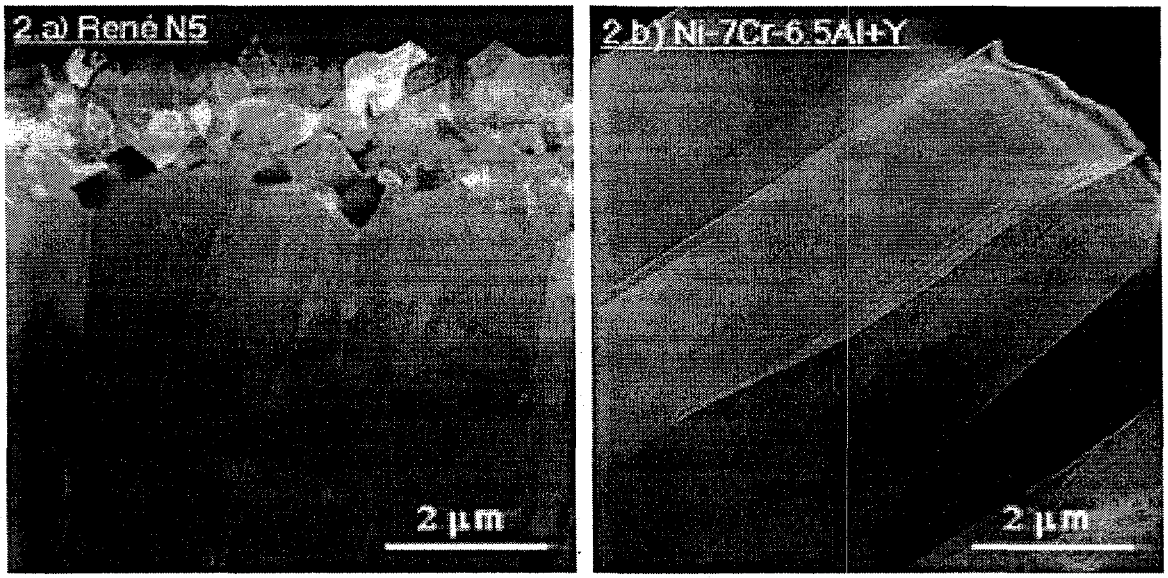
4) Research at the Oak Ridge National Laboratory (ORNL) SHaRE User Facility was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22 464 with Lockheed Martin Energy Research Corp., and by an appointment (KP) to the ORNL Postdoctoral Research Associates Program, which is administered jointly by the Oak Ridge Institute for Science and Education and ORNL.





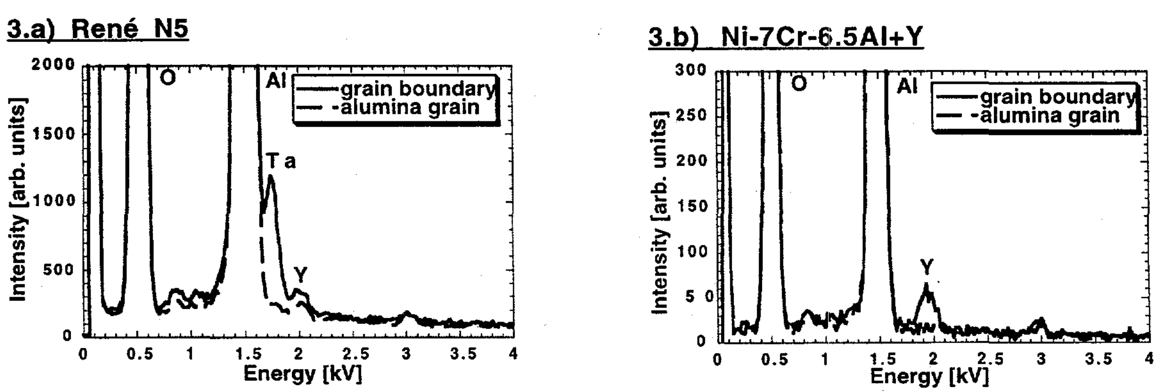


FIG. 1: SEM backscattered electron (BSE) images of polished and fractured cross sections.
FIG. 2: STEM annular dark field image of cross sections through the oxide scale.
FIG. 3: EDS spectra showing segregation of Ta and Y at alumina grain boundaries.