

Composition Effects on Aluminide Oxidation Performance: Objectives for Improved Bond Coats

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Formerly, the role of metallic coatings on Ni-base superalloys was simply to limit environmental attack of the underlying substrate. However, a new paradigm has been established for metallic coatings adapted as bond coats for thermal barrier coatings. It is no longer sufficient for the coating to just minimize the corrosion rate. The metallic coating must also form a slow-growing external Al_2O_3 layer beneath the overlying low thermal conductivity ceramic top coat. This thermally grown oxide or scale must have near-perfect adhesion in order to limit spallation of the top coat, thereby achieving a long coating lifetime.

While oxidation is not the only concern in complex thermal barrier coating systems, it is, however, a primary factor in developing the next generation of bond coats. Therefore, a set of compositional guidelines for coatings is proposed in order to maximize oxidation performance. These criteria are based on test results of cast alloy compositions to quantify and understand possible improvements as a basis for further investigations using coatings made by chemical vapor deposited (CVD). Experimental work includes furnace cycle testing and in-depth characterization of the alumina scale, including transmission electron microscopy (TEM).

The focus of these guidelines is on aluminide compositions. While MCrAlYs represent an important class of coatings, it appears that scale adhesion on MCrAlYs is inherently inferior to that on aluminides at 1100°-1200°C [1,2] and therefore does not represent a fruitful option for development. This problem may be due to the higher coefficient of thermal expansion for MCrAlYs compared to γ -NiAl [3,4].

Current aluminide bond coats often contain Pt, which clearly is beneficial in improving alumina scale adhesion in cast aluminides [5] and CVD aluminide coatings [6]. When Pt is added to CVD aluminide coatings, Pt mitigates the detrimental role of sulfur present in the superalloy substrate

on scale adhesion. However, the beneficial effect of Pt is minimal compared to the benefit of an optimized reactive element addition, particularly Hf. Hafnium not only improves alumina scale adhesion but also has been shown to reduce the scale growth rate by an order of magnitude compared to undoped γ -NiAl [5,7]. In a comparison of simple and Pt-modified aluminide coatings on General Electric alloy René N5, Pt did not (1) reduce the alumina scale growth rate, (2) alter the diffusion of heavy elements into the coating during deposition or oxidation or (3) alter the coating Al content before or after oxidation [6]. In addition, a comparison of castings of NiAl and NiAl+(2-5)at%Pt (10-20wt%Pt) showed no effect of Pt on hot corrosion resistance, Figure 1. Therefore, since incorporation of Hf in the coating would result in a significant improvement in alumina scale adhesion, the addition of Pt would be unnecessary.

However, the benefits of Hf can be compromised if additional elements are also incorporated into the coating. (Yttrium is not considered a viable alternative to Hf because it readily forms Ni₃Y precipitates, which internally oxidize and disrupt scale formation [8].) Strong detrimental effects were found from the addition of Re and Cr to Hf-doped NiAl, Figure 2. Both elements form precipitates in the γ -matrix which appear to lead to scale spallation, Figure 3. To a lesser extent, Ta and Ti incorporate into the alumina scale on Hf-doped NiAl and also increase the scale growth rate. Chromium is the only element which appears to improve the hot corrosion resistance of NiAl (Figure 1), however, the addition of Cr increases scale spallation and the isothermal scale growth rate. Thus, from the available data for cast aluminides, it appears that hot corrosion resistance and exceptional scale spallation resistance are mutually incompatible goals for coating performance.

Likely the most severe problem to overcome in producing long coating lifetimes will be the loss of Al from the coating by diffusion into the substrate. After only short exposures, γ ' formation is noted at CVD Pt aluminide grain boundaries, indicating significant Al loss. Another benefit of Hf is that it significantly improves the performance of low Al content (40-42.5at%) NiAl, Figure 2. However, there are indications that Hf-doped Ni-40at% Al may be more prone to spallation than higher Al contents.

These compositional guidelines will be difficult to implement by traditional CVD coating processes. Since elements detrimental to scale growth and adhesion, such as Cr and Re, incorporate into both inward and outward growing aluminide coatings, the coating essentially must be

formed by depositing Ni, Al and a uniform, low level of Hf on the superalloy surface. At worst, this strategy would require substrate elements (e.g. Ta, Cr, Re) to diffuse to the gas side of the coating before they could negatively effect oxidation performance. Of course, a stable diffusion barrier between the substrate and coating would further improve this strategy by reducing outward diffusion and inward diffusion of Al, but the development of such a barrier material appears problematic.

A final point is that there has been no inherent problem with a thick (125 μm , 5 mil) ceramic coating adhering to a metallic substrate. A 125 μm -thick, physical vapor deposited, Y_2O_3 -stabilized ZrO_2 coating on Zr-doped - NiAl [9] had a 20% coating spallation lifetime of 3600, 1h cycles at 1150°C and has not reached 20% spallation after 800, 2h cycles at 1200°C. These long lives indicate that when an adherent alumina layer is formed, a long coating lifetime should result. The major problem with current bond coats is that they simply do not form alumina scales with sufficient adherence. The next generation of bond coats will require more careful compositional control in order to achieve the significant improvements in performance that are required.

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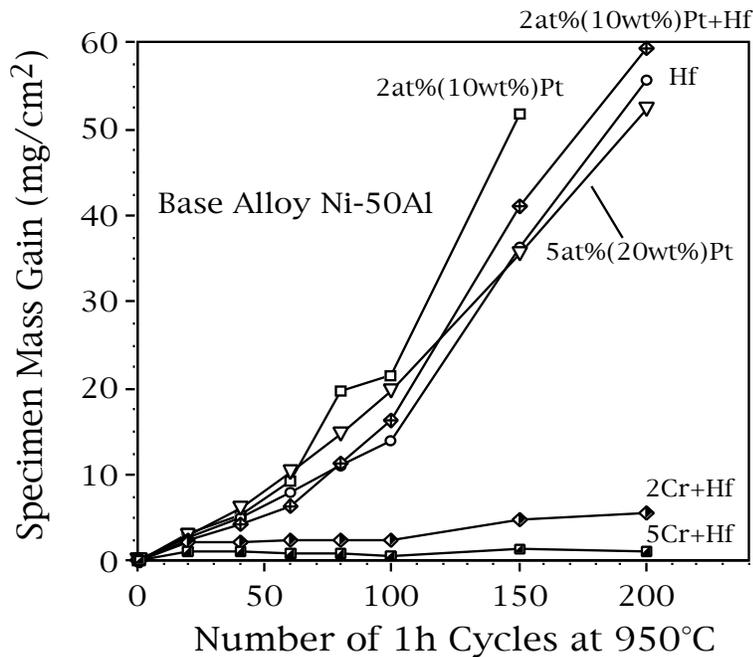


Figure 1. Hot corrosion specimen mass gains at 950°C for cast NiAl alloys with various modifications. All specimens were coated with 10 mg/cm^2 Na_2SO_4 after 1h and 100h. Chromium had a beneficial effect but Pt and Hf showed no benefit.

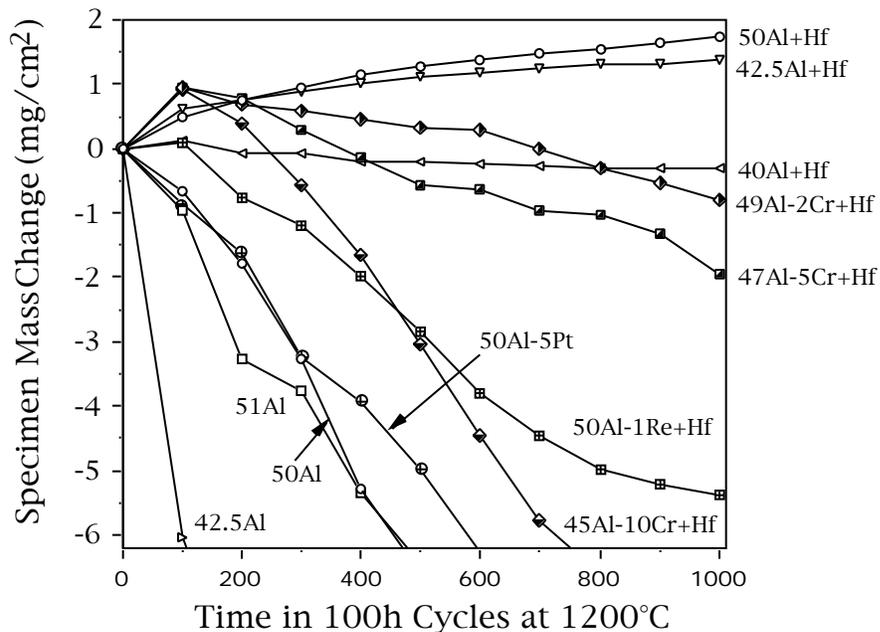


Figure 2. Specimen mass changes during 100h cycles at 950°C in air. While Hf improves Ni-Al scale adhesion, additions of Re and Cr degrade it.

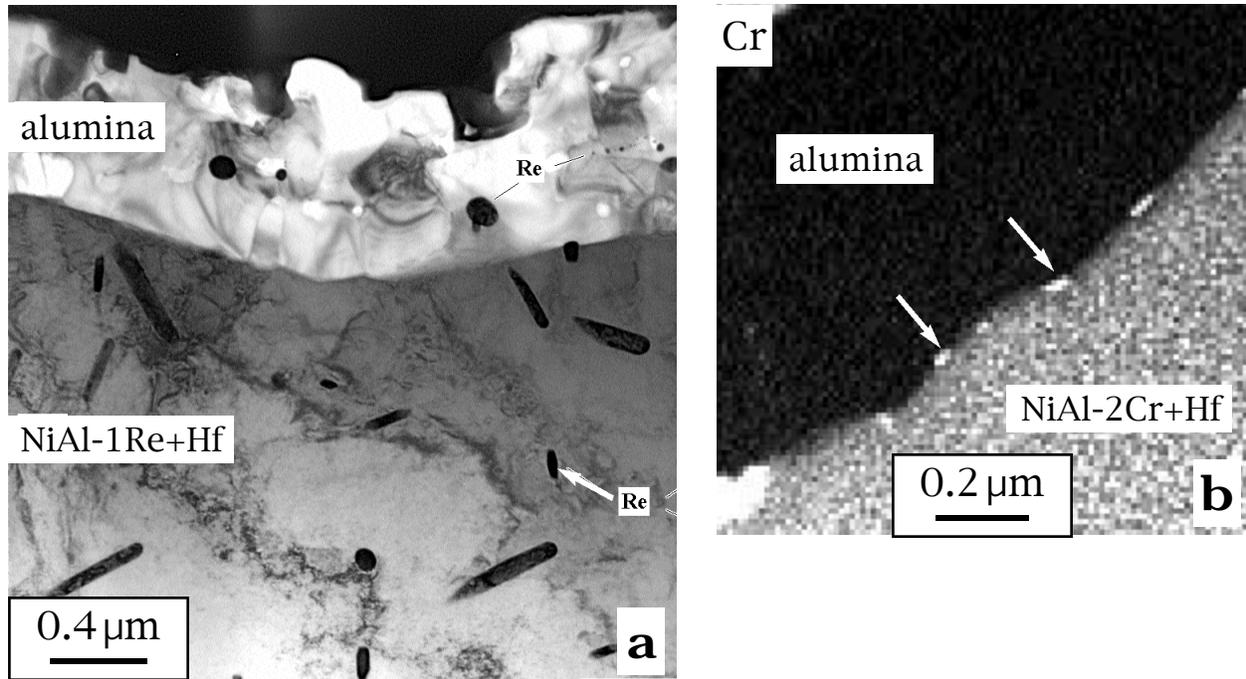


Figure 3. (a) TEM bright field image of the alumina scale formed on Ni-50at%Al-1Re-0.05Hf. Re-rich precipitates are observed in the metal and in the oxide. (b) High resolution STEM Cr x-ray map of the scale formed on Ni-49Al-2Cr-0.05Hf, arrows mark Cr precipitates at the metal oxide interface. Both scales formed after 2h at 1200°C in O_2