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The effect of grain refinement on the adhesion of an alumina scale on an aluminide coating

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ABSTRACT

To understand the effect of grain refinement on the thermally grown alumina scale adhesion to the metal substrate, two δ -Ni₂Al₃ coatings, one coarse-grained ($\sim 70\ \mu\text{m}$) and the other ultrafine-grained (generally below $\sim 500\ \text{nm}$), were prepared. The cyclic oxidation in air at $1100\ ^\circ\text{C}$ shows that the ultrafine-grained (UFG) coating is better oxidation resistant than the coarse-grained (CG) coating due to the formation of a more adherent alumina scale. The latter is intrinsically correlated with the fact that the aluminide grain refinement helps to increase the oxide/metal strength through a route to prevent the formation of large-sized voids at the interface.

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1. Introduction

Diffusion aluminide coatings are widely used on superalloys in gas turbines, especially the hot section components to protect their surface from oxidation, because they can thermally grow a protective scale of alumina [1–3]. However, the oxidation resistance and service life of an aluminide coating has been significantly limited by the detachment of the alumina scale, which mostly occurs during cooling from exposure temperatures and under thermal-cycling conditions [4–7]. One important reason for scale detachment is due to the formation of large-sized cavities at the interface between the scale and the coating [4,8–11]. The cavities form normally as a result of the condensation of vacancies during oxidation [12,13]. The vacancies are partly the cation vacancies being formed due to the outward diffusion of aluminium ions for alumina scale growth [13,14]. In addition, the oxidation of aluminium of the aluminide coating forms an aluminium depletion zone below the scale. In the depletion zone, a rapid counter-diffusion of the non-oxidized element from the interface to the coating with respect to the diffusion of aluminium from the coating to the interface induces a flux of “Kirkendall” vacancies toward the interface [15,16]. Sulfur effect is another important reason for the scale detachment. Sulfur, as a common indigenous impurity in metals, typically 1–10 ppm, usually segregates to the interface between oxide scale and metal during oxidation and consequently weakens

the interfacial bonding [17–22]. Promotion of the growth of the voids at the interface by lowering their nucleation energy was also correlated with the interface sulfur segregation by some investigators [23–25].

It is well known that the alumina scale adhesion can be greatly improved by adding a small amount of reactive elements, such as cerium, lanthanum and yttrium or their oxides into the alumina-forming alloys [26–31]. The phenomenon has been referred to as “reactive element effect” (REE). Because of a strong sulfide-forming ability, RE addition can profoundly reduce the sulfur activity in the alloy, preventing the sulfur segregation to the interface as having been reviewed elsewhere [22]. The added RE oxides have also been proposed as vacancy “sinks”, which mitigate the amounts of vacancies condensed at the interface [32–34]. Recently, Peng and co-workers found that ultrafine-grained [35,36] and nano-grained [37] alloys help to form much more adherent alumina scales. For example, significant alumina scale spallation occurred for a conventionally coarse-grained, high-sulfur Ni–25Cr–5Al–1S (wt.%), while no spallation occurred for the nanocrystalline (NC) alloy of similar composition during cyclic oxidation at high temperature [37]. The cyclic oxidation also showed that UFG Ni₂Al₃ [35] and Ni₃Al [36] coatings with respect to the CG aluminide counterparts can form better adherent alumina scales.

On these bases, we propose that grain refinement of alumina-forming alloys is an alternative to RE addition to improve the alumina scale adhesion. Alloy grain boundaries (GBs) close to the interface would be additional sites for sulfur segregation and vacancy condensation. Alloy grain refinement greatly increases the number of GBs. Numerous GBs in the alloys help to decrease

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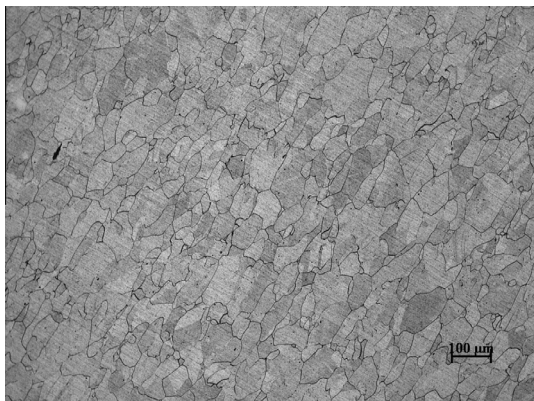


Fig. 1. Optical microscopy of the Ni plate (etched).

the concentration of not only sulfur segregated [37] but also the vacancies transported to the interface during oxidation [36]. Accordingly, the grain-refined alloys with respect to the conventional coarse-grained alloys may thermally form a more adherent alumina scale. However, the viewpoint proposed is needed to be further evidenced in system and depth.

In the work, two differently structured aluminide coatings were prepared. One is a CG Ni_2Al_3 and the other is a UFG Ni_2Al_3 . The cyclic oxidation resistance of the two coatings was investigated at 1100 °C, with a focus on the effect of the grain refinement of the aluminide on the adhesion of the alumina scale formed. The result will offer a new route to develop an aluminide coating with an ability to thermally grow an alumina scale with increased adhesion to the coating substrate.

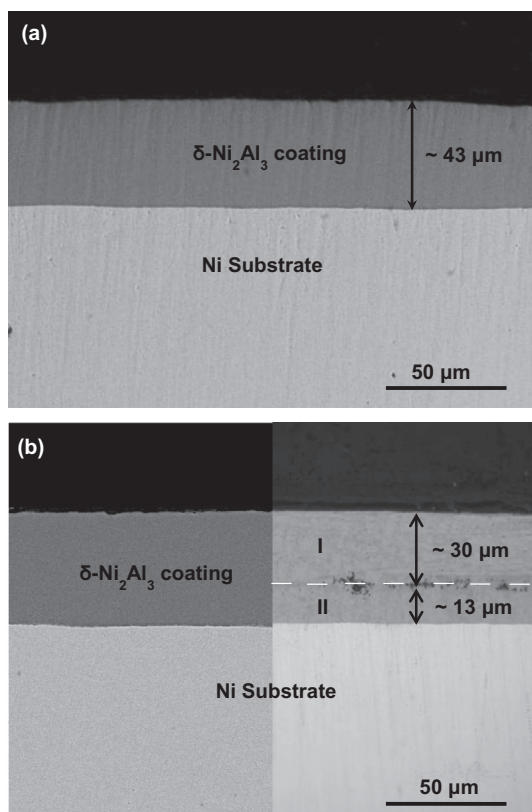


Fig. 2. Cross-sectional morphologies of the $\delta\text{-Ni}_2\text{Al}_3$ coatings on the CG Ni plates (a) without and (b) with the NC Ni film. The left and right images of (b) show the coating without and with etching which are viewed using SEM and OM, respectively.

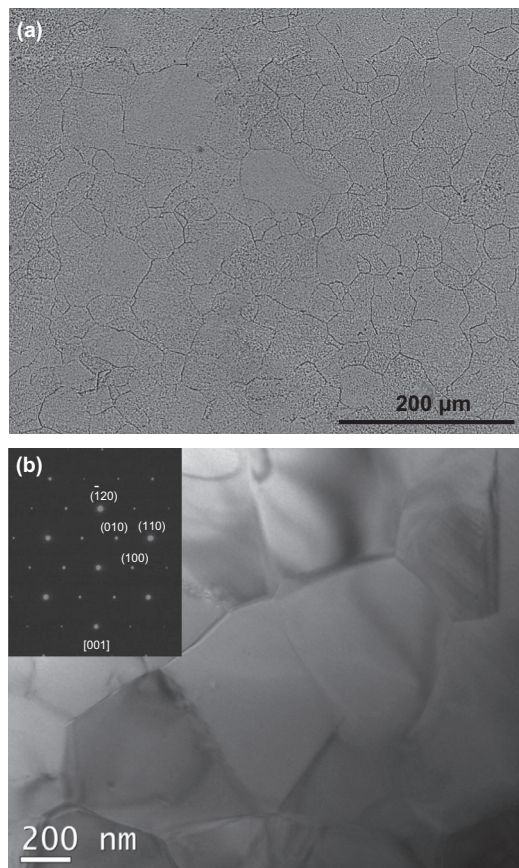


Fig. 3. (a) SEM image of the etched $\delta\text{-Ni}_2\text{Al}_3$ coating on the coarse-grained Ni and (b) TEM image of the $\delta\text{-Ni}_2\text{Al}_3$ coating on the NC Ni.

2. Experimental

The Ni_2Al_3 coating can be formed by aluminizing nickel at ~600 °C [35,38], a temperature much lower than normal. The grain size of the Ni_2Al_3 is dependent on the grain size of the Ni substrate for aluminizing because of the characteristics of the inward growth of the aluminide at low temperature. A CG Ni_2Al_3 is simply available by aluminizing the CG Ni, while a UFG Ni_2Al_3 can be

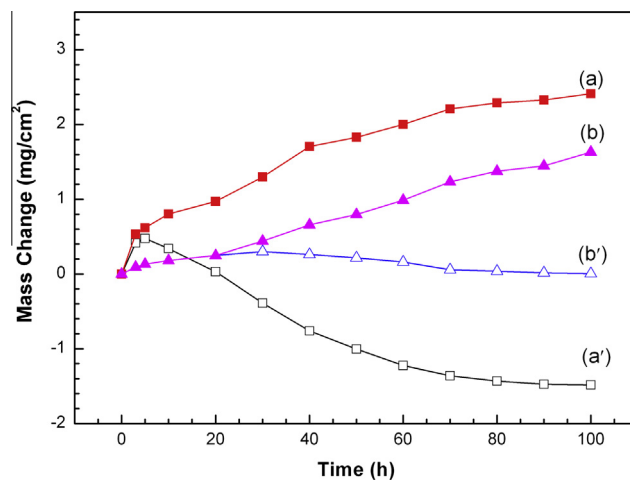


Fig. 4. The mass change vs. time curves of cyclic oxidation in air at 1100 °C for (a) (a') CG and (b) (b') UFG $\delta\text{-Ni}_2\text{Al}_3$ coatings containing and not containing the weight loss by spallation.

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