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Mechanism of the oxidation and degradation of the aluminide coating on the nickel–base single-crystal superalloy DD32M

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ABSTRACT

The aluminide coating on the single-crystal Ni–base superalloy DD32M was prepared by the low-pressure gas phase deposition, and isothermal oxidation tests were performed in the temperature range of 900–1000 °C to check the ability of the aluminide coatings to form alumina scales with the expected protective properties. Two-stage oxidation experiments were performed to describe the high-temperature oxide scales formed and the aluminide coating changed then to put forward the mechanism of oxidation and degradation of the aluminide coating on the single-crystal Ni–base superalloy DD32M, with morphological observations and chemical analysis of the oxide-scale surface by scanning electron microscope (SEM) coupled with energy-dispersive X-ray analyzer (EDX) and analysis of crystal structure by X-ray diffraction(XRD).

1. Introduction

Today the surface temperatures of gas turbine blades can reach 1400 °C or higher. Materials used in high temperature applications such as blades of aircraft engines must possess both strength and oxidation resistance. The turbine blades required for a modern gas turbine engine is often cast in single-crystal form, to avoid the grain boundaries that do harm for the creep and fatigue properties. There continues to be significant evolution in the compositions of the alloys designed for these applications, with the latest ones containing significant quantities of the transition metals such as Ta, Mo, W, and Cr and so on, which markedly improve the mechanical properties. However, the operating temperatures of the gas stream continue to rise such that the degradation of the blades during service, by oxidation or corrosion, was a strong possibility, as has been shown by these articles [1–5]. For this reason, it was usual to protect the blades using coating technology, *e.g.*, either by aluminization or by the application of a ceramic thermal barrier layer with a metallic bond coating [6–10].

Such components used in aero gas turbine engines were conventionally protected by a coating based on the intermetallic compound NiAl [11–18], which possesses several attractive properties, including a high melting point, relatively low density, good thermal conductivity, and excellent oxidation resistance because under oxidizing conditions a protective scale was formed, which was composed principally of aluminum oxide [12,13]. The formation [12,14] and degradation [12,15–17] mechanisms of aluminide coatings were fairly well known. Redden [13] reported on oxidation behavior and coating–substrate interactions of coated nickel alloys. Fleetwood [18] investigated the influence of nickel alloy compositions on the properties of aluminide coatings. The problem of resistance to oxidation and corrosion for aluminide coatings on Ni–base superalloy was well known, little is known of this problem of resistance for aluminide coatings on the single-crystal Ni–base superalloy.

In the present study, the oxidation kinetics, scale morphology, microstructure of the aluminide coating on the as-cast single-crystal superalloy DD32M in the temperature range of 900–1000 °C were investigated to abstain the characterization of the oxide scale formed and the mechanism of relevant oxidation and degradation.

2. Experimental procedures

Superalloy substrate disks ($\phi 4\times 15$ mm) used in this study were machined from Ni–base single-crystal superalloy bars, the nominal composition of DD32M (wt.%) was listed in Table 1. The as-cast specimens were ground down to 600-grit SiC paper, degreased in acetone, ultrasonically cleaned in alcohol and dried in hot air immediately before aluminizing treatment. The coating was prepared by low-pressure gas phase deposition on specimens. Aluminizing treatments were carried out in vacuum furnace by using standard high temperature and low aluminum activities (HTLA) processes, with the powder of Fe–50 wt.% Al alloy as reagent and NH_4Cl as an

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Table 1
Nominal composition of as-cast single-crystal Ni–base superalloy DD32M in wt.%.

wt.%	C	Cr	Al	Co	W	Ta	Nb	Mo	Ni
DD32M	0.014	4.5	6.0	9.0	8.5	4.0	1.6	1.0	Bal.

aluminizing activator. The gas phase deposition aluminizing treatment was carried out at 1050 °C for 1.5 h under the control of gas pressure between 0.02 and 0.06 MPa.

Isothermal oxidation kinetic tests were performed at 900 and 1000 °C for 500 h in static air to analyze the weight gain vs. time curve obtained experimentally. During oxidation, the weight gain of the specimens was measured discontinuously. The sensitivity of the electron balance used in this paper was 0.1 mg. The surface morphology and cross-sectional microstructure of the aluminide coatings of the SC nickel–base superalloy DD32M after oxidation were analyzed by scanning electron microscopy, equipped with energy-dispersive X-ray analysis (SEM/EDX). The surface structure of the coating of DD32M after oxidation was determined by X-ray diffraction (XRD).

3. Results and discussion

3.1. As-deposited coating

Surface morphology of as-coated specimen DD32M was shown in Fig. 1(a). The aluminide coating on DD32M consisted of large, polygonal aluminide grains (8–22 μm in diameter), showing flat surface morphology with the distinct network of prominent grain boundary ridges (black arrow) and containing some pores. This morphology was well characterized and typical of outwardly growing aluminide coating, which was based on the low-activity aluminizing process at high temperature. The concentration of the major elements on the surface of the coated DD32M was as follows (wt.%): 57.5% Ni–39.4% Al–1.5%Co–0.8%Cr–0.8%Nb. The as-deposited coating on DD32M was composed of single-phase β-NiAl (containing Co, Cr and Nb), which was consistent with the XRD analysis results, is shown in Fig. 1(b).

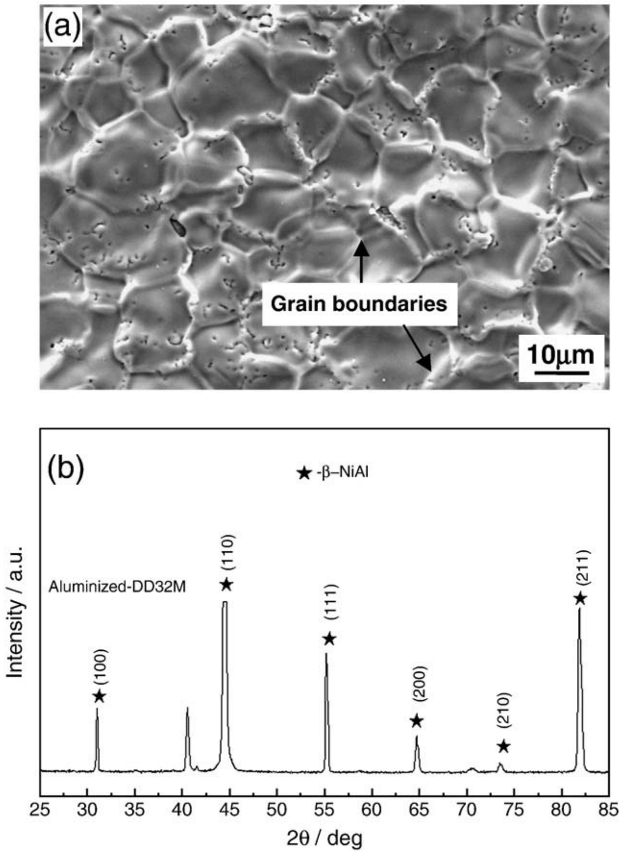

Fig. 1. (a) Surface morphologies [11], (b) XRD patterns of as-coated DD32M.

The cross-sectional microstructure of the coated DD32M prior to oxidation was shown in Fig. 2. It was clearly seen from Fig. 2(a) that the aluminide DD32M had the double-layer structure, the outer layer with approximately 14 μm thickness, and the inner interdiffusion zone (IZ) with 11 μm thickness, as described previously [19,20] with the similar structures. In the as-deposited coating on DD32M, the outer layer, from the original substrate surface to the coating surface, was mainly composed of columnar-grained single-phase β-NiAl (containing Cr and Co) (Fig. 2(c)), which was consistent with the XRD analysis results (Fig. 1(b)). The interdiffusion zone, which began at the original substrate surface and extended into substrate, consisted of two phases, determined by EDS results (Fig. 2(b)), point-like white precipitate phase rich in Ta, W, Nb and Mo, and the grey β-phase matrix (containing Cr and Co) (Fig. 2(c)).

The production of outward grown (low activity) coating was based on outward diffusion of Ni through β-NiAl. The amount of interdiffusion was mainly controlled by the Al activity in the outer zone of coating and Ni activity from the substrate. The fact that Ta with other refractory metals such as W and so on has obvious effect on the formation of the aluminide coating was further emphasized by the discovery that these refractory metals formed the precipitate phase, which can in some degree inhibit the outward diffusion of Ni and inward diffusion of Al.

3.2. Phase analysis

In order to identify the surface oxide products, XRD analysis was carried out for the coated specimens on DD32M after oxidation at 900 and 1000 °C in static air and the results were shown in Fig. 3. The peak-height comparison was used in order to make the semi-quantitative approximation of the scale fraction [21,22]. Analysis of XRD of the oxide products formed on the aluminide coating of DD32M after oxidation for 1 h revealed that the phase was only composed of minor amount of α-Al_2O_3, because of the very weak single-peak of α-Al_2O_3 relative to the very strong remainder-peaks of β-NiAl in the XRD pattern of Fig. 3(a). 10 h after exposure, the diffraction peaks of θ-Al_2O_3 occur in the XRD patterns. 100 h after exposure, even up to 500 h, the diffraction peaks of θ-Al_2O_3 and α-Al_2O_3 became stronger, when the oxidation time reached 500 h, diffraction peaks of the γ′-Ni_3Al phase appeared. After oxidation for 1100 h, the diffraction peaks of α-Al_2O_3 were further stronger, whereas θ-Al_2O_3 was weakened and that of γ′-Ni_3Al were also further stronger, but β-NiAl phase still dominated on the coatings, as shown in Fig. 3(a). For the aluminide DD32M after oxidation for 10 and 100 h at 1000 °C, the oxidation products were very similar to that of 100 h, 500 h at 900 °C, respectively. After oxidation for 1100 h at 1000 °C, $NiAl_2O_4$ was identified in addition to θ-Al_2O_3, α-Al_2O_3, γ′-Ni_3Al and β-NiAl, and the γ′-Ni_3Al phase dominated, as shown in Fig. 3(b). The XRD results cannot quantitatively indicate the amount of oxides as well as the degree of their transformation. Thus, they need to be verified with the scale growth kinetics and morphologies [4].

3.3. Oxidation kinetics

The kinetics may be described by examining the growth-time constant n or K value, which was found as the exponent in the following rate equation: $(\Delta m/A) = Kt^n$ where Δm was the change in weight gain, A the surface area, K the oxidation rate constant, t the exposure time and n the oxidation exponent.. The mass changes Δm for the aluminide DD32M at 900 °C proved to be smaller than that of the coated DD32M at 1000 °C. The oxidation exponents n at 900 °C and 1000 °C were both about equal to 0.5, which indicate the parabolic time dependence of the growth mass. Both the initial and