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Deposition of a B-modified silicide coating for Nb-Si based alloy oxidation protection

Wei Shao, Wan Wang, Chungen Zhou*

Department of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Key Laboratory of Aerospace Materials and Performance (Ministry of Education), Beijing 100191, China

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ABSTRACT

A B-modified silicide coating was prepared on the Nb-Si based alloy by Si-TiB_2 co-deposition at 1300 °C for 10 h. The results show that the two-layer coating is composed of a (Nb, X)Si_2 (X represents Al, Cr, Ti and Hf) + $NbTiB_4$ outer layer and a (Nb, X)Si_2 + Cr_2Nb inner layer. Static oxidation tests indicate that the mass gain of B-modified silicide coating was 2.39 mg/cm^2 after oxidation at 1250 °C for 100 h. The good oxidation resistance is attributed to the formation of a continuous and dense scale mainly consisting of glassy borosilicate.

1. Introduction

Nb-Si based superalloys are regarded as the promising candidates for high-temperature structural materials due to their high melting points (>1750 °C), low densities (6.6–7.2 g/cm^2) and good mechanical properties at high temperatures [1,2]. However, poor oxidation resistance seriously restricts the practical application of Nb-Si based superalloys [3,4]. Nb-Si based alloys can be oxidized and form unprotected porous oxides such as Nb_2O_5, $TiNb_2O_7$ and TiO_2 which cannot stop the inward diffusion of oxygen at elevated temperatures in oxidizing environment [5,6]. Based on the above, there are mainly two methods to improve the oxidation resistance of Nb-Si based superalloys including alloying treatment and oxidation-resistant coating. Alloying may alleviate oxidation, but alloying elements degrade the mechanical properties of substrates beyond some certain range and the improvement is not enough for the need of actual high-temperature applications under stringent environment condition. And coating is better for the improvement of oxidation resistance because it can not only enhance the oxidation resistance of substrates effectively, but also allow for the substrates to retain their mechanical properties [7].

Satisfactory oxidation-resistant coatings should be dense, adherent and slow-growing in order to impede the inward diffusion of oxygen [8]. Silicide coatings have been found suitable for protecting Nb-Si based superalloys at high temperatures due to their low densities, high melting points and self-healing ability. But binary niobium silicide coatings have limited oxidation resistance for the formation of unprotected Nb_2O_5 under oxidizing environments [9]. Therefore, many studies have been carried out to develop modified silicide coatings [10–16]. The addition of B_2O_3 solute into SiO_2 results in the formation of a glass borosilicate with higher fluidity at low temperature to heal cracks and the coefficients of thermal expansion for borosilicate are also significantly higher than that of pour SiO_2 to minimize spalling of the scale. Guo et al. [16] prepared the B-modified silicide coating containing a NbB_2 outer layer with elemental B as boron source on Nb-Si based alloy and the mass gain of the B-modified silicide coating was 2.8 mg/cm^2 after oxidation at 1250 °C for 100 h. Moreover, Cockeram et al. [17,18] investigated the growth and oxidation resistance of B-modified silicide coatings on Ti based alloy. From their research, it can be concluded that the weight gain for the B-modified silicide coating obtained by using TiB_2 as boron source is lower than that produced with B as boron source. Nevertheless, few studies have focused on the formation mechanism and the oxidation behavior of B-modified silicide coating prepared with TiB_2 as boron source on Nb-Si based superalloys.

Thus, the objective of the present study is to identify the formation mechanism of the coating prepared with Si and TiB_2 as the source of Si and B. Moreover, the oxidation behavior of B-modified silicide coating has also been investigated.

* Corresponding author.
E-mail address: cgzhou@buaa.edu.cn (C. Zhou).

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2. Experiment

2.1. Specimen preparation

The alloy with nominal composition of Nb-16Si-22Ti-17Cr-2Al-2Hf (at.%) was prepared by arc-melting using a non-consumable electrode in argon atmosphere and remelted for 5 times to ensure composition homogeneity. Then the alloy was remelted in a vacuum induction furnace and cast to be a vacuum induction melting (VIM) ingot. Finally, the ingot was annealed at 1250 °C for 50 h in a vacuum of 10^{-3} Pa so as to obtain a stable microstructure, which is composed of Nb_{ss}, $(Nb, X)_5Si_3$ and Cr_2Nb phases.

After the melting process, the ingot was cut into samples with the size of 8 mm × 8 mm × 3 mm by wire-electrode machining. All six sides of each specimen were ground with silicon carbide papers up to 800-grit. The specimens were ultrasonically cleaned in ethanol for 20 min.

2.2. Coating process

B-modified silicide coating was prepared by pack cementation in a powder mixture of 8Si-8TiB_2-5NaF-79Al_2O_3 (wt.%). Powders were weighed accordingly and mixed uniformly. The pack mixture and specimens were embedded in a cylindrical alumina retort and the specimens must be surrounded by the pack. The cylindrical alumina retort was sealed with an alumina lid and cement. After that, the retort was put into an alumina tube furnace surrounded by argon. In case of steady flow of argon, the retort with pack and specimens was heated to 1300 °C at a heating rate of 5 °C/min, sustained at 1300 °C for 10 h, and cooled down to room temperature naturally. The coated specimens were retrieved from the pack and ultrasonically cleaned in ethanol bath. All the detailed experiment procedure is also presented in our previous papers [19,20].

2.3. Oxidation tests

In order to evaluate the oxidation resistance of the B-modified silicide coating on Nb-Si substrate, static oxidation tests of the substrate and specimens with B-modified silicide coating were conducted.

The oxidation tests were carried out at 1250 °C in an open-ended tube furnace in air. The specimens for oxidation tests were taken out to weigh the mass change at intervals of 10, 20, 40, 60, 80, 100 h using an analytical balance (Model CPA225D, Germany) with the accuracy of 10^{-5} g. Three specimens for weight gain measurement at each time were taken and weight gain for three specimens was averaged.

2.4. Analyzing methods

The microstructures and phase compositions of as-packed coating and oxidized scales were analyzed. The phase compositions were identified by X-ray diffraction (XRD, Model D/M-2500PC Rigaku, Japan) with Cu Kα radiation. The microstructural characterization was carried out by scanning electron microscope (SEM, Model CamScan-3400) equipped with energy dispersive spectroscopy (EDS) and electron microprobe analysis (EPMA, Model JXA-8230, Japan, the spot diameter is 1 μm and the operation voltage is 20.0 kV) with wave dispersive spectroscopy (WDS). Moreover, in order to obtain the detailed microstructure of coating, TEM cross-sectional samples were prepared and observed by a transmission electron microscopy (TEM, Model JEM-2100) equipped with EDS. In the preparation process of the TEM samples, a film was removed from the coated specimen. Then the film was cut into 1 mm × 2 mm × 2 mm cubes and two cubes were glued together with the coating facing each other. After the glue was cured, the specimen was ground with silicon carbide papers up to 3000-grid until the thickness of the specimen was less than 50 μm. Then the specimen was bonded to a Mo aperture grid (1.5 mm inner and 3 mm outer diameter) and ion milling was utilized to prepare the transparent area for TEM investigation.

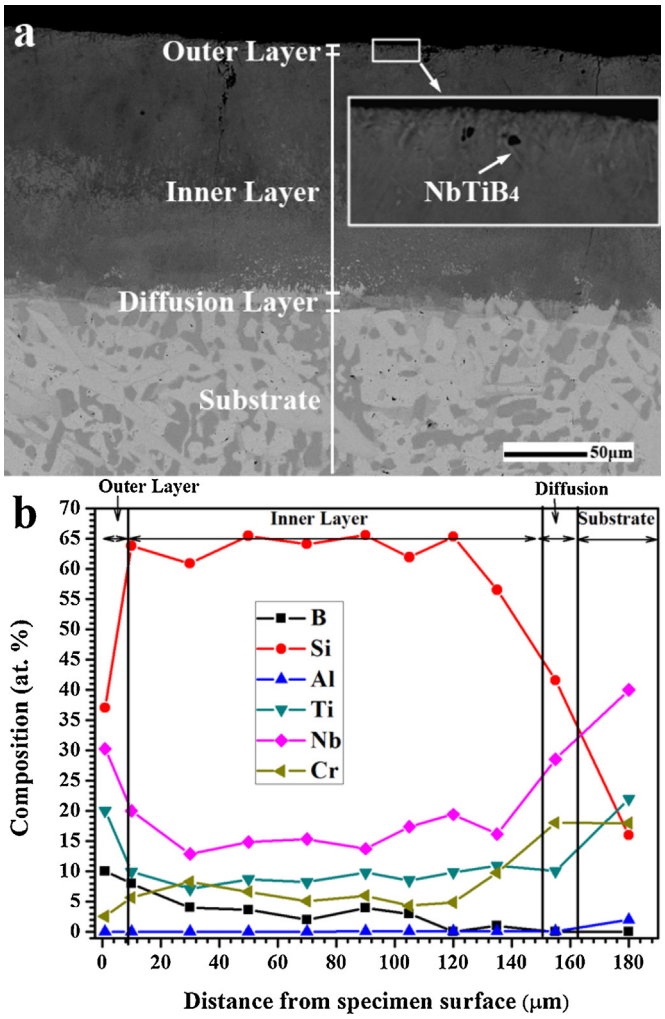

Fig. 1. (a) Cross-sectional BSE image and (b) major elemental concentration profiles of B-modified silicide coating prepared at 1300 °C for 10 h.

3. Results

3.1. Microstructure of the B-modified silicide coating

Fig. 1 illustrates the cross-sectional microstructure and major elemental concentration distributions of B-modified silicide coating prepared at 1300 °C for 10 h. As shown in Fig. 1(a), the B-modified silicide coating is composed of an outer layer, an inner layer and a diffusion zone. It can be seen that the thicknesses of the outer layer, inner layer and diffusion zone are approximately 9 μm, 141 μm and 12 μm, respectively. Accordingly, Fig. 1(b) reveals the element composition of the specimen. Three different positions in the same distance from the coating surface are detected by EDS and the average is taken. Fig. 1(b) demonstrates that the concentration of Si in the coating increases distinctly, while the concentration of Nb, Ti and Cr decreases noticeably compared to the composition of substrate. The presence of Nb in the outer layer suggests that the formation of the coating is primarily attributed to the inward diffusion of Si and B. In order to verify the distribution of the B, Ti, Nb, Si and Cr, the elemental maps of the prepared coating are shown in