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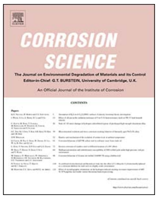

Oxidation behavior of the B-modified silicide coating on Nb-Si based alloy at intermediate temperatures

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ABSTRACT

A B-modified silicide coating on Nb-Si based alloy was prepared by the method of pack cementation. The oxidation resistance of the B-modified silicide coating was studied in the pest-oxidation temperature range (from 650 °C to 850 °C). Oxidation experiments show that the samples coated with B-modified silicide coating maintain low-rate oxidation and suffer from no pest oxidation at all experimental temperatures. The preferential oxidation of Ti and Si can suppress the formation of Nb_2O_5. Besides, the borosilicate scale with high fluidity can seal the cracks and pores in the scale. Thus, the occurrence of pest catastrophe is avoided.

1. Introduction

Nb-Si based alloys are a promising candidate for hot sections of turbine engines because of their several advantages such as high melting points, high fracture toughness at room temperatures and good strength at elevated temperatures [1–3]. However, Nb-Si based alloys suffer from a catastrophic phenomenon at moderate temperatures [4], called pesting, and have inferior oxidation resistance at elevated temperatures due to the formation of non-protective Nb_2O_5. The poor oxidation resistance limits their application to a great extent [5]. As a result, researchers have concentrated on the improvement of the oxidation resistance of Nb-Si based alloys for many years and have found that the addition of alloying elements and the preparation of coatings may be helpful [6–8]. Although significant improvement in oxidation behavior is obtained, the alloying addition makes the sacrifice of the room-temperature fracture toughness and creep property [9]. Therefore, the formation of suitable protective coating is considered a preferred method to improve oxidation resistance of Nb-Si based alloys.

Silicide and aluminide coatings have been found suitable for improving the high-temperature oxidation performance on Nb-Si based alloys. In comparison with aluminide coatings, silicide coatings can operate better due to their high application temperatures, good thermal stability and mechanical property at high temperatures. The component of silicide coatings on Nb-Si based alloys mainly consists of $NbSi_2$ which possesses good high-temperature capability due to the formation of a protective and glassy silica scale on the substrate. However, $NbSi_2$ may be subjected to pest disintegration which results in catastrophic fragmentation of the samples at intermediate temperatures especially at 750 °C [10]. Until now, there is no clear understanding of the pest oxidation of $NbSi_2$. Zhang et al. [11] compared the oxidation process of poly and single crystalline $NbSi_2$ at 750 °C and drew a conclusion that pest disintegration was mainly determined by the pre-existing cracks in the microstructure. But Kurokawa et al. [12] reported that pest oxidation of $NbSi_2$ occurred due to the transformation of SiO_2 from amorphous to crystalline. Efforts have been made to eliminate the pest oxidation of $NbSi_2$. The work by Geng et al. [4] showed that the oxidation resistance of Nb-Si based alloys at 800 °C could be improved significantly by additions such as Mo and Ti. In the open literatures, Al, Y, B, Ge etc. were also added as modified elements into the silicide coatings and the results verified that these elements could enhance the oxidation resistance of the substrate at high temperatures [1,13–15].

Among these coatings, B-modified silicide coatings were prepared on Nb-Si based alloys [16–18] and the oxidation resistance of Nb-Si based alloys at high temperatures was improved dramatically due to the formation of self-healing and dense borosilicate. The introduction of B_2O_3 to the silica scale could decrease the viscosity of SiO_2 [19] and also led to a higher coefficient of thermal expansion [20]. The oxidation resistance of boronized $MoSi_2$ at 500 °C was investigated by Yokota et al. [21] and results showed that no pest disintegration was observed and boronizing could improve the low-temperature oxidation resistance of $MoSi_2$. Thus, boron is supposed to have similar effect on the oxidation behavior on $NbSi_2$.

However, few literatures have reported any research on the oxidation behavior of B-modified silicide coatings among the pest oxidation temperature range. Thus, the object of the paper is to study the oxidation kinetics and oxidation mechanism of the B-modified silicide

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coatings at moderate temperatures.

2. Experimental method

2.1. Specimen preparation

The Nb-Si based alloy used for the coating and oxidation experiments was firstly prepared by non-consumable arc-melting under an argon atmosphere with a chemical composition of Nb-16Si-22Ti-17Cr-2Al-2Hf (at.%). The alloy was then re-melted for 5 times to ensure composition homogeneity and element partition. Then the ingot was cast in a vacuum induction furnace. After solidification, the vacuum induction melting (VIM) ingot was annealed in vacuum at 1250 °C for 50 h, which ensured the equilibrium microstructure. The microstructure of the alloy consisted of Nb_{ss}, $(Nb, X)_5Si_3$ and Cr_2Nb [22].

Prior to coating deposition, each sample was cut into coupons of $8 \times 8\,mm^2$ and 3 mm in thickness. Then the coupons were abraded from 60-grit to 800-grit using SiC paper to get a relatively rough and clean surface, followed by degreasing ultrasonically in acetone for 20 min.

2.2. Coating process

Silicon and boron were simultaneously deposited through a pack cementation process. The experimental apparatus and the handling procedures for coating were identical with previous articles [15,23]. The powder mixture used for pack cementation consisted of 8 wt.% Si, 8 wt.% TiB_2, 5 wt.% NaF and the remainder Al_2O_3 powder. The samples were then placed in a cylindrical alumina retort and completely immersed in the powder mixture. The retort was placed in an alumina tube furnace. Argon of high purity (99.99%) was filled into the furnace chamber as a protective atmosphere.

Under a steady flow of argon, samples were heated up to 1300 °C at a heating rate of 5 °C/min, kept at 1300 °C for 10 h and then cooled down to room temperature at 5 °C/min. After deposition, the coated specimens were retrieved from the pack and cleaned ultrasonically in ethanol before oxidation experiments.

2.3. Oxidation tests

For the short-time (10 min, 30 min, 1 h, 5 h and 20 h) and long-time (100 h) exposure, the oxidation experiments were performed using an open-ended tube furnace in dry air at 650, 700, 750, 800 and 850 °C, respectively. Samples were held in the hot zone of the furnace with alumina crucibles. In the long-time experiments, the weight gains of samples were measured at intervals of 1, 5, 10, 20, 40, 60, 80 and 100 h using an analytical balance (Model CPA225D, Germany) of 10^{-5} g accuracy to analysis the oxidation kinetics. The mass gains of the specimens were obtained by taking the average of three specimens.

2.4. Sample characterization

In order to understand the oxidation mechanisms, the microstructure and composition of the coating and oxidation products were analyzed from the surface and cross-section. Before observation, the cross-sections were abraded on wet SiC paper up to 2000-grit and finally polished on a tightly woven cloth with 2.5 μm diamond abrasives. X-ray diffraction (XRD, Model D/M-2500PC Rigaku, Japan) operated at 40.0 kV and 200 mA with Cu Kα radiation (1.5418 Å) was employed to identify the phases in the as-prepared coating and in corrosion products. For microstructural observation, micrographs were taken by scanning electron microscope (SEM, Model CamScan-3400 and FEI Quanta 200F) 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). Chemical component of the scale surface was examined using Auger electron spectroscopy (AES, Model PHI 710) after the removal of the absorption layer on the surface of the oxide scale. In addition, detailed microstructure of oxidation products was observed by a transmission electron microscopy (TEM, Model Tecnai G^2 F30 S-TWIN) equipped with EDS.

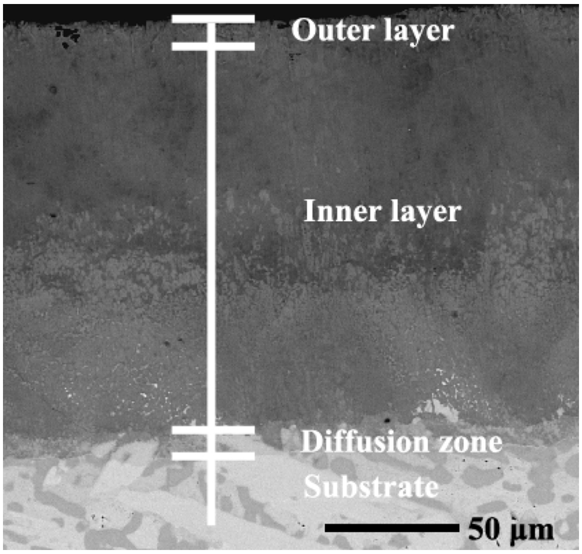

Fig. 1. The cross-section microstructure of B-modified silicide coating.

3. Results and discussion

3.1. Microstructure of B-modified silicide coating

The cross-sectional microstructure of B-modified silicide coating is presented in Fig. 1. It reveals that the as-deposited coating possesses a $(Nb, X)Si_2$ (X represents Cr, Ti and Hf) + $NbTiB_4$ outer layer and a $(Nb, X)Si_2$ + Cr_2Nb inner layer. The thickness of outer layer is about 9 μm and it is 141 μm for the inner layer. B and Ti mainly distribute in the outer layer while Cr exists in the inner layer. There is a diffusion zone between the coating and the substrate. The phases in diffusion layer are mainly $(Ti, Nb)_5Si_4$ and $(Nb, X)_5Si_3$. More details of the coating can be referred to Ref. [16].

3.2. Oxidation kinetics of the coating

The oxidation kinetics of B-modified silicide coated specimens exposed to different temperatures are shown in Fig. 2. It is noticeable that there is no pest phenomenon and the mass gains are little at all the experimental temperatures. The mass gains of the specimens are given in Table 1. Among the temperatures, the mass gain of the coating grows with a decreasing trend with time prolonging. It rises slowly from $0.17\,mg/cm^2$ at 650 °C to $0.77\,mg/cm^2$ at 850 °C as temperature develops. Oxidation is a particular case of the diffusion of an element from a gaseous atmosphere and an ensuing chemical reaction with the formation of a compound [24]. Fig. 2b shows that at initial time, the oxidation kinetics of the coated specimens approximately follow the linear law. Oxygen is easy to reach the surface of the coating. Sufficient oxygen can lead to high rate of oxidation which corresponds to the fast increase of the mass for very short time. As a result, the mass gains of the B-modified silicide coatings are controlled by oxidizing reactions. With the oxidation process going on, the diffusion of oxygen in the oxide scale becomes difficult and diffusion is the rate-limiting process. As a result, the weight gain increases tardily. Fig. 2c indicates that the weight gains obey the parabolic rate law. It can be deduced that the B-modified silicide coating is protective at moderate temperatures.