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Microstructural evolution and oxidation behaviour of Mo-Si-B coatings on an Nb-16Si-22Ti-7Cr-2Al-2Hf alloy at 1250 °C prepared by spark plasma sintering

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ABSTRACT

Mo-Si-(5, 10, 15)B ternary coatings were firstly coated on an Nb-Si based alloy using the spark plasma sintering technique. The Mo-Si-B coatings consisted of an outer $MoSi_2/MoB/SiO_2/Mo_2B_5$ (Mo_5Si_3) layer and an inter-diffusion zone, while SiO_2 was formed during SPS. The oxidation kinetics curves exhibited parabolic time dependence and 5B coating had the lowest mass gain of approximately 0.41 mg/cm^2 after oxidation at 1250 °C for 100 h. The good oxidation resistance results from a dense and protective borosilicate layer formed on coatings and the low growth rate of the inter-diffusion zone beneath the Mo-Si-B coatings.

1. Introduction

Nb-Si base alloys have great potential for use as high-temperature materials in next-generation airplane engines because of their low density, high melting point and excellent strength at temperatures higher than 1250 °C [1–4]. However, disastrous oxidation of the Nb-Si based alloys limits their practical applications at ultra-high temperatures [5,6]. The Nb-Si based alloys can be oxidized quickly due to the formation of porous oxides such as Nb_2O_5 and TiO_2 [7,8]. Therefore, improving oxidation resistance is one of the most important issues for the development of the Nb-Si based alloys with balanced properties of room temperature toughness, high-temperature strength and stability in service environment, and the alloying and coating techniques are the most effective approaches for improve the oxidation resistance of the Nb-Si based alloys. By a alloying with elements such as Cr, Al, Hf, B, the high-temperature oxidation resistance of the Nb-Si based alloys has been found to be obviously improved owing to the formation of the Laves Cr_2Nb intermetallic compound [9], while the Laves Cr_2Nb is the well-known phase that acts against the attack of oxygen [9]. Unfortunately, the multi-component Cr_2Nb phase has a low melting point and decreases the strength of the bulk Nb-Si based alloys at the temperatures beyond 1200 °C [10]. Recently, the development of modified silicide coatings on the Nb-Si based alloys has been prominently investigated for improving the oxidation resistance of the Nb-Si based alloys [11–13]. In the oxidizing environment, the modified silicide coatings can quickly form dense, adherent and flexible oxide scales that offer a promising approach to maintain the long-term environmental stability of the Nb-Si based alloys at high temperatures [11]. Meanwhile, the mechanical properties of the Nb-Si substrates cannot be degraded by the oxidation-resistant coatings [14].

It is possible to coat the Nb-Si alloys with various oxidation-resistant materials with thermal expansion coefficients that are close to those of the substrates [15,16]. A Y- and Al-modified silicide coating on the Nb-Si based alloy prepared by the pack cementation technique was found to show the mass gain of approximately 1.66 mg/cm^2 after oxidation at 1250 °C for 20 h [12]. A Ge- and Y-modified silicide coating coated on the Nb-Si based alloy by Si-Ge-Y co-deposition at 1300 °C showed the mass gain of 2.78 mg/cm^2 after oxidation at 1250 °C for 100 h [11]. A Mo-Si-B coating obtained by the deposition a molybdenum layer followed by Si and B co-deposition [17] showed better oxidation resistance than the two Y-, Al- and Ge-modified silicide coatings mentioned above. After oxidation at 1250 °C for 100 h, the mass gain of Mo-Si-B coating was only 0.92 mg/cm^2. The better oxidation resistance for the Mo-Si-B coating results from the rapid formation of a dense and self-healing protective borosilicate scale on the coating in the oxidation environment.

Unfortunately, the silicide coatings prepared using the pack cementation and the co-deposition techniques were not dense and their composition could not be precisely controlled [17]. These coatings also showed several other drawbacks such as the flaws and holes within the coating [12,17], which may act as the channels for the oxygen inward diffusion, and subsequently degraded the environmental stability of the

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silicide coatings. Spark plasma sintering (SPS) is a technology in the powder metallurgy field. The Nb-Si or Mo-Si-B samples treated by SPS show a homogeneous and controlled microstructure (including morphology, fraction and size of the constituent phase and bulk composition) with few defects obtained by the modification of the size, fraction and composition of the original powders [18–20]. The relative densities of the SPS-processed samples are usually larger than 99%, resulting in designable mechanical and oxidation properties [20]. It was reported that an $MoSi_2$ binary coating was processed by SPS on a pure Nb substrate and the mass gain of the coating was 0.25 mg/cm^2 after oxidation at 1300 °C for 80 h [16]. During the oxidation processing at 1300 °C, cracking and spallation of the SiO_2 scale formed on the $MoSi_2$ binary coating did not occur. However, the $MoSi_2$ binary phase usually oxidizes severely at temperatures between 400 °C and 600 °C, which can lead to "pest failure", i.e., cracking and powdering of the $MoSi_2$ coating to a disastrous collapse [21]. The addition of B to develop a ternary Mo-Si-B system usually introduces B_2O_3 oxide into SiO_2 and results in the formation of a protective glass borosilicate layer with higher fluidity at low temperature on the Mo-Si-B surface that heals the cracks and accelerates the formation of the oxide layer [22–24]. This glass borosilicate layer is effective for resolving the "pest failure" problem of the Mo-Si binary system in oxidative environments at the of 400–600 °C temperature range [25].

To date, little work has been done to prepare the Mo-Si-B ternary coatings on the Nb-Si based substrates using the SPS technique. The oxidation behaviour of the Mo-Si-B coatings on the Nb-Si based alloy prepared by SPS is not yet known. In this work, the Mo-Si-B coatings with a fine microstructure was firstly coated on an Nb-Si based alloy using spark SPS to obtain a dense microstructure with few defects, and the microstructural evolution of the coatings and the interface between the coatings and the substrate before and after the oxidation was investigated. The compositions of the coatings can be quantitatively controlled by adjusting original compositions of the powders used for the SPS processing. Therefore, three kinds of the coated specimens with 5B, 10B and 15B are designed and the oxidation behaviour of the Mo-Si-B coatings dependence on the different B content at high temperatures was identified.

2. Experimental procedures

2.1. Preparation of substrate specimen

The substrate alloy was prepared using a non-consumable electrode under an argon atmosphere with the nominal compositions of Nb-16Si-22Ti-7Cr-2Al-2Hf (at.%). The alloy was re-melted and cast in a vacuum induction furnace and then annealed at 1250 °C in the vacuum furnace to obtain a stable microstructure composed of the Nb solid solution (Nb_{SS}) and silicide $(Nb,Ti)_5Si_3$ [26]. The substrates with the size of Φ 8.5 mm × 3 mm were cut from the annealed ingot using by wire-electrode machining. All sides of substrate were ground up to 1500-grit with water. The surface of samples were cleaned with ethanol by ultrasound and then dried by air blower for 5 min.

2.2. Processing of coatings

Button ingots with the nominal compositions (at.%) of Mo-62Si-5B, Mo-57Si-10B and Mo-52Si-15B were prepared by arc-melting with Mo, B and Si raw powders with purity higher than 99.95 wt% under argon atmosphere. To obtain alloy powders, the arc-melted ingots were manually crushed and ball-milled until the powder size was low than 5 μm. Ball milling (BM) was milled using a planetary ball mill (QM-QX, NanDa Instrument Plant, China) under an argon atmosphere. The ball-to-powder weight was maintained at 8:1 and the rotation speed was 400 rpm. The three BM alloy powders were used as starting materials of coatings and their D_{50} values were in the 2–4 μm range [20,27]. For the SPS process, 0.5–0.8 g alloy powders were evenly spread on the bottom of a graphite die with the diameter of 10 mm, then an Nb-Si substrate specimen was placed on the powders and finally, the 0.8–1.2 g Mo-Si-B alloy powders were poured into the die to uniformly cover the substrate specimen. The preparation of the Mo-Si-B coatings on the Nb-Si substrate is schematically illustrated in Fig. 1. Note that graphite foils were used as spacers to separate the alloy powders from the graphite die. The coatings were sintered at 1400 °C for 5 min under 50 MPa in an argon atmosphere using a spark plasma sintering system (Model 1050). After the proper sanding of the specimen surfaces, three kinds of the coated specimens, referred as to the 5B coating (coated with Mo-62Si-5B alloy powders), 10B coating (coated with Mo-57Si-10B alloy powders) and 15B coating (coated with Mo-52Si-15B alloy powders), were obtained.

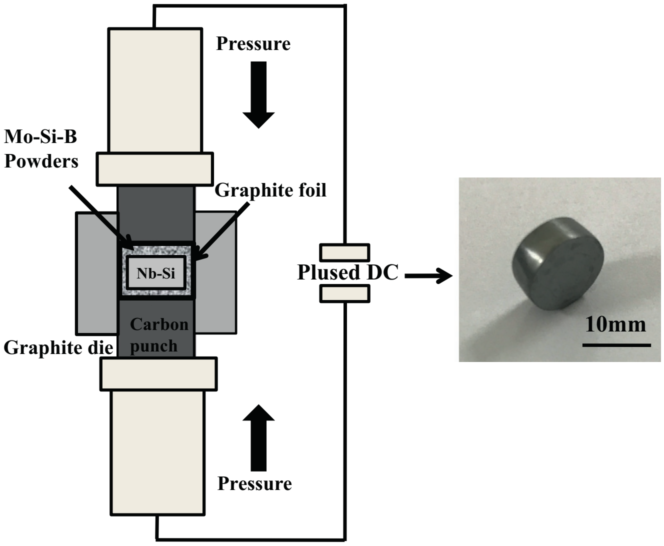

Fig. 1. Schematic drawing of Mo-Si-B coating fabricated by SPS and the SPS-coating sample.

2.3. Oxidation tests

The substrates (without coatings) and the coated samples were oxidized in order to evaluate the role of the Mo-Si-B coatings in the high-temperature oxidation behaviour. Isothermal static oxidation tests were carried out at 1250 °C for 100 h in an open-ended tube furnace in air. The alumina crucible was used for setting the specimen. The mass gains of the oxidation specimens were measured at the intervals of 5, 10, 20, 50, 80, 100 h using an analytical balance with an accuracy of 10^{-5} g (Model CPA225D, Germany). Three specimens for weight gain measurements were used at each oxidation time to get the average values. An additional batch of each specimen was isothermally oxidized for 0.5, 1, 2, 5, 20, 50 and 100 h, respectively, to investigate the oxidation mechanism and the structural evolution of oxide layer.

2.4. Characterizations

The oxidized specimens were cut from the middle line and mounted in cold setting resin, and then the cross-sections of the mounted specimens were mechanically polished for the observation of the microstructures of the oxide product layer on the substrate. The phase and the microstructural evolution of the coatings and the oxide layers were identified by X-ray diffraction (XRD, Model D/M-2500PC Rigaku, Japan) using Cu Kα radiation and by field emission scanning electron microscopy (SEM, Model 200F, Holland), respectively. The phase composition was analysed using an electron microprobe analysis instrument (EPMA, Model JXA-8230, Japan, the spot diameter is 1 μm). Raman spectroscopy (LabRAM HR Evolution, French) was operated with an excitation wavelength of 532 nm laser to detect the surface on