Corrosion Science 80 (2014) 164–168

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Formation and oxidation resistance of germanium modified silicide coating on Nb based in situ composites

Wan Wang, Bifei Yuan, Chungen Zhou *

Department of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100191, China

ARTICLE INFO

Article history:
Received 19 July 2013
Accepted 19 November 2013
Available online 26 November 2013

Keywords:
A. Intermetallics
A. Metal coatings
C. Oxidation

ABSTRACT

Ge-modified silicide coating was prepared on the Nb–Si based alloy by Si–Ge co-deposition at 1300 °C for 10 h. The pack powder for co-deposition consisted of 16Si–8Ge–5NaF–71Al_2O_3 (wt.%). It is observed that the coating is composed of an outer layer and a transitional layer. The mass gain of substrate and Ge-modified silicide coating are 190.08 and 5.42 mg cm^{-2} after oxidation at 1250 °C for 100 h, respectively. The coating can prevent substrate from oxidizing efficiently. The good oxidation resistance is attributed to the formation of glassy GeO_2 and SiO_2.

1. Introduction

The Nb–Si based alloys are composed of Nb solid solution (Nb_{SS}) and Nb_5Si_3 silicide. The Nb_{SS} and Nb_5Si_3 silicide have different properties, and they are called in-situ composites when they combine through eutectic reaction [1,2]. Nb based in situ composite has great potential as high temperature materials because of their low density, high melting points and high strength at high temperatures. However, a major barrier to the high temperature applications of the Nb based alloys is their poor oxidation resistance [1–7]. Although previous works have shown that the oxidation resistance of the Nb based in situ composite can be improved obviously by adding alloying elements such as Cr, Al, Hf, Sn and B [8–10], further alloying with especially beneficial elements like Al and Cr often lead to deterioration of mechanical properties, also the improvement is not enough for the need of actual high-temperature applications in oxidizing environments. It is now generally recognized that deposition of coatings that can form dense, adherent and slow-growing oxide scales offer the most promising approach to improving long term environmental stability at high-temperatures [11].

Many studies have focused on silicon as the coating material for Nb based high temperature alloys by pack cementation, hot dipping, molten salt, and slurry method [12–15]. Among these techniques, the pack cementation has been the most widely used process for preparing the silicide coating. There is $NbSi_2$ coating formed at the surface when silicon was deposited onto the substrate. When it was heated in the open air at high temperatures, the protective coating SiO_2 was formed. SiO_2 is a glassy substance and it will stop the oxygen coming further into the substrate. However, micro-cracks formed in the coatings due to mismatch in the coefficients of thermal expansion between the silicide coatings and the substrates, which becomes a serious problem to hinder the long-term applications of $NbSi_2$ coatings. Therefore, it is essential to develop modified silicide coatings with less micro-cracks and excellent high temperature oxidation resistance [16].

To achieve better oxidation resistance, many studies have been carried out using the pack cementation process to develop the silicide coatings modified with elements such as Al, B and Cr [16–19]. Recent investigation indicated that, the GeO_2 decreases the SiO_2 glass viscosity at high temperatures which results in a better sealant and greatly increases the expansion coefficient [20,21]. However, very little work has been carried out on the silicide coatings modified with Germanium on Nb based in situ composite. Therefore, the objective of the present work is to produce the Ge-modified silicide coating on Nb based in situ composites and to investigate the oxidation behavior of the coating.

2. Experimental part

2.1. Specimen preparation

The alloy Nb–16Si–22Ti–17Cr–2Al–2Hf (at.%) was prepared by arc melting, a mixture of high purity niobium, titanium, chromium, aluminum, silicon and hafnium in arc furnace under an argon atmosphere. To ensure composition homogeneity and element partition, the ingot was inverted and remelted more than five times. After solidification, the ingot was annealed under argon gas atmosphere at 1250 °C for 50 h in order to obtain a stable

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* Corresponding author. Tel.: +86 10 82338622; fax: +86 10 82338200.
E-mail address: cgzhou@buaa.edu.cn (C. Zhou).

0010-938X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.corsci.2013.11.029

microstructure. The alloy ingot was machined to slices of approximately 12 mm in diameter and 3 mm in thickness. The samples were ground with silicon carbide paper to 800 grit and then ultrasonically cleaned in acetone.

2.2. Coating process

The components for the pack cementation process consisting of Ge, Si powder, halide activator (NaF) and inert filter (Al_2O_3 powder) were weighed, mixed and ground. The average particle sizes of Ge, Si, NaF and Al_2O_3 powders were all less than 100 mesh. The pack 16Si–8Ge–5NaF–71Al_2O_3 (wt.%) was used to co-deposite Si and Ge. Packs were prepared by burying the substrates in a well-mixed pack powder mixture in a cylindrical alumina retort of 20 mm diameter and 35 mm length, which was then sealed with an alumina lid and cement. After that, the pack was loaded into an alumina tube furnace circulated with argon. The furnace was raised to 1300 °C at a heating rate of 5 °C min^{-1} and sustained for 10 h, then, cooled down to room temperature naturally by switching off its power supply while keeping the gas–argon flowing. The coated specimens were retrieved from the pack and cleaned in an ultrasonic water bath to remove any residual powders on their surfaces.

2.3. Oxidation tests

In order to evaluate the protective effects of Si–Ge coating on substrate, the oxidation experiments of substrate, purely siliconized coating and Si–Ge co-deposition coating specimens were performed. The substrate was also sliced into buttons with 12 mm in diameter and 3 mm in thickness, the surface was ground to an 800 grit finish. The specimen was then degreased and cleaned by ultrasonic. The substrate and the as-coated specimen were put in alumina lids which were degreased and cleaned by ultrasonic respectively.

The oxidation tests were conducted in an open-ended tube furnace with air as the oxidizing atmosphere at 1250 °C. The specimens were taken out of the furnace to cool at room temperature for a weight measurement at intervals of 1, 7, 10, 20, 40, 60, 80, 100 h and then back into the furnace to continue the oxidation tests. The total period of the oxidation experiment was 100 h. The mass gains of these specimens are measured by a precision analytical balance (Model CPA225D, Germany) with an accuracy of 10^{-5} g. Three measurements for weight gain at each time were taken and averaged.

2.4. Analyzing methods

X-ray diffraction (XRD, Model D/Max 2500PC Rigaku, Japan) analysis, scanning electron-microscopy (SEM, Model FEI Quanta600, USA) with energy-dispersive spectroscopy (EDS), electron microprobe analysis (EPMA, Model JXA-8230, Japan) with wave-dispersive spectroscopy (EDS) were used to identify the phase constituents, compositional distribution.

3. Results and discussions

3.1. Microstructure of coating

Fig. 1 presents the cross-sectional microstructure and concentration distribution of the as-coated specimen held at 1300 °C for 10 h. The coating structure is divided into an outer layer and a transitional layer underneath. From Fig. 1(a), it can be seen that the depths of outer layer and transitional layer approximately are 165 μm and 11 μm, respectively. The composition of outer layer is about 58.93Si–12.44Ti–9.71Cr–2.54Ge–15.47Nb–0.13Al–0.78Hf (at.%) by energy dispersive spectroscopy. Through the surface X-ray diffraction (XRD) (Fig. 2a), the outer layer is consist of (Nb, X)(Si, Ge)$_2$ (X represents Ti, Cr, and Hf elements). The composition of transitional layer is about 38.02Si–22.73Ti–6.47Cr–3.72Ge–27.96Nb–1.1Hf (at.%) by energy dispersive spectroscopy. Through the surface X-ray diffraction (XRD) (Fig. 2b), it is proved that the transitional layer is mainly consist of (Nb, X)$_5$(Si, Ge)$_3$. The presence of Nb in the outer layer through Fig. 1(b) suggests that the formation of the coating is primarily attributed to the

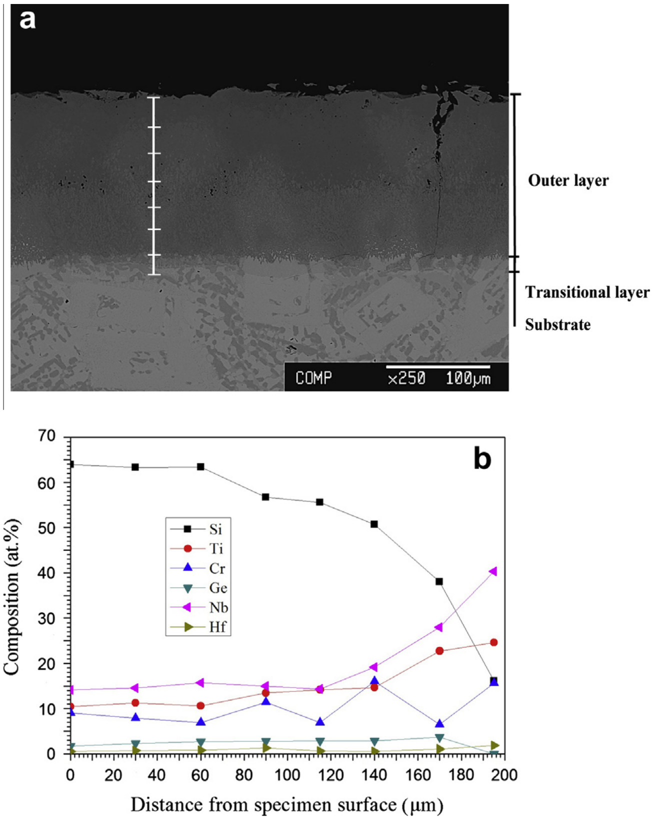

Fig. 1. Cross-sectional SEM image (a) and major elemental concentration profiles and (b) in the Ge-modified silicide coating formed at 1300 °C for 10 h.

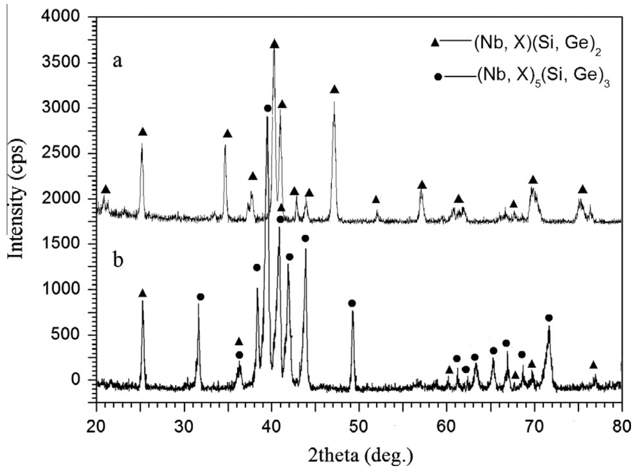

Fig. 2. XRD patterns conducted on the original surface (a) and the surface after the coating being stripped off 165 μm (b) respectively of the Ge modified silicide coating prepared at 1300 °C for 10 h.