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Improvement in the oxidation resistance of Nb–Ti–Si–Cr–Al–Hf alloys containing alloyed Ge and B

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ABSTRACT

The oxidation behaviour for Nb–Si based alloys was performed in air at 1200 °C and 1250 °C. The weight gains of Nb–24Ti–15Si–13Cr–2Al–2Hf (at.%) alloy and Nb–24Ti–15Si–13Cr–2Al–2Hf–4B–5Ge (at.%) alloy after oxidation at 1250 °C for 100 h were 156.7 mg/cm^2 and 32.5 mg/cm^2, respectively. The oxide scale of the Nb–24Ti–15Si–13Cr–2Al–2Hf (at.%) alloy was porous and loose, while that of the Nb–24Ti–15Si–13Cr–2Al–2Hf–4B–5Ge (at.%) alloy was dense and protective. The presence of alloyed B and Ge improved the protective SiO_2 phase grown during high temperature oxidation, leading to the formation of a continuous and dense oxide scale.

1. Introduction

The Nb–Si based alloys have been widely studied recently due to their attractive properties such as low density, high melting point and high temperature strength [1–3]. However, the widespread use of Nb–Si based alloys in aircraft, missiles, and certain reactors is limited because their oxidation resistance is still inadequate for structural applications [1–4].

In order to achieve a balance of properties for structural use such as high temperature strength and good oxidation resistance, a multi-component Nb–Si–Ti–Hf–Cr–Al system has been developed by General Electric Co. [2,3]. In this system, the phase constitutions are silicides, Cr_2Nb and Nb solid solution (Nb_{SS}) (the elements mainly solute in Nb are Ti and Cr). This system is of interest because the low temperature fracture toughness can be improved by Nb_{SS} and the high temperature strength and good oxidation resistance can be anticipated from the silicides and Laves phase [5–9].

One of the difficulties encountered in the oxidation resistance of Nb–Si based alloys is the formation of non-protective oxides (Nb_2O_5, $CrNbO_4$, $Ti_2Nb_{10}O_{29}$ and $Nb_2O_5{\cdot}TiO_2$) at high temperature [5,9,10]. Therefore, it is necessary to promote the formation of a protective oxide layer on the surface of Nb–Si based alloys. Extensive studies have shown that the oxidation resistance of Nb–Si based alloys can be improved significantly with the addition of Cr, Si, Al, Ti and Hf [2–4,9–12]. Alloying with B can be beneficial to the oxidation resistance [13]. Boron tends to interstitially soluble to form $Nb_5Si_3B_x$ with $D8_8$ structure (Mn_5Si_3-type, hexagonal). At the same time, when B replaces with Si, the $Nb_5(Si, B)_3$ phase is formed. The $Nb_5(Si, B)_3$ phase, i.e., so called "T_2 phase" has a body-centered tetragonal Cr_5B_3-type structure [14]. As suggested by Behrani et al., boron containing phases (T_2 and $D8_8$) show better oxidation resistance than Nb_5Si_3 [13]. Germanium addition, as a partial replacement of Si, also improves the oxidation behaviour of Nb–Si based alloy [12]. The Ge-doped silicide coating protects the refractory metals from significant oxidation and pesting by the formation of a Ge-doped silica film [15,16].

Investigation of Nb–Si based alloys without coatings is crucial to determine how they will respond in case of a failure of the coating. And understanding the oxidation kinetics of Nb–Si based alloys is of crucial importance for improving the oxidation resistance. In present study, the microstructure and oxidation behaviour of Nb–Si based alloy with compositions Nb–24Ti–15Si–13Cr–2Al–2Hf (at.%) and Nb–24Ti–15Si–13Cr–2Al–2Hf–4B–5Ge (at.%) were investigated. The results provide possibilities to develop a structural material with improved oxidation resistance for high temperature applications.

2. Experimental procedures

2.1. Specimen preparation

Two alloys with compositions of Nb–24Ti–15Si–13Cr–2Al–2Hf (at.%) (Alloy 1) and Nb–24Ti–15Si–13Cr–2Al–2Hf–4B–5Ge (at.%) (Alloy 2) were prepared by arc melting, a mixture of high purity niobium, titanium, chromium, aluminium, silicon, hafnium, boron

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and germanium in arc furnace under an argon atmosphere. To ensure composition homogeneity and element partition, the ingots were inverted and remelted four times. Oxidation specimens with a size of 8 × 8 × 5 mm^3 were cut from the ingots by electron discharge machine and all surfaces were mechanically ground with 800-grit SiC paper and ultrasonically cleaned.

2.2. Oxidation testing

The oxidation tests were performed in an open-ended tube furnace at 1200 °C and 1250 °C. Each specimen was placed in a separate alumina crucible during the test. The specimens were removed from the furnace at the intervals of 10, 20, 40, 60, 80 and 100 h and weighed together with the crucible using a precision analytical balance (Model CPA225D, Germany) with an accuracy of 0.00001 g.

2.3. Mechanical properties testing

Compression specimens with a size of 4 × 4 × 6 mm^3 were cut from the ingots by electron discharge machine and all surfaces were mechanically ground with 600-grit SiC paper prior to the experiments. Room temperature compression tests were conducted at room temperature in air at an initial strain rate of 0.09 mm/min on a SANS 5104 testing machine. High temperature compression tests were conducted at 1200 °C in argon at an initial strain rate of 0.01 mm/min on a Gleeble 1500 testing machine.

2.4. Analysing methods

X-ray diffraction (XRD) (Model O/MAX-2200, Japan) pattern of the oxidation products was investigated to identify the main phases. The surface morphologies of oxidised specimens were analysed in scanning electron microscopes (SEM) (Model CS-3400, Japan). The cross-sectional microstructure of oxidised specimens were analysed in electron probe micro-analyzer (EPMA, Model JXA-8230, Japan) equipped with wave-dispersive spectroscopy (WDS) using backscattered scanning electron (BSE) and X-ray mapping modes. Nb L_α, Si K_α, Cr K_α, Ti K_α, Al K_α, Hf L_α, B K_α, Ge K_α, O K_α were analysed with PETJ, TAP, LIFH, PETJ, LIFH, PETJ, TAP, LIFH, LDE2H, LIFH and LDE2H crystals, respectively. The ZAF corrected EPMA was calibrated by pure standards supplied by the manufacture for different operating conditions and probe sizes. Before making observations, the cross sections were cut and ground with 1500-grit SiC paper, and then polished on a tightly woven cloth with 1 μm diamond paste.

3. Results

3.1. Microstructural characterization of as-cast alloys

Fig. 1a and b demonstrate the microstructure of Alloy 1 and Alloy 2 respectively. And the XRD patterns of two alloys are shown in Fig. 1c, where the T_2 phase and $D8_8$ phase are identified according to the XRD peaks of the α-Nb_5Si_3 phase and γ-Nb_5Si_3 phase respectively [14]. All phases have been confirmed through the use of XRD and WDS analysis. Alloy 1 consists of dark grey α-Nb_5Si_3, white Nb_{SS} and black Cr_2Nb, while Alloy 2 contains light grey $Nb_5(Si, Ge)B_2$ (T_2 phase), dark grey $Nb_5(Si, Ge)_3$ ($D8_8$ phase), white Nb_{SS} and black Cr_2Nb. The EPMA analysis results of as-cast alloys are given in Table 1. As shown in Table 1, (Nb + Ti)/(Si + Ge + B) atomic ratio is close to 5:3 in the T_2 phase, while (Nb + Ti)/(Si + Ge) atomic ratio is close to 5:3 in the $D8_8$ phase. This result suggests that Ge replaces with Si in both T_2 and $D8_8$ phase, and B replaces with Si in T_2 phase but interstitially solutes in $D8_8$ phase.

3.2. Oxidation kinetics

Fig. 2a shows the weight gain per unit area as a function of the exposure time at 1200 °C and 1250 °C for two alloys. Alloy 1 displays a linear plot with the weight gains of 118.7 mg/cm^2 and 156.7 mg/cm^2 after oxidation at 1200 °C and 1250 °C respectively. Alloy 2 shows better oxidation resistance with the weight gains of 26.7 mg/cm^2 and 32.5 mg/cm^2 after oxidation at 1200 °C and 1250 °C respectively. Fig. 2b presents the weight gains of Alloy 2 as a function of the square root of exposure time after oxidation

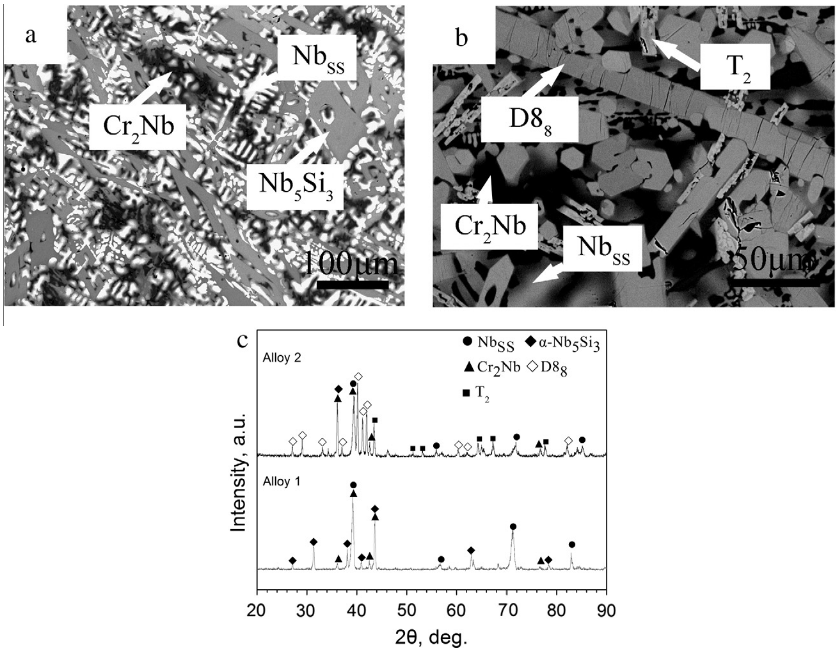

Fig. 1. (a) Microstructure of Nb–24Ti–15Si–13Cr–2Al–2Hf (at.%) alloy; (b) microstructure of Nb–24Ti–15Si–13Cr–2Al–2Hf–4B–5Ge (at.%) alloy; (c) XRD patterns of the specimens.