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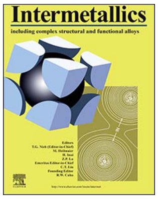

Study of the effects of Zr addition on the microstructure and properties of Nb-Ti-Si based ultrahigh temperature alloys

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ABSTRACT

The effects of alloying with Zr on the microstructure, mechanical and oxidation properties of Nb-Ti-Si based ultrahigh temperature alloys have been investigated in this study. The microstructures of the all alloys were comprised of primary $\gamma(Nb,X)_5Si_3$ blocks, Nbss and eutectic colonies, and the additions of Zr do not affect the microstructure and phase constituents of Nb-Ti-Si based alloys. Zr improves both the room-temperature toughness and the high-temperature strength. The alloy with addition of 8 at.% Zr shows the highest fracture toughness of 15.01 $Mpa{\cdot}m^{1/2}$. The compressive strengths of the alloys are improved to 278.89–293.08 MPa for the Zr-containing alloys when compare with the Zr-free alloy (194.23 MPa). The oxidation resistance of the alloys was also obviously ameliorated with Zr addition, showing a reduced weight gain with the increase of Zr content.

1. Introduction

Nb silicide *in situ* composites can offer increased temperature capability and reduced density that have the potential to replace nickel-based superalloys for aeronautic and aerospace applications [1–3]. In these composites, the hard-brittle intermetallic of Nb_5Si_3 (and/or Nb_3Si) provides high temperature strength and the ductile phase of Nb solid solution (Nbss) offers room temperature toughness. In recent years, most studies have focused on developing these alloys based on the ternary Nb-Ti-Si system [2–6], which are considered to have good combination properties. However, they still are easy to suffer from poor fracture toughness at room temperature and poor oxidation resistance at high temperatures. In order to balance the integrated properties of the alloys, various methods have been employed. One of the most commonly used method is alloying. In previous works, alloying Nb-Ti-Si based system with elements such as Cr, Al, Hf, B, Mo, Ta, Ge and Sn, etc. has been taken to investigate the alloying effect on the microstructure, phase formation, mechanical properties and oxidation behavior of the alloys [7–30]. Notably, the additions of these elements with appropriate content ranges, have been reported to be beneficial to the mechanical properties and/or oxidation resistance of the Nb-Ti-Si based alloys.

The effects of Cr on the microstructure and properties of Nb–Ti–Si based alloys have been reported in several previous publications [7–15]. Cr can destabilize $(Nb,Ti)_3Si$ phase and facilitate the formation of Laves phase (Cr_2Nb). Generally, high-temperature oxidation resistance, hardness and strength of the alloys can be ameliorated by alloying of Cr, but fracture toughness is tended to be sacrificed [9–15]. The aim of alloying Al is to improve the oxidation resistance, but also has a negative effect on mechanical properties of the alloys [9,10,12]. Alloying with Hf can stabilize the hexagonal γ-Nb_5Si_3 ($D8_8$, Mn_5Si_3-type) silicide, but there is no agreed conclusion about whether the addition of Hf in the alloys can improve the oxidation resistance or not [13,16–19]. In the case of alloying with B, the integrated properties of the alloys are usually improved, such as their oxidation resistance, room-temperature fracture toughness and strength at elevated temperatures [16,20–24]. Mo is used as alloying addition in the alloys to straighten the materials by solid solution hardening, whereas it has a detrimental effect on the oxidation resistance due to the formation of porous scale and the evaporation of MoO_3 [17,25–27]. The alloying additions of Ge and Sn in the alloys are also considered to be conducive to improvement of oxidation resistance [18–20,28,29].

In Nb-Si binary system, the addition of Zr has a significant impact to the formation of Nb/Nb_5Si_3 lamellar microstructure by eutectoid decomposition reaction of Nb_3Si [31–34]. Furthermore, with a proper content of Zr addition, the mechanical properties of the alloys can be ameliorated [34,35]. For instance, Tian et al. [35] studied the effect of Zr addition on the microstructures and mechanical properties of cast Nb-22Ti-16Si-xZr (x = 0–4) alloys, and found that the Zr addition increases the hardness of Nbss and $(Nb)_3Si$ phases as well as the yield

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strength at room temperature. From the published literature, we can find that the prior researches on alloying with Zr mainly focused on simple Nb-Si binary and Nb-Ti-Si ternary systems. Actually, the Nb-Ti-Si based alloys are always multi-alloyed, thus many researches focused on the synergistic effects of two or more elements on the microstructure characteristics, phase selection and properties of the alloys [7–13,16–20,25–29]. Thus, the present work mainly concentrates on the effects of Zr content on phase selection, microstructure, mechanical and oxidation properties of the alloys based on a multicomponent Nb-Ti-Si-Cr-Hf-Al system.

2. Experimental procedures

Five button ingots of Nb-22Ti-15Si-5Cr-3Hf-3Al-xZr ($x = 0$, 1, 2, 4 and 8, which are denoted as 0Zr, 1Zr, 2Zr, 4Zr and 8Zr respectively) (at.%) alloys were melted by vacuum non-consumable arc melting with electromagnetic stirring under an ultra high-purity argon atmosphere. Each button with a weight of 240 g was remelted six times to ensure compositional homogeneity. For microstructural analysis, cubic specimens with dimensions of $8 \times 8 \times 8$ mm^3 were cut form the ingots by electrodischarge machining (EDM).

Fracture toughness test at room temperature was measured using a three-point bending test (Instron3382). The three-point bending specimens with dimensions of $2.5 \times 5 \times 30$ mm^3 were prepared by EDM form the as-cast and heat treated ingots. The depth of the notch was 2.4–2.5 mm. The tests were conducted at a cross-head speed of 0.2 mm/min. The average value of three specimens was employed for the fracture toughness K_Q of each specimen. The details of the fracture toughness test of the alloys can refer to our previous works [13,24,36]. Vickers microhardness was measured using an HXP-1000TM hardness machine under an applied load of 0.98 N. High temperature compression tests were conducted at 1250 °C using a Gleeble 1500 testing machine in vacuum at a strain rate of 5×10^{-3} s^{-1}. The dimensions of the compression test specimens were 6 mm in diameter and 9 mm in length. The isothermal oxidation behavior of the alloys was conducted at 1250 °C for 20 h in an open-ended tube furnace. Before testing, all the surfaces of the three-point bending, high temperature compression and oxidation specimens were mechanically polished using SiC paper with water.

X-ray diffraction (XRD, Panalytical X'Pert PRO, Cu Kα) analysis and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS, TESCAN MIRA 3 and Inca X-sight) were used to identify the phase constituents, compositional distribution and microstructure of the as-cast alloys, as well as the specimens after mechanical and oxidation tests.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of all the as-cast alloys are shown in Fig. 1. As it is observed (Fig. 1a), the constituent phases of all the alloys with various Zr content are mainly composed of Nbss and γ(Nb,X)$_5$Si$_3$ (D8$_8$, Mn$_5$Si$_3$-type; X represents Ti, Hf, Cr and Zr elements). No α(Nb,X)$_5$Si$_3$ (D8$_l$, Cr$_5$Si$_3$-type), β(Nb,X)$_5$Si$_3$ (D8$_m$, W$_5$Si$_3$-type) or (Nb,X)$_3$Si phase could be detected in the alloys, which probably accounts for the stabilization effect of the alloying elements Hf and Zr on the γ(Nb,X)$_5$Si$_3$ phase [16–19,24,35]. The positions of the Nbss peaks show a shift towards lower angles with increasing the Zr content (Fig. 1a), indicating that the lattice parameters of Nbss are expanded as the larger atoms of Zr diffuse into the Nbss matrix ($r_{Nb} = 0.208$ nm and $r_{Zr} = 0.216$ nm).

3.2. Microstructure of the alloys

Fig. 2 shows typical backscattered electron (BSE) images of the as-cast alloys, and the chemical compositions of the constituent phases of these alloys are given in Table 1. In the as-cast state, the alloys show basically similar microstructure, which are mainly composed of white Nbss, dark primary γ(Nb,X)$_5$Si$_3$ blocks, Nbss/γ(Nb,X)$_5$Si$_3$ eutectics according to the XRD, BSE and EDS results as shown in Figs. 1 and 2, and Table 1. The primary γ(Nb,X)$_5$Si$_3$ blocks exhibit irregularly hexagonal, lath-like or "H" morphology. The morphology of the majority of Nbss/γ(Nb,X)$_5$Si$_3$ eutectics is irregular, and these eutectics seem to have a tendency to distribute around the primary γ(Nb,X)$_5$Si$_3$ with the additions of Zr (Fig. 2). Notably, some dark regions with higher Cr, Ti, Hf and Si concentrations (such as a composition of this region in Fig. 2a was about 20.0Nb-22.4Ti-10.7Si-40.5Cr-0.8Al-5.6Hf (at.%) for the 0Zr alloy) can also be found in the as-cast alloys. These dark regions which are inferred to be a three-phase eutectic consisting of (Ti,Nb)ss, (Nb,X)$_5$Si$_3$ and Cr$_2$(Nb,X), have been confirmed by the researches of Guo et al. [13,16,24,39], Yang et al. [37] and Shao et al. [38,39]. It should be noted that the diffraction peaks of Cr$_2$(Nb,X) were not found in the XRD patterns (Fig. 1a) due to its very low amounts. Moreover, in Nbss, many Ti and Cr rich areas (a composition of 40.8Nb-41.2Ti-3.1Si-10.0Cr-1.9Al-3.0Hf (at.%) for the 0Zr alloy shown in Fig. 2a and a composition of 50.3Nb-30.4Ti-1.5Si-8.7Cr-3.4Al-2.0Hf-3.7Zr (at.%) for the 8Zr alloy shown in Fig. 2e) were also present in the microstructure and exhibited a dark contrast, as shown in Fig. 2. Thus, the main phases present in microstructure of the as-cast alloys were: (i) the Nbss that exhibited some Ti rich areas (Ti-rich Nbss), (ii) the γ(Nb,X)$_5$Si$_3$ phase, (iii) the (Ti,Nb)ss and (iv) a Cr-rich C14 Laves phase. From the data as shown in Table 1, the concentration of Zr in γ(Nb,X)$_5$Si$_3$ is significantly higher than that in Nbss in the Zr-containing alloys, indicating that Zr mainly partitions into γ(Nb,X)$_5$Si$_3$ which was similar to the distribution behavior of Hf element. Several studies have reported that the element of Hf mainly partitioned into silicides and can promote the formation of hexagonal γ(Nb,X)$_5$Si$_3$ [11,13,15–19]. The elements Cr and Al were primarily partitioned into Nbss, which are similar to those of previous work on the Nb-Si based alloys [7–15].

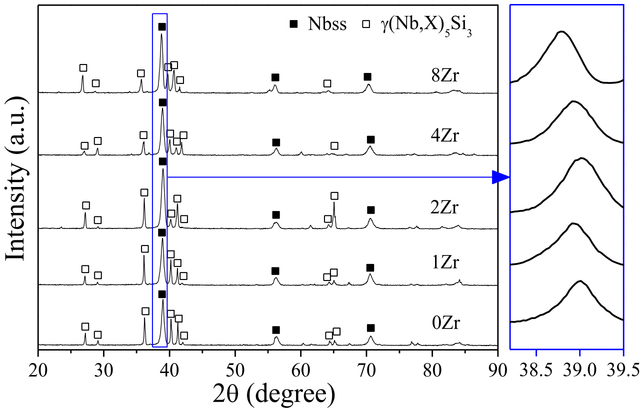

Fig. 1. XRD patterns of Nb-Ti-Si based alloys with various Zr content.

3.3. Properties of the alloys

3.3.1. Microhardness

The microhardness values of the Nbss and γ(Nb,X)$_5$Si$_3$ in the as-cast alloys are given in Table 2. The microhardness of the Nbss and γ(Nb,X)$_5$Si$_3$ was relatively stable with changing the Zr content, except for the 8Zr alloy which had a higher microhardness value for the silicide (1371 Hv).

3.3.2. Room-temperature fracture toughness

The room-temperature fracture toughness K_Q values of the alloys as a function of Zr content are given in Table 3. In the as-cast state, the average K_Q values of the alloys show an increasing trend as increasing the Zr contents. For instance, the average K_Q value of 8Zr alloy was increased to 15.01 Mpa·m$^{1/2}$ when compared with the 0Zr alloy (11.94