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Microstructure, mechanical and thermal oxidation behavior of AlNbTiZr high entropy alloy

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ABSTRACT

The developed as-cast AlNbTiZr high entropy alloy (HEA) resulted in the formation of solid solution bcc dendrites along with the inter-dendritic Zr_2Al intermetallic phase. Due to low-density of 5.74 g/cm^3 and high yield strength of about 1650 MPa (under compression testing), the alloy exhibited high specific yield strength of approximately 287 kPa m^3/kg. Further, the AlNbTiZr HEA showed high fracture strength of 1950 MPa and substantial plastic strain of approximately 17.9%. During the isothermal thermo-gravimetry analysis in the synthetic air, at 873, 973, 1073, 1173 and 1273 K for 3 h, the mass gain behavior of the alloy was nearly parabolic indicating the formation of the protective oxide layer. Further, the long-term oxidation studies of the AlNbTiZr HEA carried out in open air atmosphere for 50 h at 873, 1073 and 1273 K confirmed that the oxide layers formed were protective, intact, and spallation did not occur. Formation of complex oxides such as $AlNbO_4$ and Ti_2ZrO_6 along with Al_2O_3, NbO, ZrO_2, and TiO_2 as confirmed by X-ray diffraction could have led to the sluggish oxidation kinetics of the AlNbTiZr HEA. In contrast, the HfNbTiZr HEA showed poor oxidation resistance at 873 K.

1. Introduction

By controlling configurational entropy, researchers were able to develop multi-component single-phase solid solution alloys successfully, and this new alloy concept is being widely called as high entropy alloys (HEAs) [1,2]. The unique properties of the HEAs were ascertained to the four core effects such as high entropy effect, distorted lattice, sluggish diffusion, and cocktail effect. Miracle and Senkov have distinguished between the concept and definition of high entropy alloys (HEA) and complex, concentrated alloys (CCA) in a recently published article titled “A critical review of high entropy alloys and related concepts” [3]. Development of HEAs or CCAs either with single phase or multiple phases offers abundant opportunities for the discovery of new alloys of scientific significance and application [1–3]. The refractory HEAs were actively researched with an objective to develop new high-temperature structural alloys. The refractory HEA consist of Cr, Hf, Mo, Nb, Ta, Ti, V, W, and Zr. Though Al is not a refractory element, alloying of Al to refractory metal HEAs was also considered in several alloy system. When compared to 3 d transition metal HEAs, limited refractory HEAs are developed and studied. The Al0.4Hf0.6NbTaTiZr [4], AlNbTaTiV [5], AlNbTiV [6], HfMoNbTiZr [7], HfNbTiZr [8], HfNbTaTiZr [9,10], MoNbTaVW [11], MoNbTaW [11], NbTaTiV [5] and NbTiVZr [12,13] are reported to form solid solution of bcc alloys. The alloys Al0.5NbTa0.8Ti1.5V0.2Zr [14] and Al0.3NbTaTi1.4Zr1.3 [14] were reported to form two bcc phases, and the AlMo0.5NbTa0.5TiZr alloy consisted of bcc and B2 phase [4]. On the other hand, alloys CrHfNbTiZr [15], CrMo0.5NbTa0.5TiZr [16], CrNbTiVZr [12,13], and CrNbTiZr [12,13] were reported to form bcc and Laves phase. Furthermore, the addition of Si to the refractory HEAs was found to improve the mechanical properties of Hf0.5Mo0.5NbTiZr/M5Si3 [17], HfMo0.5NbSiTiV0.5 [18], HfNbSi0.5TiV [19] by promoting high strength silicide phases in the microstructure. A compilation of mechanical data of the refractory HEAs and the conventional superalloys such as Haynes230 (Co4Cr27Fe3Mo1Ni60W5), INCONEL 718 ((Al, Nb, Ti)5Co1Cr21Fe19Mo2Ni52) and MAR-M 247 (Al12Co10Cr10Hf1-Ni62Ta1Ti1W3) was reported elsewhere [3]. It is worth mentioning that these conventional superalloys found applications in a turbine system. Haynes 230 could be used for the thermal protective sheet (TPS) up to about 877 K, and the MAR-M 247 for turbine blades up to about 1150 K, and INCONEL 718 as disks up to about 950 K. When compared to Haynes 230 superalloy, most of the refractory HEAs exhibited high compression yield strength and specific yield strength at elevated temperatures [3]. Several refractory HEAs tested to date exceed currently used alloys in strength, specific strength, and maximum

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use temperature. It was projected that the refractory HEAs have mechanical properties that show potential for high-temperature applications in gas turbines [3].

Scientific and technological attention on the oxidation resistance of the refractory HEAs is insufficient compared to the alloy development concerning the improvement in mechanical properties. The oxidation resistance of the refractory HEAs is a serious potential barrier to the use of the alloys for an extended time at elevated temperature. The CrMo0.5NbTa0.5TiZr alloy was reported to form protective oxides and exhibit parabolic weight gain at 1273 K for 100 h [20]. Apart from Cr_2O_3 and Nb_2O_5, several complex oxides such as $CrNbO_4$, Cr_2TiO_5, $Cr_2Ti_5O_{13}$, $CrTaO_4$, MoTi-Ta_8O_{25}, $Nb_3Cr_2O_{10}$, $Nb_2Zr_8O_{21}$, Ti_2ZrO_6, Ta_4O_5, and $Ta_{12}MoO_{33}$ were found to be formed. However, refractory HEAs such as Al0.5CrNbMoTi, Al0.5CrNbMoV, Al0.5CrNbMoTiV, and Al0.5CrNbMoSi0.3TiV exhibited linear oxidation kinetics at 1573 K for 20 h indicating the formation of un-protective complex oxide layers of $CrNbO_4$, $CrVNbO_6$, $(TiCrNbV)O_2$, $(TiCrNb)O_2$ [21]. Especially the alloys with V content exhibited large pores in the oxide layer due to the volatilization of the VO_2 and V_2O_5 [21]. Although the AlCrMoTiW HEA exhibited parabolic behavior at 1273 K for 40 h, it was found to form a rather inhomogeneous mixed oxide scale consisting of Al, Cr, and Ti oxides with porosity [22]. The AlCrMoNbTi refractory HEA showed linear oxidation kinetics at 1173 K, 1273 K and 1373 K for 48 h [23]. The alloy showed a clear zone of internal oxidation, thin discontinuous Cr-rich oxide scales and as well as the formation of thick, porous, mixed oxides of Ti and Al [23]. Addition of 1 at. % Si to the AlCrMoNbTi refractory HEA has improved the oxidation resistance behavior, however, a clear mechanism was not proposed [23]. In the recent study, the oxidation behavior of the NbTiZrV alloy was found to be rapid and linear at 1273 K for 100 h [24]. The whole sample of NbTiZrV was completely oxidized, indicated that the $TiNb_2O_7$, TiO_2, and $Nb_2Zr_6O_{17}$ did not aid in oxidation resistance [24]. On the other hand, by replacing V with Cr, the oxidation behavior of the NbTiZrCr alloy has been improved when compared to NbTiZrV at 1273 K for 100 h. The improvement in oxidation resistance was attributed to the formation of $NbCrO_4$ and ZrO_2 and followed by internal oxidation [24].

In this work, an equimolar AlNbTiZr refractory HEA was designed to study the phase formation, microstructure, mechanical compression properties and oxidation behavior. The motivation for this alloy design is derived from replacing Hf by Al in the bcc HfNbTiZr, or it could be considered as replacing V by Zr in the bcc AlNbTiV. It is worth mentioning that the oxidation behavior of HfNbTiZr or AlNbTiV was not reported. The volatilization of V_2O_5 has been reported earlier in a refractory alloy, indicating that the presence of high concentration of V is not suitable for oxidation resistance properties. The replacement of Hf by Al was considered to decrease the density of the alloy and simultaneously to improve the oxidation behavior.

2. Experimental procedure

2.1. Alloy preparation

The AlNbTiZr equimolar alloy was prepared using a vacuum arc melting system (M/s. Edmund Buhler GmbH, Germany). The HfNbTiZr alloy was also produced as reference material to compare the oxidation behavior. Total weights of 10 g of the high purity (99.99%) alloying elements were melted together on the water-cooled copper hearth of the arc melting system. The alloy ingots were melted at least four times and were flipped between each melting to promote homogeneity. Further, plate-shaped samples of $2 \times 6 \times 40\ mm^3$ in dimensions were prepared by copper mold suction casting. Before melting and suction casting, the chamber was evacuated to a vacuum level of 0.035 Pa and back-filled with high purity argon.

2.2. Phase analysis and microstructural characterization

For phase analysis, the AlNbTiZr ingot and plate, samples were characterized by X-ray Diffraction technique (XRD; D3290 X'pert PRO PANalytical, The Netherlands) using monochromatic Co Kα radiation. For microscopic observation, the cross-section of the ingot and plate samples were wet ground on SiC emery paper up to 2400 grit and followed by final polishing with colloidal silica suspension to obtain a smooth mirror-like surface finish. The polished samples were etched with the Kroll-reagent (2 ml HF, 3 ml HNO_3 and 100 ml distilled H_2O) for 10 s, to reveal the microstructure. The microstructure of the AlNbTiZr samples was characterized by high-resolution scanning electron microscopy (HR-SEM, Leo Gemini 1530 microscope) and the chemical composition was analyzed with energy-dispersive x-ray spectroscopy (EDX).

2.3. Mechanical testing

The room temperature mechanical properties under compression were evaluated with rod-shaped specimens with diameter 3 mm and length 6 mm under quasistatic loading at an initial strain rate of $5 \times 10^{-4}\ s^{-1}$ using Instron type testing machine. The rod-shaped samples were machined from the as-cast ingot sample. The fracture morphologies of the samples were investigated using HR-SEM.

2.4. Thermal stability and oxidation studies

The thermal stability of the AlNbTiZr alloy up to 1473 K was studied using a differential scanning calorimetry (DSC, Perkin Elmer Inc., Massachusetts) in purified Ar atmosphere at a constant heating rate of 10 K/min.

The thermal oxidation studies on the AlNbTiZr and HfNbTiZr samples were carried out by thermogravimetric analysis (TGA; STA 449C model NETZSCH, Germany), in a high-purity synthetic air atmosphere with a constant net flow rate of 50 ml/min. For TGA studies, strip-shaped samples of $1.9 \times 3.9 \times 9.0\ mm^3$ in dimensions were machined from arc melted AlNbTiZr and HfNbTiZr alloy ingots. For both the dynamic and isothermal TGA studies, the samples were polished up to 1200 grit SiC emery paper. The polished samples were placed in a ceramic crucible in standing upright position. For dynamic TGA, the AlNbTiZr and HfNbTiZr samples were continuously heated up to 1273 K with a constant heating rate of 10 K/min. Isothermal TGA studies were conducted for the AlNbTiZr samples at different oxidation temperatures of 873, 973, 1073, 1173, and 1273 K. The isothermal oxidation study for the HfNbTiZr sample was carried out only at 873 K. A four-step procedure was followed for isothermal studies with initial fast dynamic heating with 40 K/min up to a temperature of 373 K. Followed, by slower dynamic heating with 10 K/min up to the isothermal oxidation temperature. Isothermal oxidation was conducted for 3 h and followed by a cooling step with a cooling rate of about 40 K/min.

The long-term air oxidation behavior of the AlNbTiZr alloy was studied in a horizontal tubular furnace at temperatures of 873, 1073 and 1273 K for 50 h. For these studies, the suction cast plate samples were polished up to 1200 grit SiC emery paper. The final polished strips are of $1.85 \times 5.6 \times 10.5\ mm^3$ in dimensions. After, oxidation studies, the thicknesses of the oxide layers as well as the morphology and the chemical compositions were assessed by HR-SEM, (Leo Gemini 1530 microscope) attached with EDX. Similarly, the phase formation of the oxidized samples was analyzed by XRD using monochromatic Co Kα radiation.

3. Results and discussion

3.1. Phase analysis, microstructure, and thermal stability

The XRD patterns of the arc melted ingot and suction cast plate