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Microstructure and oxidation behavior of new refractory high entropy alloys

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ABSTRACT

High-entropy alloys (HEAs) are defined as the alloys composed of at least five principal elements in equimolar or near equimolar ratios, which can facilitate the formation of simple solid solutions during solidification. Recent studies suggested that the refractory HEAs exhibited great promise for high temperature structural materials. However, their oxidation behavior had received little attention. In the present study, Cr, Al and Si elements were added to improve the oxidation resistance, four types of new refractory HEAs were designed and synthesized, including $NbCrMoTiAl_{0.5}$ (H-Ti), $NbCrMoVAl_{0.5}$ (H-V), $NbCrMoTiVAl_{0.5}$ (H-TiV) and $NbCrMoTiVAl_{0.5}Si_{0.3}$ (H-$TiVSi_{0.3}$). Their microstructures and oxidation behavior were studied. As expected, these refractory HEAs mainly consist of a simple body-centred cubic (BCC) refractory metal solid solution (RM_{ss}) due to the high mixing entropy effect. Solidification process and thermodynamic analysis were investigated to explain the formation mechanism of their microstructures. For all the refractory HEAs, the oxidation kinetics at 1300 °C follows a linear behavior. The oxidation resistance of the HEAs is significantly improved with Ti and Si addition, but reduced with V addition.

1. Introduction

Refractory metals have the potential to be the next generation of high temperature structural materials because they have high melting points, good performances of high temperature strength and ambient temperature ductility [1–4]. However, their poor oxidation resistance at elevated temperatures limits their application. Considerable works have been performed to solve this problem. It is found that doping high content of Cr, Al and Si elements can cause the formation of protective oxide layers (i.e., Cr_2O_3, Al_2O_3, SiO_2) [5–7]. Unfortunately, at the same time, large quantities of brittle intermetallic compounds (Nb_5Si_3, $NbCr_2$, $MoSi_2$, Nb_3Al, etc.) are easy to form, leading to low fracture toughness at room temperature, which will also restrict their application [8]. This raises the question: can we avoid or reduce the formation of brittle intermetallic compounds when doping some amounts of Cr, Al, Si elements? Furthermore, can the refractory alloys remain ductile solid solution phase? The design idea of new alloy system named “high entropy alloys” (HEAs) may offer a pathway towards solving this problem.

The concept of HEAs is proposed by professor Yeh [9]. The HEAs are composed of at least five principal elements with each elemental concentration between 5 and 35 at.%. The high mixing entropy effect can facilitate the formation of simple solid solutions during solidification instead of brittle intermetallic compounds [9–15]. Recently, NbMoTaW, VNbMoTaW, TaNbHfZrTi refractory HEAs have been successfully produced by vacuum arc melting [3,4,16]. These refractory HEAs consist of single BCC solid solution phase, and are proved to be usable at high temperatures due to their high strength, but studies on their oxidation behavior are limited [17]. Besides, considering that these refractory HEAs contain no Cr, Al, Si elements, their high temperature oxidation resistance should be poor.

Based on the analysis above, high content of Cr, Al and Si elements were added to increase the oxidation resistance [5–7], and the design idea of HEAs was applied to avoid the formation of complex brittle phases. The base composition $NbMoCrAl_{0.5}$ (1:1:1:0.5 in atomic molar ratios) was selected, because Nb metal had good ductility and fracture toughness [18], Mo could increase high temperature strength [1], Cr and Al could improve the oxidation resistance of the alloys [5,6]. Then, four types of new refractory HEAs including $NbCrMoTiAl_{0.5}$ (H-Ti), $NbCrMoVAl_{0.5}$ (H-V), $NbCrMoTiVAl_{0.5}$ (H-TiV) and $NbCrMoTiVAl_{0.5}Si_{0.3}$ (H-$TiVSi_{0.3}$) alloys were designed. Here, H was used to represent $NbMoCrAl_{0.5}$ in this paper to facilitate discussion. The mixing enthalpy between Nb, Mo, V, Cr, Ti refractory elements was small (see Table 1) [19,20]. This was beneficial to the preparation of HEAs [10]. To fully augment the mixing entropy, Nb, Mo, V, Cr and Ti elements were designed in equimolar ratios [9]. But the mixing enthalpy between Al, Si and other elements were more negative, therefore the amount of their addition was relatively low to avoid the formation of intermetallics.

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Table 1
The values of ΔH_{mix} (kJ/mol) calculated by Miedema's model for atomic pairs between elements with Ti, V, Cr, Nb, Mo, Al, Si [19].

Element	V	Cr	Nb	Mo	Al	Si
Ti	−2	−7	2	−4	−30	−66
V		−2	−1	0	−16	−48
Cr			−7	0	−10	−37
Nb				−6	−18	−56
Mo					−5	−35
Al						−19

In this paper, the microstructure and oxidation behavior of these refractory HEAs were investigated with two purposes. One was to verify whether the single phase refractory solid solution with high content of Cr, Al and Si elements can be obtained. The other was to investigate the effect of the alloying elements on the microstructure and oxidation resistance, which would provide a reference for the optimization of the alloy compositions.

2. Experimental

The alloys were prepared from commercial purity (all in 99.9 wt.%) Nb, Cr, Mo, Ti, V, Al and Si by electric arc melting under argon atmosphere in water cooled copper crucible. To prevent the loss of Al and Si, the Nb, Cr, Mo, Ti, V, Al and Si were not added in the copper crucible at the same time during the arc melting. The elements Ti, V, Al and Si were firstly melted, and the first alloy ingot was obtained. Similarly, the Cr, Nb, Mo were melted, and the second alloy ingot were obtained. Then, the final HEAs ingots of about 100 g were prepared by these two alloy ingots. To ensure homogeneity, the alloys were remelted for at least five times.

The crystal structures were characterized using X-ray diffractometer (XRD, Rigaku Dmax 2200) with Cu Kα radiation scanning from 20 to 100 degrees in 2θ at a scanning rate of 6°/min. Microstructures of the cast samples were examined by Cambridge-S360 scanning electron microscopy (SEM) using backscattered electron (BSE) imaging. The chemical compositions of the constituent phases were analyzed by electron-probe microanalysis (EPMA) using a JEOL JXA 8100 superprobe equipped with energy dispersive X-ray (EDX) and wavelength dispersive X-ray (WDX) spectrometers. The precipitate phases were identified by transmission electron microscopy (TEM, JEOL JEM-2100) with thin-foil specimens that were prepared by polished thinning and ion milling. The area fractions of secondary phase in H-Ti and H-TiV alloys were measured using BSE images and the metallographic image analysis software SISC IAS v8.0.

The oxidation coupons with dimensions of approximately 4 mm × 6 mm × 10 mm were ground to 1000 grit and ultrasonically cleaned in ethanol. Isothermal oxidation tests of the samples were undertaken at 1300 °C in air with the exposure times of 5, 10, 15 and 20 h. The weight of samples was examined and recorded. Weight gain per unit area as a function of the time was used to determine the alloy oxidation resistance. The oxidation products were characterized by XRD. The cross-section of the oxide scales was observed and analyzed by EPMA.

3. Results and discussions

In this paper, the microstructures of the HEAs were investigated firstly. To fully understand the formation mechanism of these microstructures, the solidification processes were analyzed, and a simple thermodynamic analysis of the phase formation in each alloy was proposed. Afterwards, the oxidation behavior was studied, and the effect of Ti, V and Si alloying elements on oxidation resistance were discussed.

3.1. Microstructure

The XRD patterns of the refractory HEAs are shown in Fig. 1. As expected, their structure is simple. H-Ti, H-V and H-TiV alloys display a single BCC structure. The H-TiVSi$_{0.3}$ alloy is composed of two phases, including BCC phase and a compound phase $(Nb,Ti)_5Si_3$ (JCPDS, 63-3599).

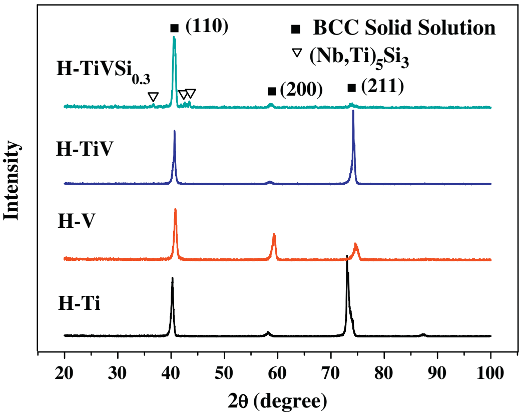

Fig. 1. XRD patterns of the HEAs.

3.1.1. Microstructure characterization

Fig. 2 shows the microstructures of the refractory HEAs. A common observation can be depicted. There is serious dendritic segregation although the matrix is of refractory metal solid solution (RM_{ss}) type. Furthermore, except for H-V alloy, all alloys have the secondary phase in interdendritic regions. To facilitate discussion, the microstructures are mainly distinguished as dendrite, interdendrite and secondary-phase regions. Table 2 gives the chemical compositions in each region, which is determined by EDX. It is noticeable that Mo element segregates preferentially to the dendritic regions, while Cr, Ti, Al and Si elements prefer to the interdendritic regions. The distribution of Nb and V elements is relatively homogeneous.

For H-V alloy, it only consists of RM_{ss} as shown in Fig. 2b. For H-TiVSi$_{0.3}$ alloy, it should be the hypoeutectic or hypereutectic microstructure as shown in Fig. 2d. Combining the EDX results and the corresponding XRD patterns (see Fig. 1), it can be summarized that the H-TiVSi$_{0.3}$ alloy consists of RM_{ss} and $(Nb,Ti)_5Si_3$ eutectic microstructure (see Fig. 2d).

It seems that H-Ti (see Fig. 2a) and H-TiV (see Fig. 2c) exhibit hypomonotectic microstructure. And there are RM_{ss} dendritic and black secondary phase in interdendritic regions. The black secondary phase exhibits irregular or lamellar shape. According to the EDX results in Table 2, the secondary phase is mainly composed of Ti element with the atomic percentage of 71.05% in H-Ti and 79.36% in H-TiV. To further identify the secondary phase, TEM is applied. The selected area diffraction (SAD) (see Fig. 3) pattern analysis indicates that it is a BCC structure with the lattice parameter of about 3.29 Å, very closed to the lattice parameter of the β-Ti solid solution (3.331 Å). Considering its high composition of Ti, it is reasonable to presume that secondary phase is a solid solution of β-Ti. However, β-Ti is not identified in the XRD patterns of H-Ti and H-TiV. This is because that β-Ti has BCC structure and similar lattice parameter with RM_{ss}, and has little concentration. Furthermore, the area fraction of β-Ti is measured by differentiating the phases using the BSE contrast. It is found that the area fraction of β-Ti in H-TiV (4.6%) is slightly higher than that in H-Ti (2.5%). This suggests that the addition of V element promotes the formation of β-Ti. This observation of β-Ti is seldom reported. The related reasons will be qualitatively analyzed in Section 3.1.3.

3.1.2. Solidification process

According to Fig. 2a, the H-Ti alloy should be the hypomonotectic microstructure. To better understand it, the hypomonotectic reaction during solidification of H-Ti alloy is schematically illustrated by the phase diagram in Fig. 4, where element A represents the mixture of Nb, Cr, Mo and Al. The solidification path (along the dotted line) of H-Ti can be described as follows: (1) Melting liquid experiences reaction by $L \rightarrow RM_{ss} + L_1$. Primary RM_{ss} form with dendrite growth, and liquid L_1 is left in interdendritic regions, as