Glass formation in a high entropy alloy system by design

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ABSTRACT

The alloys $(TiZrNbCu)_{1-x}Ni_x$ $x = 0.125, 0.15, 0.2, 0.25$ were produced by vacuum arc melting and investigated as a potential high entropy alloy and glass forming system. The alloys $x = 0.125$ and 0.15 were capable of forming either amorphous or high entropy alloy phases, increasing the Ni content destabilised the high entropy alloy phase. This behaviour is explained by considering the enthalpy and entropy of mixing of the alloys and decomposition products. The unique feature of the high entropy alloys in this study was the high vacancy formation energies compared to other reported high entropy alloys and this is believed to be responsible for their ability to form an amorphous phase and their relative sensitivity to Ni content.

1. Introduction

Two metallic materials receiving extensive interest are bulk metallic glasses (BMGs) [1] and the more recently reported high entropy alloys [2,3] (HEAs). Amorphous or glassy alloys have been extensively studied, resulting in a good understanding of the essential considerations for obtaining glass formation, with models to predict glass forming compositions based on the need for a high density of atomic packing. Inoue proposed three parameters that promote glass formation by encouraging dense random packing; a large negative enthalpy of mixing between atom pairs, three or more components and large differences in atomic radii between the constituent species [4]. BMG compositions also tend to occur close to eutectic compositions, where the melting point is suppressed and so the temperature difference between it and the point at which the glassy structure is frozen in (termed the glass transition temperature, T_g) is at a minimum. Mutual frustration of several possible competing eutectic phases also aids in shifting the nose of the crystalline phase field on a time-temperature-transformation (TTT) diagram to the right, reducing the critical cooling rate for glass formation [5].

HEAs were defined by Yeh et al. [2] as alloys comprising 5 or more components in roughly equiatomic proportions between 5 at

% and 35 at% and possessing the ability to form simple solid solution phases with face centred cubic (fcc) or body centred cubic (bcc) crystal structures. This ability to form simple solid solutions rather than the expected complex mixture of intermetallic phases (which are typically observed on devitrification of BMGs) was first observed by Cantor et al. [6] in 2004. Yeh [2] later introduced the phrase "high entropy alloy", to describe these systems, with their unique ability to precipitate solid solution phases from the melt in preference to intermetallics, which would be expected according to the Gibbs phase rule and the Hume-Rothery rules for alloying. This phenomenon forms alloys which, as a result of heavy alloying solid solution strengthening, have high strengths comparable to those of BMGs in some instances [2,3,7,8] whilst exhibiting work hardenability [9] and good ductility up to 26% strain to failure [2,3,7–9]. These combinations of high strength and ductility are not realized in conventional alloys where high yield strength and ductility are often competing properties and, for these reasons, HEAs are attracting interest as potential structural materials.

The ability of HEAs to form such simple microstructures is the key to their properties; the large number of component elements results in a solid solution, which has sufficiently high configurational entropy to overcome the effects of the heat of mixing of the alloy. The molar configurational entropy (ΔS^{conf}) of the alloys is related to the number of equivalent microstates (Ω), which may result in an observable macrostate by Boltzmann's equation, which states $S^{conf} = R\ln\Omega$, where R is the universal gas constant. In the case of HEAs Ω is the number of ways of arranging N component species

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Table 1
Theoretical elastic moduli (calculated from method in Ref. [25]) and kinetic fragility index, m (m = 12(B/G+0.67)) [17].

Alloy	Δr (%)	ΔH^{mix} (kJ mol^{-1})	G (GPa)	B (GPa)	m
A-HEA1	12.0	−35	43.4	124.5	42
A-HEA2	12.15	−40	43.9	125.6	42
A-HEA3	12.36	−49	45.0	127.8	42
A-HEA4	12.5	−55	46.2	130.0	42

onto the n non-equivalent lattice points of the crystal unit cell [10,11]. Calculating S^{conf} in this way it can be seen that (1) the entropy of the bcc lattice is highest for 5 component HEAs, (2) the fcc lattice has the highest entropy for 6−10 component HEAs and (3) for compositions above 10 components an hexagonal close packed (hcp) lattice would have the greatest entropy. This may be the reason why no hcp HEAs have been reported although electronic structure undoubtedly plays an important role in the lattice type [12].

The high S^{conf} of the HEA solid solutions must be large enough to overcome the enthalpy of mixing of the metals composing the alloy. Many of the reported HEA compositions have positive heats of mixing when calculated using the Miedema model [13] and the regular melt model [14]. The compositions CoCrCuFeNiAl (fcc) [8] and WNbMoTaV (bcc) [15] have heats of mixing 18.7 kJ mol^{-1} and 13.9 kJ mol^{-1} respectively and would normally be expected to segregate, though at high temperature the configurational entropy of each solid solution of 22.5 J K^{-1}mol^{-1} and 19.1 J K^{-1}mol^{-1} respectively would make a random solid solution the more stable state. It may be that compositions with positive heats of mixing and prone to segregation form HEAs most readily, as the increase in entropy from a segregated alloy to a random solid solution is greater than that for a polysubstituted intermetallic to a random solid solution [16]. Thus if the formation of random solid solution phases in HEAs depends wholly upon sufficiently high entropy of mixing then a zero or positive value of enthalpy of mixing must be a requirement of the alloy system, and one that is incompatible with glass formation. To date, no high entropy alloy system, consisting of 5 or more elements and forming a simple fcc or bcc solid solution [2] with the ability to form an amorphous phase on rapid cooling has been reported. Identification of an alloy system which forms both an HEA solid solution and a glassy phase would allow novel processing routes for high entropy alloys and create he possibility of HEA reinforced amorphous alloy composites but would also force a re-evaluation of the explanation of HEA formation. The compositions (TiZrNbCu)$_{1-x}$Ni$_x$; x = 0.125, 0.15, 0.20, 0.25 fulfil the main requirements of a glass former discussed above, as calculations using Miedema's model [2,14] give negative ΔH^{mix} in the range −35 to −55 kJ mol^{-1}, the size mismatch of the alloys

varies from 12.0 % to 12.5 % and the kinetic glass index, m, was calculated using the method of Park et al. [17] to be the intermediate value of 42 (based on theoretical elastic moduli) see Table 1. The compositions also all fulfil the requirements of an HEA former, save for the inferred requirement for a positive enthalpy of mixing. In this work we investigate the extent to which this alloy system may form an HEA solid solution or amorphous phase depending on chemistry and cooling rate.

2. Experimental procedures

Four alloys in the (TiZrCuNb)$_{1-x}$Ni$_x$ system with x = 0.125, 0.15, 0.20, 0.25, A-HEA1, A-HEA2, A-HEA3 and A-HEA4 respectively and the reported HEA compositions CoCrNiFeTi [18] and CoCrNiFeAl [19] were prepared from high purity elements by arc melting in the presence of a Ti "getter". The chamber was evacuated to a pressure of 10^{-3} Pa and backfilled with high purity argon. The ingots were flipped and re-melted 4 times to ensure complete melting and then suction cast into a water-cooled copper die of 6 mm diameter. Ribbons with a thickness of approximately 20 microns of each alloy were generated by melt spinning. The suction cast rods were investigated by: (1) X-ray diffraction (XRD) using a Siemens D500 diffractometer with a Cukα source, and (2) scanning electron microscopy (SEM) using an FEI Sirion, with energy dispersive spectrometry (EDS) capability. The melt-spun ribbons were also analysed by XRD, with a slow scan rate of 0.2°/min, and by differential scanning calorimetry (DSC) with a Perkin Elmer Diamond DSC, using gold sample pans and a heating rate of 20 Kmin^{-1}.

3. Results and discussion

The A-HEA alloys solidified to form the dendritic microstructure seen in Fig. 1a and EDS analysis found that the dendrites consisted mainly of Nb − see Fig. 1b. XRD traces in Fig. 2 confirm that the cast alloys A-HEA1 and A-HEA2 solidified to form two phases, the first corresponding to niobium and the second an unknown bcc HEA phase with a = 2.51 nm. The compositions A-HEA3 and A-HEA4 also precipitated niobium dendrites but the HEA peak is suppressed in the XRD trace of A-HEA3 and absent in A-HEA4, being replaced by Ni$_{42}$(Ti,Zr)$_{58}$ and Cu$_{10}$Zr$_7$ signals. This corresponds to increased Ni content causing the enthalpy of mixing of the alloys to become more negative. High concentrations of Ni push the equilibrium between the solid solution and the decomposition products towards formation of Ni-X intermetallic phases. Heats of mixing calculated using the Miedema model [13] imply that at these compositions Ni would react most favourably with Ti and Zr to form intermetallic phases of the type Ni$_{42}$(Ti,Zr)$_{58}$, ΔH^{mix} −64 kJ mol^{-1}.
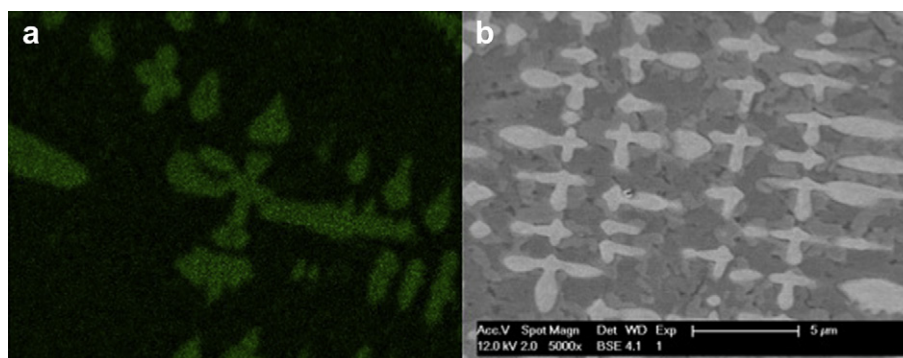

Fig. 1. (a) Nb Kα EDS map A-HEA3 Nb (green) partitions to dendrites the remaining elements form the matrix phase, (b) back scattered electron image of A-HEA3 microstructure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)