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Study of Glass Forming Ability of Different Bulk Metallic Glass Alloys

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Abstract

Zr based, Cu-Zr based and equiatomic TiZrHfNiCu metallic glasses have been prepared by suction casting and characterised by using X-Ray Diffraction and Differential Scanning Calorimetry. Fully glassy rods with wide supercooled liquid region (ΔT_x) have been obtained at 3 mm diameter for both Zr based and Cu-Zr based alloys while glassy equiatomic TiZrHfNiCu exhibit low ΔT_x at 1.5 mm. The glass forming ability for BMG compositions are analysed and characterised using three parameters: atomic size difference (δ), mixing enthalpy (ΔH_{mix}) and mixing entropy (ΔS_{mix}).

Keywords Bulk metallic glasses; Glass-forming ability; Suction casting.

1. INTRODUCTION

Bulk Metallic Glasses (BMGs) are an amorphous alloys which absent in grain boundaries and crystal defects. High cooling rates (10^2 to 10^6 K/s) is required in order to prevent crystallisation during solidification [1]. BMGs have excellent strength, low Young's modulus, high elastic strain limit and improved wear resistance. However, BMGs suffer from catastrophic failure owing to localised plastic flow upon loading at room temperature. Several types of BMGs have been fabricated in order to enhance the ductility. Among various kinds of BMGs, Zr-based BMGs have been drawing extensive attention due to the high glass forming ability (GFA). The GFA commonly relates to the potentiality of the alloy to form a glass. It can be estimated by critical casting size of metallic glass and supercooled liquid region (ΔT_x), which is the temperature difference between the onset crystallisation temperature (T_x) and glass transition temperature (T_g). Another type of BMG is reported by Cantor as high Entropy-BMG (HE-BMG) from alloying with elements of similar chemical natures in equiatomic proportions [2]. The high configurational entropy of these alloys induces the confusion principle hence easing glass formation [3]. Inoue's empirical rule [4] have been employed to identify conditions required for glassy phase. It states that metallic glasses can be formed by: (1) more than three elements in the system; (2) large atomic size differences (≥12%); and (3) large negative mixing enthalpies. High entropy of mixing (ΔS_{mix}) and higher critical cooling rate are also favourable for glass formation [5].

In this paper, we have characterised three types of BMG (Zr-BMG, CuZr-BMG and HE-BMG) using X-ray diffraction (XRD) and differential scanning calorimetry (DSC) and explained variations of their GFA based on empirical rule of metallic glass formation.

2. EXPERIMENTAL TECHNIQUE AND MATERIAL

Ingots of HE-BMG TiZrHfNiCu (S1), Zr-based $Zr_{55}Cu_{30}Al_{10}Ni_5$ (S2) and $Cu_{45.5}Zr_{47.5}Al_5Co_2$ (S3) were prepared by arc melting high-purity elements (≥99.8%) in a Ti-gettered argon atmosphere. Ingots were remelted at least four times to ensure their homogeneity and then suction cast into a water-cooled copper mould to produce cylindrical rods with diameters of 1.5 mm (S1) and 3 mm (S2 and S3). The amorphous phase and crystalline phase were characterised using X-ray diffraction (XRD) on a Siemens D5000 X-Ray Diffractometer with a Cu Kα radiation source ($\bar{\lambda}$=1.5418 Å). Differential Scanning Calorimetry (DSC) at heating rate of 0.67K/s was used to identify the crystallisation temperature (T_x) and glass transition temperature (T_g). All the data have been repeated twice for validity of the results.

3. RESULTS

Fig. 1 (a) shows X-ray diffraction patterns of sample S1, S2 and S3. Characteristic diffused peaks located between 35° and 45° of S1 and S2 indicates the presence of an amorphous state. S1 is fully crystallized when casting diameter is larger than 1.5mm (the result is not shown here). The overlapping of a small sharp peak with a diffuse peak in S3 indicates the formation of amorphous phase together with crystalline phase. Considering the XRD results and casting size of studied compositions, S2 exhibits best GFA (S1 is fully crystallized when d > 1.5mm, S2 is fully amorphous when d=3mm and S3 is partially crystallized when d=3mm).

Fig.1 (b) shows DSC curves of sample S1, S2 and S3. Table 1 listed related thermal stability parameters, T_g, T_x and supercooled liquid region (ΔT_X) of S1, S2 and S3. T_g for S1, S2 and S3 is 658±2K, 675±2K and 698±2K, respectively, and their T_x is 706±2K, 729±2K and 756±2K, correspondingly. Lower T_g and T_x of S3 is indicative of relative liquid stability at lower temperature and therefore better GFA. On the other hand, its relatively larger ΔT_X, for S3 provides evidence of stability of supercooled liquid.

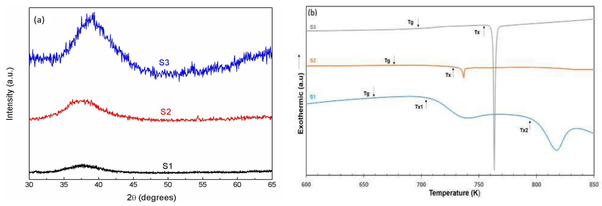

Figure 1. (a) The X-ray diffraction patterns (b) DSC curves of sample S1, S2 and S3.

Table 1. Glass transition temperature, crystallization temperature and supercooled liquid region of S1, S2 and S3

Sample	T_g (K)	T_x(K)	ΔT_x(K)
S1	658±2	706±2	48±2
S2	675±2	729±2	54±2
S3	698±2	756±2	58±2

The GFA of a designed composition, theoretically, may also be estimated by calculating mixing enthalpy (ΔH_{mix}), mixing entropy (ΔS_{mix}) and atomic size difference (δ). *Miedema's* model is used for the related calculation [6]. Table 2 lists values of ΔH_{mix}, ΔS_{mix} and δ for S1, S2 and S3. It is reported [4] that the values of ΔH_{mix}, ΔS_{mix} and δ required to form (HE)BMGs are in the limited range of -49 kJ·mol^{-1} ≤ΔH_{mix}≤ -5.5 kJ·mol^{-1}, 7 J·K^{-1}·mol^{-1} ≤ ΔSmix ≤ 16 J·K^{-1}·mol^{-1}, δ≥9. ΔH_{mix} and δ for these three alloys are roughly around -30 kJ·mol^{-1} and 10 respectively, which perfectly match the empirical rule [7]. Even though values of ΔS_{mix} for three BMGs are in the reported range, there shows some difference between S1 and S2/S3.

Table 2. ΔH_{mix}, ΔS_{mix} and δ for S1, S2 and S3.

Materials	ΔH_{mix}/(kJ·mol^{-1})	ΔS_{mix}/(J·K^{-1}·mol^{-1})	δ
S1	-27.36	13.38	10.33
S2	-32.57	8.90	10.41
S3	-29.49	7.82	10.85

4. DISCUSSION

HE-BMG is designed with equiatomic compositions to reduce the eutectic point temperature [8]. However, high mixing entropy alone is not sufficient to form an alloy with good GFA. Large negative heat of mixing is favourable for glass formation by increasing the energy barrier thus restraining long range diffusion of atoms. The formation of crystalline phases will thus be suppressed during rapid solidification hence inducing high GFA. The ΔH_{mix} value of S1 (-27.36 kJ·mol^{-1}), however, is less negative than S2 (-32.57 kJ·mol^{-1}) and S3 (-29.49 kJ·mol^{-1}), thereby exhibiting lower GFA. Another factor that could examine GFA is the atomic size ratio δ. S2 (δ=10.41) and S3 (δ=10.85) have higher atomic size mismatch compared to S1 (δ=10.33). The constituent elements in S1 are similar chemical species, which gives insignificant difference in their atomic size. From the DSC results the supercooled liquid regions of S2 (ΔT_x=54K) and S3 (ΔT_x=58K) can be obtained, both of these alloys have relative wide supercooled liquid region compared with S1 (ΔT_x=48K) and show good glass forming ability.

5. CONCLUSION

Three BMGs (HE-BMG and two CuZr-based) have been produced by copper mould casting. CuZr-based BMGs has higher glass forming ability compared to HE-BMG. The produced BMGs match the empirical law where ΔS_{mix}, ΔH_{mix} and δ meet the requirements for glass formation. It is generally shown that Inoue's empirical rule can be used for predicting glass formation, even for new BMG types such as (HE)BMGs.

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