Formation of Cu-Zr-M ternary bulk metallic glasses based on atomic clusters

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Abstract. Ternary Cu-Zr-M (M= Al, Ti and Ag) bulk metallic glasses are investigated using a cluster line approach. New bulk metallic glass rods with compositions lying along the cluster line $\text{Cu}_5\text{Zr}_6-M$ were fabricated by copper mould suction, where binary cluster $\text{Cu}_5\text{Zr}_6$ is an Archimedean octahedral antiprism, M being about 4~13.2 at.% for Al, 8.3 at.% for Ti and 9 at.% for Ag. The relevant mechanism was discussed in the light of the cluster-plus-glue-atom model.

1. Introduction

Cu-Zr-based bulk metallic glasses (BMGs) have been extensively studied [1, 2] due to their good mechanical properties [3, 4], wide metallic glass formation region [5], and low cost. In our previous works [6, 7, 8, 9], a series of Cu-rich ternary Cu-Zr-based BMGs were obtained by using a cluster line approach and they are all related to a dense-packed $\text{Cu}_5\text{Zr}_5$ icosahedral cluster and a $\text{Cu}_6\text{Zr}_5$ Archimedean antiprism cluster [10]. In a ternary phase diagram, a cluster line is a straight composition line linking a binary cluster composition to the third element. The specific binary cluster is a nearest-neighbor coordination polyhedron that usually exists as a local structure of crystalline phases. In other words, this is a cluster-plus-glue-atom model where the third element serves as glue atoms linking atomic clusters.

In the present work, we investigate the Zr-rich BMG formation in Cu-Zr-M (M =Ag, Ti and Al) ternary systems based on another Archimedean antiprism $\text{Cu}_5\text{Zr}_6$ cluster, which has the same cluster type as the $\text{Cu}_6\text{Zr}_5$ cluster (see figure 1). Thus, the cluster-line alloys (Cu$_5$Zr$_6$)$_x$M$_y$ along the Cu$_5$Zr$_6$-M cluster line are designed to study the BMG formation.

2. Experimental

(Cu$_5$Zr$_6$)$_x$M$_y$ (M = Ag, Ti and Al) alloys were prepared by using arc melting mixtures of constituent elements under argon atmosphere. The purities of elements are 99.9 wt% for Zr, 99.999 wt% for Al and 99.99 wt% for Cu, Ag and Ti. Alloy rods with a diameter of 3 mm were prepared by means of copper mould suction casting. Structural identification was carried out by X-ray diffraction (XRD) with Cu K$_\alpha$ radiation. Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are employed to study the thermodynamic behaviors of the BMGs at a heating rate of 0.33 K/s.
**Figure 1.** Cluster lines and BMG compositions in Cu-Zr-Al ternary system.

**Figure 2.** XRD patterns of the suction-cast (Cu<sub>5</sub>Zr<sub>6</sub>)<sub>x</sub>M<sub>x</sub> (M=Al, Ti, Ag) alloy rods.
3. Results and discussions

XRD results indicate that the (Cu,Zr)xAl1-x BMGs are formed over a wide composition range with x=0.46–1.7 (Al 4–13.2 at.%), while the BMG formations in (Cu,Zr)xAg1-x and (Cu,Zr)xTi1-x alloys depend strongly on the composition and only (Cu,Zr)xAg1.09 (Cu1.4Zr0.6Ag0) and (Cu,Zr)xTi1 (Cu4.7Zr50Ti8.3) can form BMGs, which are nearly point-like. As shown in figure 2, exceeding this point composition, the Cu-Zr-Ag and Cu-Zr-Ti alloys become crystallized.

The thermal analyses give the glass transition temperature Tg, the onset temperature of crystallization Ts, the melting temperature Tm, and the liquidus temperature Tl of the (Cu,Zr)xMx BMGs, as listed in table 1.

It can be seen from the data that the (Cu,Zr)xMx BMGs have not only large Tg and ATs values, and hence high thermal stabilities, but also large GFA indicators Tg/Tl and γ (γ = Ts/(Tg+Tl)) [12]. The best BMG composition is probably (Cu,Zr)xAl1.67 with the largest Tg = 731 K, Tg/Tl = 0.638 and can form a BMG rod with diameter of 4mm. However its ATs is the lowest and it does not have the maximum γ parameter. The largest ATs is found for the BMGs with compositions close to (Cu,Zr)xAl1, with ATs = 67–68 K, so that they may be good formers as well. The thermal parameters of the (Cu,Zr)xAl1 BMG are Tg =707 K, Tg/Tl = 0.605, ATs = 67 K. Those of the other two best glass formers with M=Ag and Ti are Tg =679 K, Tg/Tl = 0.575, ATs = 53 K for (Cu,Zr)xAg1.09 and Tg =632K, Tg/Tl = 0.522, ATs = 53 K for (Cu,Zr)xTi1.

We note that the proportions of M with respect to the cluster are all close to x=1. In fact we have also found similar composition formula in our previous works [7, 8, 9], where they can be expressed in terms of a cluster-plus-glue-atom model into a simple unified formula of (Cluster)x(Glue atom). For instance, two good BMG compositions Cu58.7Zr35.9Al6 [8] and Cu50.0Zr41.7Al8.3 [9] can be expressed with (Cu,Zr)xAl1.68 and (Cu,Zr)xAl1. In the present work, the BMGs (Cu,Zr)xAg1.09 (Cu1.4Zr0.6Ag0) and (Cu,Zr)xTi1 (Cu4.7Zr50Ti8.3) all match this model. As for (Cu,Zr)xAl1, the x range is quite large and experimental composition zone also covers (Cu,Zr)xAl1 (Cu4.7Zr50Al8.3). This (Cluster)x(Glue atom) formula is supported by the efficient cluster packing model proposed by Miracle [11]: dense-packed clusters centered by primary solute atoms are packed in a close-packing face-centered-cubic (fcc) like structure and the secondary solute atoms (or glue atoms as we call them) are located in the interstitial sites. An fcc unitcell includes four lattice sites and four octahedral interstices. The ratio 1:1 for the number of clusters to that of glue atoms indicates that glue atoms only occupy the octahedral interstices.

Table 1. Experimental data of the Cu-Zr-M BMGs. The last two BMGs are from the literature.

| (cluster)xMx | Atomic percent | Tg (K) | Tl (K) | ATs (K) | Ts (K) | Tg/Tl | γ   |
|--------------|----------------|--------|--------|---------|--------|-------|-----|
| (Cu,Zr)xAl0.46 | Cu43.9Zr52.1Al4 | 685    | 733    | 48      | 1195   | 0.573 | 0.390 |
| (Cu,Zr)xAl0.74 | Cu42.3Zr50.8Al6.3 | 692    | 753    | 61      | 1174   | 0.589 | 0.404 |
| (Cu,Zr)xAl0.95 | Cu41.4Zr50.2Al8 | 708    | 776    | 68      | 1174   | 0.603 | 0.412 |
| (Cu,Zr)xAl1 | Cu41.7Zr50Al8.3 | 707    | 774    | 67      | 1169   | 0.605 | 0.413 |
| (Cu,Zr)xAl1.09 | Cu41Zr60Al9 | 711    | 778    | 67      | 1163   | 0.611 | 0.415 |
| (Cu,Zr)xAl1.26 | Cu40.7Zr48.4Al10.9 | 715    | 782    | 67      | 1150   | 0.622 | 0.419 |
| (Cu,Zr)xAl1.67 | Cu39Zr47.1Al13.2 | 731    | 769    | 38      | 1145   | 0.638 | 0.410 |
| (Cu,Zr)xTi1 | Cu41.7Zr50Ti8.3 | 632    | 685    | 53      | 1210   | 0.522 | 0.372 |
| (Cu,Zr)xAg1.09 | Cu41Zr60Ag9 | 679    | 732    | 53      | 1181   | 0.575 | 0.394 |
| (Cu,Zr)xAl0.83 [8] | Cu58.7Zr35.9Al6 | 730    | 790    | 39      | 1173   | 0.648 | 0.413 |
| (Cu,Zr)xAl1 [9] | Cu50.0Zr41.7Al8.3 | 738    | 788    | 50      | 1173   | 0.629 | 0.412 |
4. Conclusions
Series of (Cu₅Zr₆)ₓM, BMG compositions were designed according to our cluster line criterion where M stands for Al, Ti and Ag respectively. When x is about 0.46~1.7 for Al, 1.09 for Ag and 1 for Ti, BMG rods with diameter of 3mm were obtained by copper mould suction. The best BMG compositions correspond to a simple composition formula (cluster)₁(⟨glue atom⟩). 

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