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Structural essence of abnormal crystallization behaviors during the annealing of $Cu_{33}Zr_{67}$ metallic glass

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ABSTRACT

During the non-isothermal annealing of $Cu_{33}Zr_{67}$ metallic glass (MG), two abnormal crystallization behaviors were detected. Nano-crystal growth ceasing leads to amorphous/nano-crystalline dual-phase structure, and residual amorphous crystallization is accompanied by grain coarsening. The structural evolutions of $Cu_{33}Zr_{67}$ MG at atomic-level were observed by high-resolution transmission electron microscopy. By analyzing structural factors, the nano-crystal growth ceasing is attributed to the spatially variation of icosahedral short-range order density arising from the structural heterogeneity of $Cu_{33}Zr_{67}$ MG, and the concurrence of crystallization and grain coarsening is due to higher thermal stability of residual amorphous as compared to bct-$CuZr_2$ nano-structure.

1. Introduction

Metallic glasses (MGs), as a new class of disordered materials, have been attracted much attention. In the absence of defects such as dislocations or grain boundaries, the yielding of MGs can occur only at stresses approaching ultimate theoretical strength [1,2]. However, the actual strength of MGs is far below this value [3] due to shear-band softening [4]. Therefore, tremendous research efforts have been dedicated to alleviate the shear-band softening and to improve the strength. Over the past decades, it has been indicated that nano-grain (NG) reinforced MG is found to be one of promising ways to strengthen MGs [5–8], because the NGs embedded in the MG matrix will block the propagation of shear bands and promote the formation of multiple shear bands [9]. According to this principle, a Mg-Cu-Y alloy with amorphous/nano-crystalline dual-phase structure was ingeniously designed most recently [10]. The reported strength is very close to the ultimate theoretical strength of Mg-based materials, which shows the strong application potential of NG reinforced MGs.

In many cases, the NG reinforcement in MG matrix is in-situ formed by annealing fully amorphous alloys [5,11,12]. Therefore, it is particularly important to reveal the structural factors governing nano-crystallization. Recently, great advances have been made to understand the atomic structure of MGs, which shed a light on the structural essence of nano-crystallization, e.g., the importance of icosahedral short-range order (ISRO) during the crystallization was realized [13,14], and the effect of structural heterogeneity on crystallization was discussed [15]. However, the knowledge frame of the relationship between MG structure and nano-crystallization is far from well-established. For example, the crystallization of MGs generally has a very high nucleation rate due to large driving force, but some Zr-based MGs crystallize into a structure with coarse grains [16]. This puzzle derives from a vague understanding of its structural essence. In this work, the non-isothermal crystallization of $Cu_{33}Zr_{67}$ MG was studied, two abnormal crystallization behaviors of nano-crystal growth ceasing and concurrence of crystallization and grain coarsening were reported, and their atomic-level structural factors were then analyzed.

2. Experimental

A master ingot of $Cu_{33}Zr_{67}$ was first prepared by arc melting pure Zr (99.9 wt%, purity) and Cu (99.999 wt%, purity) elements under an argon atmosphere. Then, MG ribbons (40–50 μm, thickness) were fabricated by the use of a melt-spinning. The specimens with different degrees of crystallization were obtained by annealing the MG ribbons in a differential scanning calorimetry instrument (DSC, DSC8500, Perkin Elmer). The applied temperature-time program was heating each melt-spun specimen to a certain temperature (i.e., 663 K, 665 K and 703 K) with the rate of 20 K/min followed by rapid cooling down to room temperature. The microstructures of amorphous and partially crystallized specimens were observed by X-ray diffraction (XRD, Panalytical

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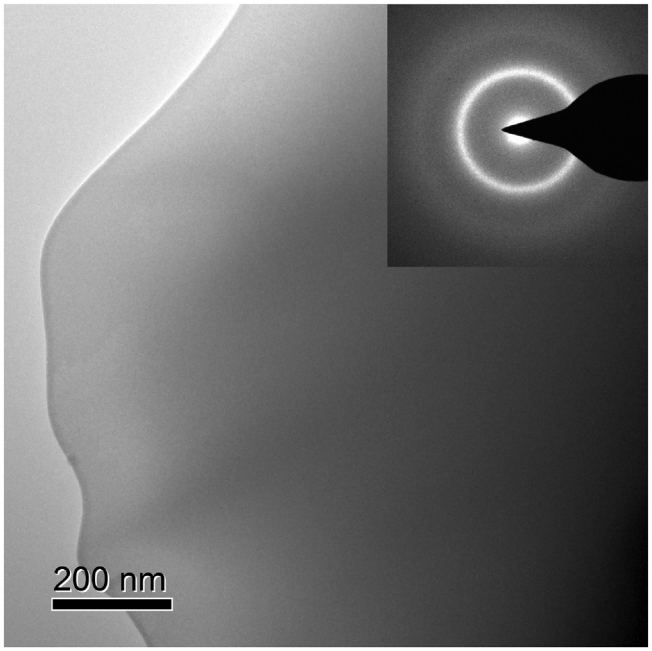

Fig. 1. Bright-field TEM image and selected area diffraction pattern of melt-spun $Cu_{33}Zr_{67}$ amorphous alloy.

X'pert PRO) and transmission electron microscopy (TEM, Tecnai F20, FEI). Specimens for TEM observation were thinned in a Precision Ion Polishing System (PIPS, Model 691, Gatan).

3. Results

The chemical composition of $Cu_{33}Zr_{67}$ ingot was tested to be Zr-32.76 at.%Cu by inductively coupled plasma atomic emission spectrometry. The Cu-Zr binary alloy with such composition has strong glass forming ability, and the cooling rate of melt-spinning is sufficient for forming fully amorphous structure. Fig. 1 shows the bright field (BF) TEM image of the melt-spun $Cu_{33}Zr_{67}$ specimen. Only featureless contrast is observed over the entire image. The selected area electron diffraction (SAED) pattern in the inset of Fig. 1 consists only of halo rings with no spotty diffraction pattern. The TEM analysis results indicate that the melt-spun $Cu_{33}Zr_{67}$ specimen is composed of a single amorphous phase.

It has long been known that the crystallization kinetics of $Cu_{33}Zr_{67}$ MG is controlled by a simple polymorphic transformation proceeding by a single stage transformation directly to stable bct-$CuZr_2$ phase [17]. In Fig. 2, the diffraction peaks in XRD patterns of annealed specimens at different crystallization stages can only be indexed to the bct-$CuZr_2$ phase. A DSC curve obtained by annealing to 703 K shows only one sharp exothermic peak; see Fig. 3. The information shown in Figs. 2 and 3 confirms that the $Cu_{33}Zr_{67}$ MG crystallizes directly into final structure by a polymorphic transformation. However, a close observation of microstructure is required to determine whether the crystallization behavior is simple or not.

Fig. 4 is the TEM images and the corresponding SAED patterns of annealed $Cu_{33}Zr_{67}$ specimens at different crystallization stages. The TEM image of specimen at initial crystallization stage (Fig. 4a) shows that NGs with grain size in the range of several to tens of nm is present in the MG matrix. In its SEAD pattern, diffraction rings corresponding to bct-$CuZr_2$ phase together with halo rings corresponding to amorphous phase are identified; see the inset of Fig. 4a. With the progress of crystallization, a large numbers of bct-$CuZr_2$ grains of several tens of nm with amorphous shell form, and exceptionally large grains are also observed; see the TEM image and the corresponding SAED pattern shown in Fig. 4b. According to classical theory, once hard impingement

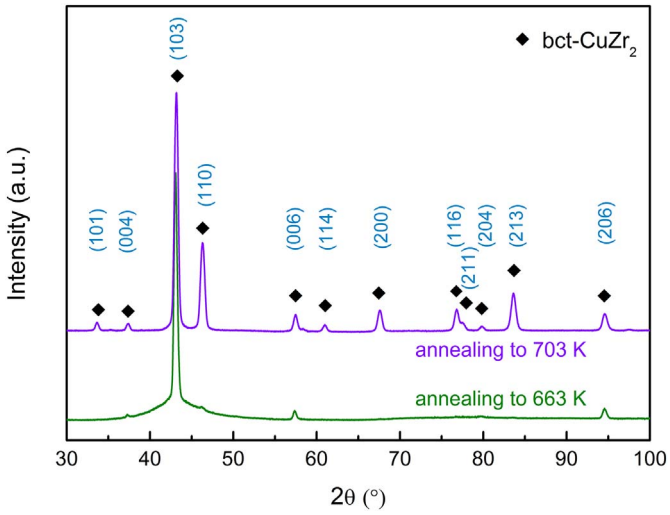

Fig. 2. XRD patterns (Co Ka radiation) of annealed $Cu_{33}Zr_{67}$ alloy by heating to different temperatures.

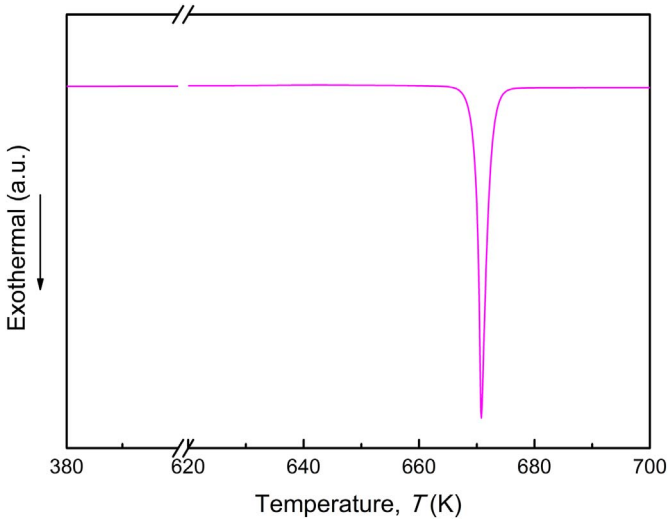

Fig. 3. DSC scan of $Cu_{33}Zr_{67}$ MG by heating to 703 K with the heating rate of 20 K/min.

of two neighboring polymorphic grains occurs, the grain growth will stop [18]. However, an abnormal phenomenon observed from Fig. 4a and b is that the growth of bct-$CuZr_2$ NGs ceases at the size of several tens of nm even though the hard impingement do not take place. The further crystallization of residual amorphous shell involves another abnormal phenomenon of concurring grain coarsening. Finally, the microstructure of completely crystallized specimen is constituted of only coarse bct-$CuZr_2$ grains (~0.5 μm); see Fig. 4c. The TEM observations indicate that the polymorphic crystallization of $Cu_{33}Zr_{67}$ MG involves two stages, i.e., the first stage is crystallization into a structure of bct-$CuZr_2$ NGs embedded in amorphous shells, and the second stage is the concurrence of residual amorphous crystallization and grain coarsening. Note that, due to the overlapping of the two stages, the DSC curve in Fig. 3 shows only one exothermic peak.

4. Discussion

4.1. Nano-crystal growth ceasing

A key point for revealing the structural essence of $Cu_{33}Zr_{67}$ MG crystallization is to clarify the growth ceasing of polymorphic NGs. The structure of bct-$CuZr_2$ NGs embedded in amorphous shells is very similar with the dual-phase structure reported in ternary Mg-Cu-Y system