Cooling rate, structure, thermal stability and crystallization behaviour of Cu-based bulk glass-forming alloys

D. V. Louzguine-Luzgin, G. Xie, W. Zhang, T. Saito, K. Georgarakis, A. R. Yavari, G. Vaughan and A. Inoue

1 WPI Advanced Institute for Materials Research, Tohoku University, Aoba-Ku, Sendai 980-8577, Japan
2 Institute for Materials Research, Tohoku University, Aoba-Ku, Sendai 980-8577, Japan
3 SIMAP-LTPCM, Institut National Polytechnique de Grenoble, St-Martin-d’Hères Campus, Grenoble, BP 75, 38402, France
4 European Synchrotron Radiation Facility, 6 rue Jules Horowitz, 38042, Grenoble, France
e-mail: dml@imr.tohoku.ac.jp

Abstract. We summarize the structural features of several Cu-based alloys known so far having high glass-forming ability and investigate the influence of Ag addition on their crystallization behavior. According to synchrotron-beam X-ray radiation studies, an c68 Cu10Zr7 phase is found to be a good approximant to the Cu-Zr-Ti and Cu-Zr-Ag glassy phases. The structure of the bulk glassy Cu36Zr48Al8Ag8 and Cu44Ag15Zr36Ti5 alloy samples studied by high-resolution TEM was found to contain well developed medium-range order zones and nanoparticles, respectively. An influence of the cooling rate on the structure and properties of the Cu-based glassy alloys on heating was also studied. The crystallization kinetics of Cu55Zr45, Cu50Zr50, Cu55-xZr45Agx (x = 0, 10, 20), Cu44Ag15Zr36Ti5, Cu45Zr45Al5Ag5 and Cu36Zr48Al8Ag8 glassy alloys was also analyzed substantially. Cu35Zr45Ag20 alloy was found to exhibit possible phase separation upon heating within a supercooled liquid region.

1. Introduction

Bulk metallic glassy (BMG) alloys are promising structural and functional materials owing to their superior properties [1,2]. Cu-based BMG alloys were reported to exhibit a high mechanical strength exceeding 2 GPa [3,4]. A quaternary Cu55Zr30Ti10Co5 glassy alloy showed the highest ultimate compressive strength of 2.3 GPa [5]. Binary Cu-Zr and Cu-Hf bulk glassy alloys were also formed but only in the narrow composition ranges [6,7] and their glass-forming ability (GFA) is rather low. The nanocrystal-glassy Cu-Zr composite showed a room temperature compressive plastic deformation of 50% [8]. An addition of the third element like Ti [3,9] or Al [10], for example, enhances the GFA of a binary alloy in accordance with the “confusion” principle [11] if some other important principles known as Inoue rules [12] are satisfied. The devitrification behavior of the binary Cu-Zr alloys [13],
ternary Cu-Zr-Ti [14,15], quaternary Cu-Zr-Ti-Ni[16] and quinary [17] glassy alloys has been also studied. Cu_{47.5}Zr_{47.5}Al_{5} glassy alloy exhibits a relatively large ductility [18].

Cu_{45}Zr_{45}Ag_{10} alloy exhibited one of the highest GFA's (the critical diameter is 6 mm) among Cu-Zr-Ag glassy alloys [19]. Ag also drastically improves the GFA of a Cu-Zr-Ti alloy [20], Cu-Zr-Al [21] alloys. The formation of the nanoscale icosahedral phase was observed in some Cu-Zr-Ti-Pd alloys [22]. The thermal stability and devitrification behaviour of Cu-based alloys as important features of metallic glasses influencing their applications are studied in the present work.

2. Experimental Procedure
The ingots of the Cu_{55}Zr_{45}, Cu_{50}Zr_{50}, Cu_{55-x}Zr_{45}Ag_{x} (x = 0, 10, 20), Cu_{44}Ag_{15}Zr_{36}Ti_{5}, Cu_{45}Zr_{45}Al_{5}Ag_{5} and Cu_{36}Zr_{48}Al_{8}Ag_{8} alloys (composition is given in nominal atomic percentages) were prepared by arc-melting mixtures of pure metals having 99.9 mass% purity in an argon atmosphere. From these ingots, ribbon samples of about 20 µm in thickness were produced by the melt spinning technique while bulk samples were prepared by Cu mould casting. The cooling rate was measured by a thin (0.3 mm) thermocouple connected to analogue-to digital converter. The structure of the samples was examined by X-ray diffractometry (XRD) with monochromatic CuKα radiation. The phase transformations were studied by differential scanning calorimetry (DSC) and differential isothermal calorimetry. Transmission electron microscopy (TEM) investigation was carried out using a JEM 2010 (JEOL) microscope operating at 200 kV. The samples for TEM were prepared by an ion polishing technique. Synchrotron radiation X-ray diffraction in transmission was carried out using a high energy monochromatic beam of the European Synchrotron Radiation Facility (ESRF). The photon energy was 94 keV. The radial distribution RDF(r) and pair distribution PDF(r) functions were obtained by the Fourier transformation of the interference function Q(f(Q)) [23].

3. Results
The cooling rate was measured on casting Cu_{44}Ag_{15}Zr_{36}Ti_{5} alloy. As it is expected the cooling rate was found to depend on the ingot size and change with temperature and within the ingot. The cooling rate in the center of the ingot in the temperature range of 900-1200 K ranges from 1000 to 3000 K/s for 3 mm ingot, from 200 to 800 K/s for 5 mm ingot and from 100 to 300 K/s for 10 mm ingot. Thus, one can see that even in case of BMG alloys their solidification is a highly non-equilibrium process and the cooling rate is much higher then that at which conventional equilibrium phase diagrams are built.

Fig. 1 shows pair distribution function of the Cu_{45}Zr_{45}Ag_{10} glassy alloy. One can also assume that the Cu-Zr interatomic pair is the most probable interatomic distance corresponding to left shoulder of the first PDF function maximum in the present alloy while Ag-Zr peak fills the space between two peaks related to Cu-Zr and Zr-Zr distances. It is found that the medium-range order in this and similar alloys maintains up to 2 nm distance. According to TEM investigation most of Cu-based glassy samples have a fully amorphous structure except for the Cu_{44}Ag_{15}Zr_{36}Ti_{5} alloy in which some nanoparticles (~3 nm in size, likely AgZr phase) were found in a bulk glassy state Fig. 1 (insert).

oC68 Cu_{10}Zr_{7} phase is a stable phase forming in some Cu-Zr, Cu-Zr-Ti and Cu-Zr-Ag alloys after crystallization of the glassy phase. It is isomorphous to oC68 Ni_{10}Zr_{7} one. During the exothermic reactions the supercooled liquid of Cu_{55-x}Zr_{45}Ag_{x} (x = 0, 10, 20) alloys crystallizes forming oC68 Cu_{10}Zr_{7} phase in Cu_{55}Zr_{45} alloy and a mixture of oC68 Cu_{10}Zr_{7} ss and tP4 AgZr ss (ss denotes solid solution) phases in Ag-bearing alloys.

Different Cu-Cu and Cu-Zr interatomic distances observed in the oC68 Cu_{10}Zr_{7} compound varying in wide ranges from about 0.24 to 0.31 nm for Cu-Zr pair and from about 0.22 to 0.31 for Cu-Cu pair explain the shape of the main PDF(r) peak in Cu-Zr-Ti and Cu-Zr-Ag alloys and the oC68 Cu_{10}Zr_{7} phase can be used as a good approximant to describe the structure features of these glassy alloys.
The linearity of the Avrami plot of \( \ln(-\ln(1-x)) \) vs. \( \ln(t) \) found for Cu-Zr-Ag alloys indicates that the crystallization of the alloys obeys the well-known kinetic law \( x(t) = 1 - \exp(-Kt^n) \) for the volume fraction \( x \) transformed as a function of time \( t \) provided that the nucleation and growth rates are time-independent. The values of the Avrami exponent obtained are close to 4 which indicates a steady-state nucleation and 3-dimensional interface-controlled growth of nuclei typical for an eutectic-type reaction. XRD results (see Fig. 2) indicate that Cu_{10}Zr_{7}^{ss} phase is the main structure constituent in the Cu_{45}Zr_{45}Ag_{10} alloy while the Cu_{35}Zr_{45}Ag_{20} alloy contains a large fraction of AgZr^{ss} phase. The phase composition was confirmed using TEM. A small volume fraction (~10 vol.%) of a residual globular glassy phase is observed in the structure of the Cu_{35}Zr_{45}Ag_{20} alloy annealed at 722 K while no phase separation was found in the case of the as-solidified sample and the sample annealed at \( T_g \). According to EDX analysis the residual amorphous phase is depleted in Ag compared to the crystalline region. This is explained to be a result of phase separation in the supercooled liquid region.

During the exothermic reactions the supercooled liquid of Cu_{44}Ag_{15}Zr_{36}Ti_{5} glassy alloy crystallizes forming Cu_{10}Zr_{7}^{ss} and AgZr^{ss} phases, though some peaks remained unidentified which indicates possible existence of a third phase. The Cu_{36}Zr_{48}Al_{8}Ag_{8} alloy has an exceptionally high GFA and its critical diameter \( (D_{cr}) \) is exceeds 20 mm. The structure of the as-solidified bulk sample was also studied by TEM and the as-solidified structure was found to be fully amorphous, while, on prolonged observation in the TEM, it partially crystallized. On heating AgZr^{ss} phase precipitates. TEM EDS analysis showed that, in comparison to the residual glassy matrix, the precipitating crystalline phase is enriched in Zr and Ag, which is consistent with the primary formation of the tP4 AgZr^{ss} phase. Additionally, an unidentified phase is also present. There is no significant difference in the crystallization products obtained from both the ribbon and bulk glassy samples. The Cu_{10}Zr_{7}, Zr_{2}Cu and unidentified phases have formed at higher temperatures. The isothermal calorimetry data showed two shoulders of the exothermic peak which likely indicates two competitive phase transformations related to the formation of AgZr^{ss} phase and the unidentified phase taking place simultaneously. Contrary to the Cu_{36}Zr_{48}Al_{8}Ag_{8} alloy, the Cu_{45}Zr_{45}Al_{8}Ag_{8} alloy \( (D_{cr}=9 \text{ mm}) \) formed a mixture of Cu_{10}Zr_{7}, Cu_{2}AlZr and AgZr phases by eutectic-type reaction on heating.

4. Discussion

The medium-range order in Cu-Zr-Ti and Cu-Zr-Ag glassy alloys maintains above 2 nm distance. It is also shown that the interatomic distances correspond to those of oC68 Cu_{10}Zr_{7} compound. The structure of the Cu_{45}Ag_{15}Zr_{36}Ti_{5} glassy alloy depends on the cooling rate. It is rather fully amorphous in the case of ribbon samples while the nanoscale clusters of the crystalline phase (highly ordered regions) are formed in the bulk samples. As it is expected the cooling rate depends on the ingot size.
and it changes with temperature. There is also a temperature gradient inside the ingot. The as-solidified structure of the bulk glassy Cu_{36}Zr_{48}Al_{8}Ag_{8} alloy sample was found to be disordered.

Cu_{55}Zr_{45}, Cu_{55-x}Zr_{45}Ag_{x} (x = 0, 10, 20), and Cu_{45}Zr_{45}Al_{5}Ag_{5} glassy alloys crystallize by the eutectic mechanism. Cu_{44}Ag_{15}Zr_{36}Ti_{5} and Cu_{36}Zr_{48}Al_{8}Ag_{8} glassy alloys (which are much better glass-formers) have a complex crystallization behaviour involving several crystalline phases precipitating continuously. Thus, the GFA is higher at the off-eutectic compositions. It has also been noted before that some particular alloy compositions lying away from the equilibrium eutectic composition possess better GFA than the eutectic one [24] which is explained by non-equilibrium solidification conditions on casting BMG alloys [25]. The Avrami exponent obtained in the initial crystallization stage of the Cu_{36}Zr_{48}Al_{8}Ag_{8} alloy ribbon sample (3.5) is slightly higher than that of the bulk Cu_{36}Zr_{48}Al_{8}Ag_{8} alloy sample (3.0). This phenomenon can be related to preferential crystallization at the surface (surface-induced crystallization needs much lower activation energy) [26,27]. It is also reflected in the increase in T_{x} of the ribbon sample compared to the bulk one at high enough heating rate.

5. Conclusion

The medium-range order in Cu-based glassy alloys maintains above 2 nm distance. The interatomic distances nearly correspond to those of c68 Cu_{10}Zr_{7} compound. The structure of the Cu_{44}Ag_{15}Zr_{36}Ti_{5} glassy alloy depends on the cooling rate. It is rather fully amorphous in the case of ribbon samples while the nanoscale clusters of the crystalline phase are formed in the bulk samples. As it is expected the cooling rate depends on the ingot size as well as it changes with temperature and within the ingot. The as-solidified structure of the bulk glassy Cu_{36}Zr_{48}Al_{8}Ag_{8} alloy sample was found to be disordered. Cu_{55}Zr_{45}, Cu_{55-x}Zr_{45}Ag_{x} (x = 0, 10, 20), and Cu_{45}Zr_{45}Al_{5}Ag_{5} glassy alloys crystallize by the eutectic mechanism but the best glass-forming compositions rather have a slightly off-eutectic composition.

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