Nano structure of rapidly quenched Cu–(Zr or Hf)–Ti alloys and their devitrification process

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Abstract

The structure and primary devitrification process of the melt-spun Cu_{60}(Zr or Hf)$_{30}$Ti$_{10}$ alloys were investigated. It was confirmed that the compositional segregation in the diameter range of 5–10 nm exists in the as-quenched state. The nanocrystalline particles with cubic structure are observed in the glassy matrix in the high-resolution transmission electron microscopy images, of which size is corresponding to the scale of compositional segregation. Small-angle X-ray scattering measurement also indicates the development of nanoscale inhomogeneity with the same size as that of nanocrystalline particles. The nanocrystalline region has high Cu content. In contrast, Zr or Hf and Ti elements are enriched in the glassy region. These results are recognized as the formation of novel structure consisting of the glassy and nanocrystalline phases. It is suggested that the precipitation of bcc CuZr phase as a primary crystallization phase proceeds in the glassy phase remaining the nanocrystalline phase in the Cu–Zr–Ti alloy. Meanwhile, the glassy and nanocrystalline phases are transformed to an orthorhombic Cu$_8$Hf$_3$ phase at the initial crystallization stage in the Cu–Hf–Ti alloy. These differences of crystallization process are consistent with the results of thermodynamic and kinetic analyses of the transformation mode.

Keywords: Cu-based metallic glass; Nanocrystal; Nanostructure; Transformation; Crystallization; Kinetics

1. Introduction

Recently, new Cu-based bulk glassy alloys with high mechanical strength have been reported in the Cu–(Zr and Hf)–Ti systems [1]. These bulk glassy alloys have attracted attention in the aspect that they do not satisfy the three empirical rules for high glass-forming ability (GFA), which has applied to most of bulk glassy alloys in various systems [2]. The atomic size ratios of the constitutional elements are 1.28 for Zr/Cu, 1.25 for Hf/Cu, 1.10 for Zr/Ti, 1.09 for Hf/Ti and 1.14 for Ti/Cu, which indicates a small size mismatch in the Zr–Ti, Hf–Ti and Ti–Cu pairs. Heats of mixing have been estimated to be −23 kJ/mol for Cu–Zr, −17 kJ/mol for Cu–Hf, 0 kJ/mol for Zr–Ti and Hf–Ti and −9 kJ/mol for Cu–Ti [3], which are comparatively smaller than those in the typical alloys with high GFA [4,5]. It is noted that Zr–Ti and Zr–Hf pairs have no chemical affinity. These facts are expected to create a novel structure in the glassy state in the Cu–(Zr and Hf)–Ti alloys. It is also expected that the local atomic structure in the as-quenched state and the transformation behavior are different from those in the previously reported bulk-forming metallic glasses [6,7]. In this paper, we evaluated the structure of the melt-spun Cu$_{60}$(Zr or Hf)$_{30}$Ti$_{10}$ alloys using X-ray diffraction (XRD), transmission electron microscope (TEM) and small-angle X-ray scattering (SAXS) in order to investigate the feature of the novel structure in these alloys. We also examined the primary devitrification process of these alloys.

2. Experimental procedure

Melt-spun Cu$_{60}$(Zr or Hf)$_{30}$Ti$_{10}$ ternary alloys with a cross section of 0.03 × 1 mm$^2$ were produced from alloy ingots prepared by arc melting high-purity metals of 99.999 mass% Cu, 99.9 mass% Zr, 99.9 mass% Hf and 99.9 mass% Ti in a purified argon atmosphere. The structure and thermal
property of the melt-spun alloys were studied by XRD with Cu–Kα radiation operated at 40 kV-30 mA and differential scanning calorimetry (DSC) with a heating rate of 0.67 K/s. The microstructure was examined by high-resolution transmission electron microscopic (HREM) observation using field-emission transmission electron microscopy (FE-TEM) with an accelerating voltage of 300 kV (JEOL JEM-3000F). The sample for TEM observation was prepared by the ion milling technique with liquid nitrogen cooling. The compositional analysis was performed by nanobeam energy dispersive X-ray spectroscopy (EDX) and high-angle annular detector dark-field scanning transmission electron microscopy (HAADF-STEM). The nanoscale inhomogeneity was also evaluated by SAXS measurement using a pinhole collimation type SAXS instrument (RIGAKU PSAXS-3S) with Mo target.

3. Results and discussion

3.1. Structure in the as-quenched state

Figs. 1 and 2 show XRD patterns and DSC curves of the melt-spun Cu₆₀Zr₃₀Ti₁₀ and Cu₆₀Hf₃₀Ti₁₀ alloys, respectively. No obvious diffraction peaks are observed in both the alloys in the XRD patterns. The exothermic reactions with more than three peaks appear after the glass transition in the crystallization process in the DSC curves. The onset temperatures of glass transition, \( T_g \) and crystallization, \( T_x \) are 711 and 745 K in the Cu₆₀Zr₃₀Ti₁₀ alloy and 755 and 813 K in the Cu₆₀Hf₃₀Ti₁₀ alloy, respectively. The supercooled liquid region defined by the interval of these temperatures in the Cu₆₀Hf₃₀Ti₁₀ alloy (58 K) is wider than that in the Cu₆₀Zr₃₀Ti₁₀ alloy (34 K), which implies a difference of stability of supercooled liquid state between the alloys. We can also find the difference in the exothermic reactions in the alloys. The transformation proceeds through the sharp exothermic peak at the initial stage in the Cu₆₀Hf₃₀Ti₁₀ alloy, which is in contrast to the two exothermic peaks with similar intensities in the Cu₆₀Zr₃₀Ti₁₀ alloy. The enthalpy of the first exothermic peak in the Cu₆₀Hf₃₀Ti₁₀ alloy is 3.1 kJ/mol. It is nearly equal to the sum of enthalpies of the first (1.8 kJ/mol) and second (1.7 kJ/mol) peaks in the Cu₆₀Zr₃₀Ti₁₀ alloy. The temperature interval between the first and second exothermic peaks of approximately 54 K in the Cu₆₀Zr₃₀Ti₁₀ alloy is much smaller than that (approximately 77 K) in the Cu₆₀Hf₃₀Ti₁₀ alloy. These results lead to the difference of the transformation behavior, especially primary crystallization process, in the present alloys.

In order to examine the microstructure, HREM observation was carried out. Fig. 3 shows the HREM images and selected-area electron diffraction patterns (SADPs) of the as-quenched Cu₆₀Zr₃₀Ti₁₀ ((a), (b)) and Cu₆₀Hf₃₀Ti₁₀ ((c), (d)) alloys, respectively. In the SADPs taken from the region of approximately 1 μm in diameter ((b) and (d)), only the broad rings are observed with no obvious diffraction spots, which is consistent to the XRD results. However, the HREM images ((a) and (c)) exhibit the inhomogeneous structure. We can confirm the fringe contrast in the dark regions in the glassy matrix in the HREM images, which indicates the existence of particles with crystalline structure. The crystalline particles have a fine size of approximately 5 nm in diameter and are dispersed randomly. Thus, it is found that the mixture phases of nanocrystal and glass are contained in the melt-spun Cu₆₀(Zr or Hf)₃₀Ti₁₀ alloys.

3.2. Characterization of nanocrystalline phase

The HAADF-STEM (Z-contrast) images [8] of the as-quenched Cu₆₀Zr₃₀Ti₁₀ (a) and Cu₆₀Hf₃₀Ti₁₀ (b) alloys...
are shown in Fig. 4 for the examination of the atomic deviation in the as-quenched state. The brighter region in the image has relatively high concentration of the heavy atom (Zr or Hf) since the thickness is regarded as a constant due to the very small area for HAADF-STEM. The significant compositional segregation, of which the scale is in range of 5–10 nm in diameter, can be observed. The size of compositional segregation is corresponding to the results of HREM observation. It is, therefore expected that the compositional segregation originates from the structural difference of nanocrystalline and glassy phases in the as-quenched state of the Cu60(Zr or Hf)30Ti10 alloys.

The nanoscale inhomogeneity of the as-quenched Cu60Hf30Ti10 alloy is also evaluated by the SAXS measurement. Fig. 5(a) and (b) shows the SAXS results of the as-quenched Cu60Hf30Ti10 alloy. The increase in the intensity in the low q-range is due to the fluorescence exited by Mo Kα radiation. The significant peak with a q-value of approximately 1.2 nm⁻¹ is observed in the intensity profile for melt-spun Cu60Hf30Ti10 alloy. The peak is corresponding to the inhomogeneity in electron density due to the concentration difference, which is also clarified by HAADF-STEM. The average distance among the inhomogeneity is estimated to be approximately 5 nm. In order to evaluate the average grain size of nanocrystalline particle, Guinier plot is shown in Fig. 5(b). This plot was obtained by subtraction of the SAXS profile for the Cu60Hf30Ti10 alloy by that of the Cu50Hf50Ti10 alloy, which has completely homogeneous glassy structure [9]. Assuming spherical morphology, the estimated diameter of the nanocrystalline particles is 3.4 nm, which is in agreement with that in the HREM observation.

For the determination of the composition of the two phases, nanobeam EDX was performed. The average compositions of five data points in the nanocrystalline and glassy phases are Cu68.8Zr25.7Ti5.5 and Cu56.1Zr35.6Ti8.3 in the Cu60Zr30Ti10 alloy and Cu67.5-Hf27.2Ti5.3 and Cu48.0Hf43.2Ti8.8 in the Cu60Hf30Ti10 alloy, respectively. It is clarified that the Zr or Hf and
Ti atoms are enriched and the Cu element is rejected in the glassy phase. Therefore, it is concluded that the melt-spun Cu$_{60}$(Zr or Hf)$_{30}$Ti$_{10}$ alloys contain the structural and compositional inhomogeneity consisting of nanocrystalline and glassy phases.

The structural identification for nanocrystals was examined by nanobeam electron diffraction (NBD). Fig. 6 shows the NBD patterns taken from the nanocrystalline particles in the as-quenched Cu$_{60}$Zr$_{30}$Ti$_{10}$ ((a), (b)) and Cu$_{60}$Hf$_{30}$Ti$_{10}$ ((c), (d)) alloys. The beam diameter for NBD is approximately 2.4 nm. These patterns are recognized as a cubic structure along with the \( \frac{1}{2}1\overline{2}1/3C_{138} \) (a), \( \frac{1}{2}10/1C_{22} \) (b), \( \frac{1}{2}103/3C_{138} \) (c) and \( \frac{1}{2}241/2C_{138} \) (d) zone axes. The lattice constants of the nanocrystalline phases in Cu$_{60}$Zr$_{30}$Ti$_{10}$ and Cu$_{60}$Hf$_{30}$Ti$_{10}$ alloys are estimated to be \( a = 0.45 \) and \( 0.51 \) nm, respectively. Considering that the Cu content of nanocrystalline particles have approximately 70 at% and there are no cubic phases in the Cu–Zr, Cu–Hf and Cu–Ti systems with the lattice constants as described above, it is suggested that the cubic structure of Cu-rich nanocrystalline particles is a metastable phase. We can identify that the dark regions (i.e. Zr or Hf poor regions) in the HAADF-STEM images in Fig. 4 correspond to the nanocrystalline particles with the metastable cubic structure. Therefore, we can conclude that the melt-spun Cu$_{60}$(Zr or Hf)$_{30}$Ti$_{10}$ alloys have a novel structure consisting of the Cu-rich nanocrystalline particles with the metastable cubic structure in the glassy matrix with a nanoscale compositional segregation.

### 3.3. Mechanism of nanocrystalline phase formation

It is clarified that the glassy phase has comparatively high Zr or Hf and Ti contents in the compositional analysis of the melt-spun Cu$_{60}$(Zr or Hf)$_{30}$Ti$_{10}$ alloys. From the viewpoint of the alloy composition with higher GFA, we prepared the Cu$_{50}$Hf$_{40}$Ti$_{10}$ alloy ribbon, which has a similar composition with the glassy region in the melt-spun Cu$_{60}$Hf$_{30}$Ti$_{10}$ alloy. We have already reported that the HREM image of the as-quenched Cu$_{50}$Hf$_{40}$Ti$_{10}$ alloy has a homogeneous glassy structure and no fringe contrast corresponding to the nanocrystalline particle [9]. These results indicate that no nanocrystalline phase can be formed in the slightly Cu-poor alloy composition deviated from the Cu$_{60}$Hf$_{30}$Ti$_{10}$ alloy. It is, therefore, realized that the nanocrystalline phase formation is attributed to an excess of Cu (i.e. a lack of Hf) in the Cu$_{60}$Hf$_{30}$Ti$_{10}$ alloy. In contrast, the homogeneous single glassy phase has not been obtained in the Cu$_{50}$Zr$_{40}$Ti$_{10}$ melt-spun alloy. Although the reason is still unclear, we suppose that the formation of nanocrystalline phase in the Cu$_{50}$Zr$_{40}$Ti$_{10}$ alloy is correlated with the precipitation of metastable bcc CuZr phase. We have found that the CuZr nanocrystalline phase is transformed from the glassy phase in the Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy as discussed below.

We also suggest that the stability of Cu-rich nanocrystalline cubic phase is attributed to the Ti element. Ti has the atomic size between Cu and Zr or Hf with the absence of chemical affinities with Zr or Hf, which contributes to the increase of packing density of the cubic phase as well as glassy phase [10]. This investigation is supported by the increase of number density (i.e. number of atoms in the unit volume) by addition of Ti in the Cu–(Zr or Hf) melt-spun alloy [11]. For example, the number density increases by 1.4 % by substituting Ti for 10 at% Zr in the Cu$_{60}$Zr$_{40}$ alloy. The calculated number of densities in the Cu$_{60}$Zr$_{30}$Ti$_{10}$ and Cu$_{60}$Zr$_{40}$Ti$_{10}$ alloys are 0.0626 and 0.0617 \( \text{Å}^{-3} \), respectively. The coordination number around Zr in the Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy is approximately 12.8, which is larger.
than that (10.6) in the Cu_{60}Zr_{40} alloy. These results are also consistent with the investigation of increase of the packing density by addition of Ti. It is suggested that the high packing density contributes to the suppression of the rearrangement of the constitutional elements, which are one of the main factors for the formation of stable Cu-rich nanocrystalline phases in the as-quenched state [10].

3.4. Devitrification process

The primary crystallization behaviors of the melt-spun Cu_{60}(Zr or Hf)_{30}Ti_{10} alloys containing nanocrystalline particles in the glassy matrix have been investigated by XRD and TEM. Fig. 7 shows XRD patterns of the Cu_{60}Zr_{30}Ti_{10} alloy annealed for 600 s at 753 K and the Cu_{60}Hf_{30}Ti_{10} alloy annealed for 300 s at 813 K, which are subjected to the first exothermic reaction in the DSC curves. No obvious diffraction peaks are observed in the annealed Cu_{60}Zr_{30}Ti_{10} alloy, suggesting the precipitation of crystalline phase with a fine grain size. In contrast, the diffraction peaks corresponding to the orthorhombic Cu_{8}Hf_{3} phase are confirmed in the Cu_{60}Hf_{30}Ti_{10} alloy. For further identification of the primary phases, TEM observation was carried out for both the alloys. Fig. 8 shows the bright-field TEM images and NBD patterns of the Cu_{60}Zr_{30}Ti_{10} alloy annealed for 600 s at 753 K ((a)–(c)) and the Cu_{60}Hf_{30}Ti_{10} alloy annealed for 300 s at 813 K ((d), (e)). Very fine grains in the diameter less than 10 nm are observed in the Cu_{60}Zr_{30}Ti_{10} alloy, which is corresponding to the XRD result. The NBD pattern taken from the precipitated particles shown in (b) is identified as a cubic structure along with [111] zone axis with a lattice constant of 0.35 nm. We can realize that the primary precipitation phase has the bcc CuZr structure due to its lattice constant of 0.326 nm. Simultaneously, we obtained the NBD pattern characterized as a cubic structure along with [210] zone axis.
as shown in (c), which has a lattice constant of 0.53 nm. This lattice constant is similar to that of the Cu-rich nanocrystalline phase in the as-quenched state. These results lead the suggestion that the glassy phase crystallizes into the bcc CuZr phase remaining the Cu-rich nanocrystalline cubic phase at the first exothermic reaction. It is also consistent to the compositional analysis of the glassy phase in the as-quenched state. The Cu content of glassy phase is poor (approximately 56 at%) comparing with those of the nanocrystalline phase and average composition of the whole area in 1 μm diameter. It is almost equivalent with that of the CuZr phase. The precipitated particles have comparatively large grain size in the diameter of 20–50 nm in the Cu60Zr30Ti10 alloy shown in (d). The typical NBD pattern in Fig. 8(e) taken from the particles is identified as the orthorhombic Cu8Hf3 phase along with [013] zone axis, which is in good agreement with the XRD result. Since no NBD pattern corresponding to a cubic phase is obtained in the annealed Cu60Zr30Ti10 alloy, it is suggested that the glass and nanocrystalline phases are transformed to the orthorhombic Cu8Hf3 phase at the first exothermic reaction in the DSC curve. Therefore, we can summarize the primary devitrification process in both the alloys as follows;

\[
\text{glass} + \text{nanocrystal (cubic)} \rightarrow \text{nano-CuZr} + \text{nanocrystal (cubic) in the Cu60Zr30Ti10 alloy}, \\
\text{glass} + \text{nanocrystal (cubic)} \rightarrow \text{nano-Cu8Hf3} \text{ in the Cu60Hf30Ti10 alloy.}
\]

It is realized that the difference in the primary crystallization processes between the alloys contributes to

![Fig. 8. Bright-field TEM images and nanobeam diffraction patterns of the Cu60Zr30Ti10 alloy annealed for 600 s at 753 K ((a)–(c)) and the Cu60Hf30Ti10 alloy annealed for 300 s at 813 K ((d), (e)).](image-url)
the difference in the exothermic reactions in the DSC curves. The large amount of enthalpy of the first exothermic reaction in the Cu_{60}Hf_{30}Ti_{10} alloy is attributed to the transformation of two metastable phases of glass and nanocrystal into the nano Cu_{60}Hf_{30} phase. We suggest that the Ti element plays the important role for the formation of nanocrystalline phase in the as-quenched state and nanoscale Cu_{60}Hf_{30} phase in the primary crystallization process by the suppression of rearrangement of constitutional elements.

The kinetics for the devitrification process were also examined by Johnson–Mehl–Avrami (J–M–A) analysis [12]. Fig. 9 shows the J–M–A plots of the primary crystallization reaction of the Cu_{60}Zr_{30}Ti_{10} (a) and Cu_{60}Hf_{30}Ti_{10} (b) alloys, where Y is volume fraction transformed and t_a is isothermal annealing time. The Avrami exponents, n of the Cu_{60}Zr_{30}Ti_{10} and Cu_{60}Hf_{30}Ti_{10} alloys are approximately 2.5 and 3.4, respectively. It is suggested that the primary crystallization mode is growth from quenched-in nuclei with constant nucleation rate for the Cu_{60}Zr_{30}Ti_{10} alloy and interface-controlled growth with decreasing nucleation rate for the Cu_{60}Hf_{30}Ti_{10} alloy [13].

![Fig. 9](image_url)  
Fig. 9. J–M–A plots of the melt-spun Cu_{60}Zr_{30}Ti_{10} (a) and Cu_{60}Hf_{30}Ti_{10} (b) alloys.

The difference of transformation mode between the alloys is strongly consistent to the investigation of the crystallization process described above. Fig. 10 shows the Arrhenius plot of the incubation period, \( \tau \) as a function of isothermal temperature, \( T \) for the primary devitrification process of the melt-spun Cu_{60}Zr_{30}Ti_{10} and Cu_{60}Hf_{30}Ti_{10} alloys.

![Fig. 10](image_url)  
Fig. 10. Arrhenius plots of incubation period, \( \tau \) as a function of isothermal temperature, \( T \) for the primary devitrification process of the melt-spun Cu_{60}Zr_{30}Ti_{10} and Cu_{60}Hf_{30}Ti_{10} alloys.

The calculated activation energies are 383 kJ/mol for the Cu_{60}Zr_{30}Ti_{10} alloy and 443 kJ/mol for the Cu_{60}Hf_{30}Ti_{10} alloy. The higher activation energy in the Cu_{60}Hf_{30}Ti_{10} alloy is originated from the transformation process of both the nanocrystalline and glassy phases at the primary stage. In contrast, since the nanocrystalline bcc CuZr phase is precipitated from the quenched-in nuclei in the glassy phase with remaining the nanocrystalline particles with cubic structure, we suggest that higher activation energy for nucleation is not necessary in the Cu_{60}Zr_{30}Ti_{10} alloy.

4. Conclusions

It is clarified that the Cu-rich nanocrystalline cubic phases are directly formed during the melt-quenching process in the Cu_{60}(Zr or Hf)_{30}Ti_{10} alloys and the high stability of the Cu-rich nanocrystalline cubic phases leads to the coexistence with the glassy phase in the nanometer scale. The formation of Cu-rich nanocrystalline phase is attributed to the excess of Cu content for the single glassy phase formation. It is also suggested that the Ti element stabilizes the nanocrystalline phases. The primary crystallization phases with a nanometer scale are confirmed. However, we found the difference of
the primary crystallization process between the alloys. The nano bcc CuZr phase is precipitated with remaining the Cu-rich nanocrystalline phase in the Cu_{60}Zr_{30}Ti_{10} alloy. In contrast, the glassy and Cu-rich nanocrystalline phases are transformed to the orthorhombic Cu_{8}Hf_{3} phase in the Cu_{60}Hf_{30}Ti_{10} alloy at the first exothermic reaction in the DSC curve. These behaviors are also consistent to the difference of the DSC curves and the kinetic analysis for the transformation mode in the present alloys.

References

[1] A. Inoue, W. Zhang, T. Zhang, K. Kurosaka, Acta Mater. 49 (2001) 2645–2652.
[2] A. Inoue, Mater. Trans. JIM 36 (1995) 866–875.
[3] F.R. de Bore, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, Cohesion in Metals, North-Holland, Amsterdam, 1988, pp. 361–492.
[4] A. Inoue, T. Zhang, T. Masumoto, J. Non-Cryst. Solids 150 (1992) 396–400.
[5] A. Inoue, T. Zhang, T. Masumoto, J. Non-Cryst. Solids 156–158 (1993) 473–480.
[6] J. Saida, C. Li, M. Matsushita, A. Inoue, J. Mater. Res. 16 (2001) 3389–3401.
[7] M. Imafuku, S. Sato, H. Koshiba, E. Matsubara, A. Inoue, Mater. Trans. JIM 41 (2000) 1526–1529.
[8] S.J. Pennycook, D.E. Jesson, Phys. Rev. Lett. 64 (1990) 938–941.
[9] M. Kasai, J. Saida, M. Matsushita, T. Osuna, E. Matsubara, A. Inoue, J. Phys. Condens. Matter. 14 (2002) 13867–13877.
[10] M. Kasai, E. Matsubara, J. Saida, M. Nakayama, K. Uematsu, T. Zhang, A. Inoue, Mater. Sci. Eng. A, in press.
[11] K. Uematsu, Master Thesis, Tohoku University, 2002.
[12] W.A. Johnson, R.F. Mehl, Trans. Am. Inst. Min. Engrs. 135 (1939) 416–458.
[13] J.W. Christian, The Theory of Transformations in Metals and Alloys—PART I, Oxford, Pergamon, 2002, pp. 538–546.