Relaxation and Crystallization Behavior of the $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ Metallic Glass

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We examined relaxation and crystallization behavior of the ternary $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ metallic glass by using positron annihilation and transmission electron microscopy (TEM). Observed changes in positron annihilation lifetime of the alloy annealed isothermally at 673 K, which is below the glass transition temperature, correlate well with observed density changes; while coincidence Doppler broadening (CDB) spectra exhibit no significant change. These observations demonstrate that free volume decreases without a rearrangement of atoms during structural relaxation. On the other hand, CDB spectrum has exhibited considerable changes when the same alloy was annealed at 773 K. TEM observations suggested that crystallization occurs via growth of spherulites of several hundred nm in diameter, which themselves are composed of radially grown grains. Chemical analysis revealed that Cu atoms are partitioned out during the growth of the spherulites. Diffraction study indicated that the unit cell of the crystalline phase belong to an orthorhombic system with $a = 0.892$, $b = 0.550$, and $c = 1.060$ nm; while remaining inter-spherulite regions are found to crystallize into an fcc phase with $a = 1.28$ nm, which is probably isostructural to the τ_3 phase.

(Received June 20, 2005; Accepted August 18, 2005; Published December 15, 2005)

Keywords: bulk metallic glass, structural relaxation, crystallization, positron annihilation, transmission electron microscopy

1. Introduction

Stability of bulk metallic glasses has been attributed to several factors, including a robustness of the amorphous structure itself and hindrance to crystallization. Chemical affinities and atomic size differences among constituent elements provide thermodynamical and topological conditions for the stability of metallic glasses.¹⁾ On the other hand, the existence of a crystalline or quasicrystalline phase at a composition close to that of the matrix amorphous alloy, as well as an ease of transportation of atoms within the amorphous phase, is among the ruling criteria for the presence of a crystallization path. The first crystalline phase to appear may or may not be an equilibrium phase.

A dominant structural change of an amorphous material prior to crystallization is relaxation to a more stable amorphous structure.²⁻⁴⁾ That is, atomic positions in the frozen-in liquid phase change slightly without a significant reshuffling of chemical bondings, so that local configurations become those of a lower free energy. During the relaxation process, however, many physical properties, such as atomic diffusivity,⁵⁾ viscosity,⁶⁾ mechanical ductility,⁷⁻¹⁰⁾ are known to change, and the nature of the relaxation process has been a subject of investigation for a long time. For example, Greer and Leake discussed structural relaxation and crossover effect, using a two-relaxation model.¹¹⁾ They suggested that one needs to take into account a distribution of relaxation times and possible non-linear effects in order to interpret changes of physical properties of amorphous materials upon annealing below the glass transition temperature (T_g). Tsao and Spaepen, in order to account for temperature-dependent viscosity changes of a Pd-Si amorphous alloy, pointed out that a reversible atomic rearrangement must take place without nearest neighbor changes or changes in chemical order, which is different from the irreversible changes of free volumes.¹²⁾ As for Zr-based bulk metallic glasses, Busch and Johnson¹³⁾ and Busch *et al.*¹⁴⁾ demonstrated that isothermal

changes in viscosity are well represented by a stretched exponential relaxation function. Quite recently, Yokoyama *et al.* showed that mechanical properties, especially Charpy impact values, of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ metallic glasses depend sensitively on the extent of annealing below T_g .¹⁵⁾ This finding is quite interesting and practically important since supercooled regions of Zr-based metallic glasses are among the largest in glass forming alloys. However, details of the structural changes in the supercooled liquid regime of this alloy, as well as its crystallization behaviors, has not been investigated so far.

The purpose of the current investigation is thus (i) to follow the observed macroscopic structural changes, as manifested by densification, by the use of positron annihilation techniques; and (ii) to examine crystallization behaviors by using TEM.

2. Experimental Procedure

A master alloy ingot of a ternary Zr-Cu-Al alloy was prepared by arc-melting mixtures of pure Zr, Cu and Al metals in an argon atmosphere. To maintain a low-oxygen concentration in the alloys, a special Zr crystal rod with an oxygen content of less than 0.05 at% was employed. A metallic glass having a composition of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ was cast into a rod-shaped specimen with 8 mm in diameter and 60 mm in length by a tilt casting technique, described previously.^{16,17)} The densities of the as-cast and annealed rod-shaped specimens were measured with an Archimedes method. For positron annihilation measurements, the rod-shaped alloy was sliced into discs 0.5 mm thick. A pair of the disc specimens were then annealed isothermally at 673 K for 100, 300, 1000, 1800, 2800, 3600, 7200 and 18000 s. At each annealing step, we carried out positron annihilation lifetime (PL) measurements by using a conventional fast-fast circuit with a time resolution of about 200 ps (FWHM), and coincidence Doppler broadening (CDB) experiments at room

temperature. The PL and CDB spectra consist of 1.5×10^6 and more than 10^9 counts, respectively. All the PL spectra were analyzed with the POSITRONFIT program.¹⁸⁾ As a positron source, we used $^{22}\text{NaCl}$ with an activity of 300 kBq, which was sandwiched by thin Kapton foils. Windows for S- and W-parameters were defined as $|p_L| < 5.0 \times 10^{-3} m_0 c$ and $1.3 \times 10^{-2} m_0 c < |p_L| < 3.0 \times 10^{-2} m_0 c$ regions in Doppler broadening spectra, where p_L is an electron momentum, c the speed of light and m_0 the electron rest mass. It is well established that changes in S-parameter correlate well with free volume changes, and that a detailed profile of Doppler broadening spectrum especially at a high electron momentum region (W-parameter) reflects the local atomic structure.¹⁹⁾

In order to prepare TEM specimens, the aforementioned samples were at first mechanically polished to 80 μm thick, and then dimpled. A small hole was then made by ion-milling with an incident angle of 15° at an acceleration voltage of 4 kV, followed by final thinning with an incident angle of 10° at 3 kV. We employed JEOL JEM-2010 and JEM-2100, both operating at 200 kV, for conventional TEM observations and energy dispersive X-ray spectroscopy (EDS) mappings, respectively. SAD patterns are presented after proper rotation calibration.

3. Experimental Results

Figure 1(a) summarizes basic properties of the $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ metallic glass in the form of a DSC curve (heating rate: 40 K/s), which shows calorimetric T_g of 706 K as well as crystallization temperature of 792 K.¹⁵⁾ Also, Fig. 1(b) shows changes in density when the specimen is isothermally kept at 673 K. As seen, after annealing for 10^2 – 10^3 s, the density increases rapidly by about 0.4%, and then reach a

plateau. This observed rise in density is comparable to 0.5%, a value reported for a Pd–Cu–Si alloy.⁷⁾

Figure 2 shows changes in PL of the $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ metallic glass during isothermal annealing at 673 K. The initial lifetime of 162 ps can be compared with 167 ps, a reported value for pure Zr metal.²⁰⁾ As annealing proceeds, PL decreases gradually until it reaches a plateau of about 147 ps. As seen, the decrease starts at an annealing time of approximately 100 s and reach a plateau at about 3000 s. This time span coincides with the time interval, during which a marked increase in density was observed, as shown in Fig. 1(b). This observation thus suggests that volume changes, as observed by a macroscopic density measurement, correspond well with free volume changes observed at the atomic level by the PL measurement.

Figure 3 shows CDB spectra of as-prepared and isothermally annealed specimens (at 673 K) for 100 to 18000 s, in the form of the ratio of the observed CDB intensity to that obtained for Zr metal. For comparison, we also showed CDB spectra of Cu and Al pure metals, in the form of ratios to Zr. (For the sake of clarity, error bars are given for the spectrum

Fig. 1 (a) DSC profile obtained at a heating rate of 0.67 K/s, and (b) density changes during isothermal annealing at 673 K of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ bulk glass. (ref. 15)

Fig. 2 Positron lifetime during isothermal annealing at 673 K. Note that the decrease in lifetime correlates well with increase in density (Fig. 1).

Fig. 3 CDB spectra of as-cast and isothermally annealed $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ metallic glasses, expressed in the form of a ratio of observed CDB intensity to the intensity of pure Zr metal. Annealing was carried out at 673 K, while the measurement was done at an ambient temperature. Also shown are CDB spectra of Cu and Al metals in the form of ratios to Zr.

Fig. 4 Transition in S- and W-parameters during annealing at 673 K, showing that changes in these parameters are small and have an approximate reciprocal relationship.

of pure Al only, and the extent of the errors of other data sets are similar to that shown for pure Al.) These profiles indicate that (i) in a low electron momentum region ($<0.01 m_0c$), the spectra of $Zr_{50}Cu_{40}Al_{10}$ metallic glass are similar to that of Zr metal, (ii) in higher electron momentum regions ($>0.02 m_0c$), they become similar to Al, and to a lesser extent, to Cu; and (iii) overall profile does not change significantly throughout annealing, except that taken for the specimen annealed for 100 s, which exhibits a slight decrease in the peak height at about $0.02 m_0c$. Although this decrease is within an experimental error, its implication will be discussed later.

In order to extract possible changes in the electronic structure of open volumes, to which positrons are presumably attracted, we obtained S- and W-parameters as a function of annealing time. Figure 4 shows changes in S- and W-parameters during annealing at 673 K. As also observed in the PL spectra, these parameters change slightly during the isothermal treatment. However, it can be noticed that the changes of the S-parameter correlate more or less inversely with those of the W-parameter. This type of systematic behavior is known for other systems, and suggests that the chemical environments of annihilation sites for positrons do not change significantly.¹⁹⁾ In other words, the observed behaviors of S- and W-parameters show that the decrease in free volume does not accompany rearrangements of atoms which form a free volume.

Figure 5 shows CDB spectra of $Zr_{50}Cu_{40}Al_{10}$ metallic glasses, (a) relaxed at 673 K, and (b) crystallized at 773 K, expressed in the form of ratio to the CDB intensity of the as-cast specimen. It can be recognized that the CDB spectrum of the relaxed specimen is essentially the same as that of the as-cast alloy, while that the spectrum obtained after crystallization differs fundamentally from both as-cast and relaxed alloys. This observation thus demonstrates that crystallization of the metallic glass results in the total modification of atomic arrangements of the alloy.

Figure 6 shows bright field (BF) image and selected area diffraction (SAD) pattern of a $Zr_{50}Cu_{40}Al_{10}$ metallic glass annealed at 773 K for 1.8 ks. As seen, crystallization proceeds via formation of spherical agglomerates, approximately 600 nm in diameter, of radially growing crystalline grains. These spherical structures are often observed in crystallization of amorphous metals, semiconductors, and organic materials, and known as spherulites; and suggest that

Fig. 5 CDB spectra of $Zr_{50}Cu_{40}Al_{10}$ metallic glasses annealed at (a) 673 K and (b) 773 K, expressed as a ratio of CDB intensity of annealed specimens to that of the as-cast specimen, showing that a considerable change in chemical environment of open volumes have taken place in the latter specimen.

Fig. 6 TEM BF image of a $Zr_{50}Cu_{40}Al_{10}$ metallic glass annealed at 773 K for 1.8 ks, and inset SAD pattern, showing that crystallization proceeds by nucleation and growth of radially growing crystalline agglomerates, or 'spherulites'.

crystallization proceeds by the nucleation and growth mechanism. It should also be pointed out that there are also crystallized grains between spherulites.

In order to examine possible compositional changes during crystallization, we carried out an EDS elemental analysis. Figure 7 summarizes the results of the EDS analysis: (a) BF image, (b) Zr, (c) Cu, and (d) Al elemental mapping. It can be seen that Cu atoms are enriched in inter-spherulite regions, while that Zr and Al atoms are depleted there. These observations thus show that Cu atoms are partitioned out during the growth of spherulites.

Crystallographic details of spherulites have been examined by conventional diffraction techniques. For example, Fig. 8 is a BF image of a spherulite, showing that radially-grown grains often exhibit a fringe-like contrast in the radial direction. The inset SAD pattern was obtained from one of the radially-grown grains, as indicated by a circle in the figure. In addition to the overall twofold symmetrical distribution of diffraction spots, there are strong streaks perpendicular to the fringe-like contrasts in the corresponding BF image, suggesting that the fringe-like contrasts arise

Fig. 7 (a) BF image, and EDS mapping of spherulites for the following elements: (b) Zr, (c) Cu, and (d) Al. Cu atoms are segregated and enriched in inter-spherulite regions.

Fig. 8 BF image of a spherulite and inset SAD pattern. (The pattern is rotation-calibrated.) Note the presence of fringe-like contrasts in the radial direction in most of radially-growing grains. The SAD pattern was obtained from an area indicated by a circle, showing, correspondingly, strong streaks perpendicular to the fringe contrasts.

Fig. 9 SAD patterns of radially-grown grains in a spherulite. Each spots can be indexed by assuming that an orthorhombic unit cell with $a = 0.892$, $b = 0.550$, and $c = 1.06$ nm. With this setting, these patterns can be identified as (a) [010], (b) [100] and (c) [103] zone axis patterns.

from numerous stacking faults. Note that stacking fault planes exist almost always in the radial directions.

Figure 9 shows SAD patterns obtained from other radially-grown grains. We took SAD patterns along seven different zone axes, and found that diffraction spots can consistently be assigned using an orthorhombic unit cell with $a = 0.892$, $b = 0.550$, and $c = 1.06$ nm. For example, Figs. 9(a), (b) and (c) have been assigned to [010], [100] and $[10\bar{3}]$ zone axis patterns, respectively. With this setting, the aforementioned stacking faults exist on the $\{100\}$ planes. We were not able to uniquely deduce the space group but systematic extinction of diffraction spots suggested that the crystalline phase belong to the one of the following space groups: $Pc2m$, $Pcm2_1$ or $Pcmm$.

Figure 10 is a BF image of an inter-spherulite region, together with an inset SAD pattern obtained from the grain indicated by the arrow. This pattern exhibits clear twofold symmetry and can be assigned to the $[110]$ zone axis pattern of a face-centered cubic (fcc) structure. Other SAD patterns obtained from inter-spherulite regions include $[111]$ and $[123]$ of an fcc structure. The unit cell parameter obtained was $a = 1.28$ nm, which can be compared with $a = 1.18$ nm, a value determined for the τ_3 phase.^{21,22)}

4. Discussion

We have shown that annealing at 673 K brings about a gradual decrease in PL, which corresponds well with the increase in density, while the CDB spectra does not alter significantly. These observations demonstrate that structural relaxation proceeds via decrease of the size of a free volume, while the local chemical surroundings of the free volume remain unchanged. On the other hand, the CDB spectrum obtained for crystallized specimens is fundamentally different from that of as-cast or relaxed specimens. Correspondingly, our TEM observations showed that crystallization proceeds by a growth of spherulites, from which Cu atoms are partitioned out. The resultant crystallized specimens are found to consist of dominant orthorhombic and minor cubic phases. In what follows, we discuss our observations from points of view of relaxation and crystallization.

4.1 Relaxation behavior

Structural relaxation of a metallic glass below T_g occurs when a frozen-in metastable liquid relaxes into a more stable state. This is an irreversible process and achieved by

Fig. 10 BF image of an inter-spherulite region, and inset SAD pattern taken from a grain indicated by a white arrow. The SAD pattern can be assigned to a $[110]$ zone axis pattern of an fcc structure with $a = 1.28$ nm, suggesting that the inter-spherulite grain is composed of the τ_3 phase.

elimination of excess free volume. On the contrary an equilibrium amount of free volume must also exist in liquids and in supercooled liquids, since its presence is a prerequisite for a number of dynamical properties, such as diffusion and viscosity.

In the past, structural relaxation has been studied by measuring a number of different physical properties, including diffusivity,⁵⁾ viscosity,⁶⁾ mechanical ductility,^{7–10)} and average structure itself.²³⁾ Changes in PL has also been measured for several glass forming systems, including $\text{Pd}_{77}\text{Cu}_6\text{Si}_{17}$ ²⁴⁾ and $\text{Ni}_{81}\text{P}_{19}$.²⁵⁾ Unlike our present investigation, these measurements were carried out for isochronally annealed specimens at different temperatures. Interestingly, these reports showed that the lifetime initially increases by a low temperature annealing (≈ 350 K), followed by a decrease by annealing at a temperature higher than 550 K. For example, Chen and Chuang ascribed an initial increase at around 350 K and a subsequent decrease at around 550 K to the localization of positrons around strained regions caused by clustering of atoms, and to the elimination of the strained area by growth of the clusters, respectively.²⁴⁾ As for Zr-based metallic glasses, there also exist several reports on PL and Doppler broadening measurements.^{26–30)} For example, Flores *et al.* reported, in the study of straining and hydrogen charging effects on Zr–Ti–Ni–Cu–Be glasses, showed that annealing at 348 K slightly decreases PL, whereas that straining and hydrogen charging resulted in the increase and decrease of PL, respectively.³⁰⁾ They attributed the observed increase in PL to an increase in open volume by the plastic strain.

In our positron annihilation experiments for isothermally

annealed samples, the decrease in PL was found to agree very well with an increase in density. Thus, the present result is a direct confirmation that the density change during relaxation is achieved by gradual reduction in free volume. This is in a general agreement with a suggestion made by Nagel *et al.* for Ni- and Be-containing Zr based alloys.^{28,29)} It should be pointed out here, however, that the observed PL in the present study represents an average value of lifetimes of positrons that annihilated at different open volumes within single specimen. This means that the present technique can not probe a possible distribution of PL. On the contrary, a structural relaxation process is often represented by assuming a distribution of relaxation lifetime. For example, Busch *et al.* showed that changes in the viscosity can be fitted well with a stretched exponential function, in which the exponential decay term was powered to a stretching exponents of 0.74–0.84.¹⁴⁾ Thus the changes in PL, and in fact most of the macroscopic properties of an amorphous phase, should be interpreted as an average behavior. In the current study, the observed PL transition from about 162 to 147 ps can be compared to the reported PL of 165, 163 and 110 ps for pure Zr, Al and Cu metals, respectively.²⁰⁾ It can be realized that the reduction of lifetime by 15 ps during the annealing at 673 K is indeed significant; suggestive of a change in the average size of open volumes or a large change in the electronic structure itself. Looking at the CDB spectra obtained for annealed specimens (Figs. 3 and 4), one realizes that these spectra are similar to each other and that the changes caused by annealing are indeed quite small. Especially, a close agreement in a low electron momentum region of the spectra of the annealed $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ glass with

that of pure Zr should be pointed out. This suggests that the electron density of the annihilation sites of the annealed metallic glasses is similar to that of Zr metal, and that it does not change significantly during the relaxation process, despite the marked decrease in PL. At the same time, the CDB spectra in a high electron momentum region ($>0.010 m_0c$) suggests that the electronic structure of the $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ glass is neither that of Zr, Al nor Cu. Only a slight decrease in the peak of the CDB profile was observed for the specimen annealed for 100 s (Fig. 3). A possible change in chemical order in such a short period when annealed at relatively high temperatures was reported by Koebrugge *et al.* in order to explain changes in the velocity of sound, or equivalently Young's modulus, of an annealed $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ amorphous alloy.³¹⁾ They described the observed change of velocity toward equilibrium by a competing process of temperature-dependent chemical short range order and a decrease in free volume. Similarly, an approach to equilibrium was reported by Mao and Altounian for enthalpy relaxation of $\text{Zr}_{67}(\text{Ni}_{1-x}\text{Cu}_x)_{33}$ metallic glasses.³²⁾ They showed that the positive formation enthalpy for Cu–Ni resulted in the increase in Cu–Cu and Ni–Ni bonding by annealing, whose kinetics also depend on annealing temperatures because the activation energy itself depends on composition. These studies showed that an approach to a chemical order, which is specific to a given temperature, is a rather fast process, especially at a temperature close to T_g . In the present CDB results, a peak at $0.02 m_0c$ showed an apparent slight decrease after annealing for 100 s, but the overall profile became that of as-cast specimen after annealing for 300 s. If the annealing for 100 s had brought about a chemical short range order, then the CDB profiles should have remained the same because it is an irreversible process at a fixed temperature. Considering that the observed change was on the order of an experimental error, and that the profile re-established that of the as-prepared state, we can not make a positive statement as to the chemical short range order in the present study. This is especially true considering that both the PL and CDB probe only an average structure as mentioned before. These considerations therefore led us to conclude that the observed structural relaxation during annealing at 673 K, which is below the glass transition temperature, is likely to be a both topologically and chemically invariant process and involves only a decrease in excess free volume.

4.2 Crystallization behavior

On the other hand, the CDB spectrum of the metallic glass annealed at 773 K was fundamentally different from those annealed at 673 K. Namely, the electron momentum at low energy regions ($<0.005 m_0c$) exhibited a slight decrease, whereas that at high energy regions ($>0.010 m_0c$) increased considerably. In other words, the spectrum became qualitatively more similar to Cu than to Zr. Nevertheless, it should be pointed out that the overall shape of the spectra is similar to none of the spectra obtained for pure metals (Zr, Cu or Al), an indication that the electronic structure of the alloy is fundamentally different from those of the pure metals. Our TEM study showed that this transition in CDB spectra is due to crystallization of the amorphous alloy. It showed that crystallization proceeds via nucleation and growth of

spherulites, which themselves are composed of radially-grown grains of about 150–200 nm. Diffraction studies suggested that these grains belong to a metastable orthorhombic phase with $a = 0.892$, $b = 0.550$, and $c = 1.06$ nm, although the present data set has not yet allowed us to unambiguously determine the space group. From a kinetic point of view, it is interesting to point out that (i) Cu atoms are partitioned out from the spherulites, *i.e.*, from the orthorhombic phase; and (ii) numerous stacking faults are created on the $\{100\}$ planes.

In the past, crystallization behaviors of Zr-based metallic glasses have been investigated by several groups.^{33–38)} Inoue *et al.*, in the study on the $\text{Zr}_{65}\text{Cu}_{27.5}\text{Al}_{7.5}$ metallic glass, showed that crystallization takes place through the precipitation of a body-centered tetragonal (bct) Zr_2Cu phase ($a = 0.322$, and $c = 1.12$ nm), in which Al atoms are presumably dissolved.³³⁾ They also showed that the morphology of crystallized structures strongly depends on the annealing temperature: above T_g it exhibits a dendritic morphology, while below T_g it shows a more smooth morphology. Based on these observations, they suggested that redistribution of constituent elements at supercooled liquid-crystalline interfaces may have taken place during the growth. Nagase and Umakoshi also showed that the bct Zr_2Cu phase is the dominant phase that emerges after the crystallization of the $\text{Zr}_{65}\text{Cu}_{27.5}\text{Al}_{7.5}$ and $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ metallic glasses.³⁷⁾

It should be mentioned here that an important intermetallic compound in the Zr–Cu binary system is $\text{Zr}_7\text{Cu}_{10}$ (orthorhombic, $a = 0.935$, $b = 0.931$, and $c = 1.27$ nm), which is richer in Cu than the bct Zr_2Cu phase. Considering the composition of the alloy investigated in the present study, $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$, which is also rich in Cu, it can be understood that the bct Zr_2Cu phase is no longer a favorable phase to emerge without a significant redistribution of constituents. Also there is no equilibrium phase in the composition range between Zr_2Cu and $\text{Zr}_7\text{Cu}_{10}$ below 988 K. It can thus be understood that the crystallization proceeds via formation of a metastable phase, containing Zr, Cu and Al. Interestingly, our elemental mapping revealed that Cu atoms are still partitioned out during the growth of spherulites, indicating that the metastable orthorhombic phase can contain only a moderate amount of Cu.

Redistribution of elements during crystallization of metallic glasses have been reported by several authors. Saida *et al.* showed, in the study of the crystallization behavior of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ metallic glass, that crystallization proceeds via formation of the Zr_2Ni phase with Cu and Al atoms being rejected into the amorphous matrix.³⁹⁾ Chen *et al.* showed that Ag atoms enrich into quasicrystals while Zr and Al atoms are slightly depleted during quasicrystallization of the $\text{Zr}_{65}\text{Cu}_{7.5}\text{Ni}_{10}\text{Al}_{7.5}\text{Ag}_{10}$ metallic glass.³⁸⁾ These studies showed that redistribution of constituent elements within the supercooled region frequently occurs, and that crystallization proceeds via growth of thermodynamically favorable crystalline or quasicrystalline phase having a limited stoichiometric range. This also means, however, that polymorphous crystallization, *i.e.* crystallization without redistribution of elements, becomes increasingly difficult in multicomponent bulk metallic glasses, providing a condition for the stability of supercooled liquids.

Thus, unlike previously studied Zr-based metallic glasses, with an approximate composition of $\text{Zr}_2(\text{Cu,Ni,Al})_1$, the present study on the $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ alloy showed that the first crystalline phase to appear is neither Zr_2Cu nor Zr_2Ni , but a metastable ternary phase, which is tentatively assigned to the orthorhombic class with $a = 0.892$, $b = 0.550$, and $c = 1.06$ nm. However, Cu atoms are still partitioned out during the spherulitic growth of the orthorhombic phase, and the residual amorphous matrix crystallize into an fcc phase with $a = 1.28$ nm, which is presumably isostructural to the τ_3 phase.

5. Conclusions

The relaxation and subsequent crystallization behavior of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ metallic glass have been studied by positron annihilation and TEM. During isothermal annealing at 673 K, which is below T_g , positron annihilation lifetime exhibited a gradual decrease, which correlates well with the observed increase in density of this alloy. The CDB spectra obtained for the same series of annealed specimens, on the other hand, showed no appreciable change, suggesting that the free volumes in the $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ metallic glass reduce in size during sub T_g annealing, while that local chemical environments around the free volumes remain essentially the same. Annealing at 773 K, brings about crystallization of the metallic glass. It crystallizes via spherulitic growth of a metastable ternary phase, with Cu atoms being partitioned out. The metastable phase was tentatively assigned to the orthorhombic class with $a = 0.892$, $b = 0.550$, and $c = 1.06$ nm, containing Zr, Cu and Al; while amorphous matrix enriched in Cu crystallizes into an fcc phase with $a = 1.28$ nm, which is probably isostructural to the τ_3 phase.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research by the Ministry of Education, Culture, Sports, Science and Technology of Japan (Grant number 15074218).

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