Electron irradiation induced crystallization of the amorphous phase in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ metallic glass

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Abstract

The electron irradiation effect on microstructure change of the amorphous phase in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ metallic glass with the largest supercooled liquid region was examined under electron irradiation at 103 and 298 K using an ultra high voltage electron microscope. The nanocrystalline structure composed of f.c.c.-Zr$_2$Cu with a mean grain size on the order of 10 nm order and an amorphous matrix was formed by electron irradiation induced crystallization, while by thermal annealing b.c.t.-Zr$_2$Cu, f.c.c.-Zr$_2$Ni and Zr$_6$Al$_2$Ni phases were formed and the nanocrystalline structure could not be realized. The crystalline structure obtained by electron irradiation induced crystallization was different from that formed by the thermal crystallization of the amorphous phase in terms of the constituent phases and the size of crystalline precipitates. This noble result indicates that electron irradiation to an amorphous phase in metallic glasses is very effective in obtaining the nanocrystalline structure, and encourages future industrial application of amorphous alloys.

Keywords: Electron irradiation; Zirconium-based alloy; Amorphous; Metallic glass; Nanocrystalline structure; Phase stability; Thermal stability; Crystallization

1. Introduction

New amorphous alloys called metallic glasses have been found in Mg- [1], Lanthanide- [2], Zr- [3,4], Fe- [5], Pd–Cu- [6], Ti- [7], Ni- [8], Co- [9] and Cu- [10] based alloy systems. Metallic glasses show extremely high phase stability against thermal crystallization: a wide supercooled liquid region and high glass-forming ability. In addition, these glasses are known to show superior superplastic deformation at supercooled liquid temperature [11]. The high strain rate sensitivity (m-value) of the glasses is about 1.0 which leads to a viscous Newtonian flow and induces an ideal superplasticity resulting in good deformability for the fabrication of amorphous alloys in the forms of complex-shaped components and microparts for micro-electro-mechanical-systems [12,13]. It is thus very important for industrial application to widen the supercooled liquid region ($\Delta T_L$) which is defined by the difference between the glass transition temperature ($T_g$) and the onset temperature of crystallization ($T_x$).

Nanocrystalline structures were recently realized in Zr–Cu based metallic glasses by thermal crystallization and induced superior mechanical properties [14,15]. This novel result indicates that the crystallization of the amorphous phase in metallic glasses is a superior method of forming various nanocrystalline components. However, the expansion of a supercooled liquid region induces high phase stability of the glassy phase against thermal crystallization and results in an increase in crystallization temperature and/or change in crystallization mode to the eutectoid like reaction. These phenomena lead to difficulty in nanocrystallization of the amorphous phase. As a result, only a limited number of Zr–Cu based metallic glasses can form the nanocrystalline structure through crystallization of the amorphous phase by thermal annealing.

The crystallization of the amorphous phase is induced not only by thermal annealing but also by other external factors such as electron irradiation [16,17], focused ion beam (FIB) [18], electropulsing [19,20] and high pressure [21]. We found that electron irradiation can induce
nanocrystallization of an amorphous phase in metallic glasses in which the nanostructure cannot be easily realized by thermal annealing [17,22]. The metastable nanocrystalline phase was formed from an amorphous phase by electron irradiation [23,24] and the formation of crystallographically oriented nanocrystals under FIB irradiation [18] was reported. These results imply that electron irradiation to an amorphous phase is a new method to obtain the controlled nanocrystalline structure in metallic glasses. But there are few reports on the electron irradiation effects on the structure change in an amorphous phase of metallic glasses, and no reports on amorphous alloys with $\Delta T_x$ of more than 100 K.

This paper reports the effects of electron irradiation on crystallization and microstructural change in Zr$_{65.0}$Al$_{17.5}$Ni$_{10.0}$Cu$_{17.5}$ metallic glass with the largest $\Delta T_x$ of 127 K [25] focusing on the difference in crystallization behavior by thermal annealing and by electron irradiation.

2. Experimental procedure

A master ingot of quaternary Zr$_{65.0}$Al$_{17.5}$Ni$_{10.0}$Cu$_{17.5}$ (at%) alloy was prepared by arc melting in a purified Ar atmosphere. Rapidly quenched ribbons with a cross section of about 2.0 mm $\times$ 0.02 mm were produced from the ingot at a rotation speed of 42 m s$^{-1}$ by a single roller melt-spinning method in an Ar atmosphere. Some specimens were annealed at 613 K whose temperature were 20 K lower than $T_g$. The thermal properties and crystallization behavior of melt-spun ribbon were examined by differential scanning calorimeter (DSC) at a heating rate of 0.67 K s$^{-1}$ and different thermal analysis (DTA) at a heating rate of 0.33 K s$^{-1}$ in an Ar atmosphere. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HREM) observations were carried out in a JEM-3010 operating at 300 kV and JEM-2010 electron microscope operating at 200 kV, respectively. No change in microstructure during conventional TEM and HREM observations can be seen in the present study. Thin foils for TEM and HREM observation were prepared from the ribbons by twin jet polishing in a solution of 30% nitric acid and 70% methanol at about 243 K. The foils were electron irradiated at 103 and 298 K by an ultra-high voltage electron microscope (UHVEM) H-3000 operating at 1 and 2 MV. The applied dose rate was in the range of $1.8 \times 10^{24}$ m$^{-2}$ s$^{-1}$ to $4.0 \times 10^{24}$ m$^{-2}$ s$^{-1}$, with the maximum total dose of $8.5 \times 10^{23}$ m$^{-2}$. Change in the microstructure during electron irradiation was examined by bright field (BF) images and selected area diffraction (SAD) patterns in UHVEM. Structures of the melt-spun, annealed and electron irradiated ribbons were examined by X-ray diffractometry using Cu K$\alpha$ radiation, TEM and HREM. The grain size was measured by a linear intercept method.

3. Results

3.1. Thermal crystallization behavior

The formation of an amorphous single phase with no crystallinity was confirmed in Zr$_{65.0}$Al$_{17.5}$Ni$_{10.0}$Cu$_{17.5}$ ribbon by X-ray diffraction pattern, BF image and SAD pattern in TEM observation and HREM image [24].

Many systematic studies on the crystallization behavior of Zr$_{65.0}$Al$_{17.5}$Ni$_{10.0}$Cu$_{17.5}$ metallic glass were reported [26–28] but only a few attempts at thermal crystallization of the amorphous phase below $T_g$ were carried out because of the extremely long annealing time required. In the present study, thermal crystallization of Zr$_{65.0}$Al$_{17.5}$Ni$_{10.0}$Cu$_{17.5}$ metallic glass was investigated focusing on the crystallization of the amorphous phase.

Fig. 1(a) shows a conventional DSC curve at a heating rate of 0.67 K s$^{-1}$ in Ar atmosphere. The melt-spin ribbon began to transform from an amorphous phase to supercooled liquid at $T_g$ and maintained the supercooled liquid state over a wide temperature range, followed by crystallization at $T_x$. The $T_g$, $T_x$ and $\Delta T_x$ were 634, 752 and 119 K, respectively. The $\Delta T_x$ of the present Zr$_{65.0}$Al$_{17.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy was comparable to that reported by Inoue et al. as the maximum value among metallic glasses found up to date [25]. Fig. 1(b) shows an isothermal DSC curve at 683 K. Isothermal annealing in a DSC furnace began just after the rapid heating of the alloy up to the required temperature at a constant heating rate of 0.83 K s$^{-1}$. The exothermic peak was observed at about 70 K lower than $T_x$. To examine the reason for the exothermic reaction, a specimen annealed at 683 K for $8 \times 10^3$ s was prepared, together with specimen annealed with a constant heating rate of 0.33 K s$^{-1}$ to 763 K. XRD patterns are shown in Fig. 1(c). The melt-spin specimen shows a typical broad halo peak for an amorphous single phase. The XRD patterns taken from the specimens annealed at a constant heating rate was identified as the b.c.t.-Zr$_4$Cu, f.c.c.-Zr$_6$Ni and Zr$_6$Al$_3$Ni crystalline phases. Thermal crystallization of this alloy occurs through the simultaneous precipitation of more than two kinds of constituent phases. The specimen annealed at 683 K for $8 \times 10^3$ s shows not a broad halo peak but sharp diffraction peaks corresponding to crystalline phases. The exothermic reaction is due to the crystallization reaction and thermal crystallization occurs accompanied by an incubation period at a temperature below $T_x$. This indicates that the annealing condition has a great effect on thermal crystallization behavior such as the phase selection.

A TTT-diagram provides an annealing condition to control the microstructure and thermal crystallization of the supercooled liquid and an amorphous phase. Fig. 2 shows TTT-diagram of the melt-spinning Zr$_{65.0}$Al$_{17.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy constructed by isothermal annealing in DSC furnace. $T_g$ was determined by conventional DSC measurement. We define the onset and offset time of crystallization ($t_{\text{onset}}$ and $t_{\text{offset}}$) as being the intersection of two lines extrapolated from
The curves of $t_{\text{onset}}$ and $t_{\text{offset}}$ were estimated by the following equation proposed by Shingu [29].

\[
t = t_0 \exp \left( \frac{E}{RT} \right)
\]

(1)

where $t$, $T$ and $R$ is time, temperature and gas constant, respectively. In Eq. (1), $t_0$ and $E$ can be estimated by fitting the experimentally observed $t_{\text{onset}}$ and $t_{\text{offset}}$ at the temperature $T$ to the following relation.

\[
\ln(t) = \frac{E}{R} \frac{1}{T} + \ln(t_0)
\]

(2)

One can note that a wide supercooled liquid region is observed above $T_g$ in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy. At the temperature just above $T_g$, the supercooled liquid state can remain for an extremely long time interval reaching about $10^5$ s before crystallization. Moreover, the amorphous phase can maintain a fully glassy structure for over $10^5$ s under $T_g$, indicating that thermal crystallization of the amorphous phase rarely occur because of the extremely high phase stability of this phase.

To investigate the thermal crystallization behavior of the amorphous phase, partially and fully crystallized specimens were prepared by annealing at 613 K lower than $T_g$ by 20 K. The annealing conditions are indicated by the cross makers in the TTT-diagram and the XRD patterns are shown in Fig. 3. XRD patterns of the annealed specimens consist of sharp diffraction peaks corresponding to a crystalline phase accompanied by the overlapping of a broad peak corresponding to an amorphous phase at around $2\theta = 38$ degrees. The intensity of the sharp diffraction peaks monotonously increases with increasing annealing time, while that of a broad peak gradually weakens. XRD pattern of Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy annealed at 613 K for $3.6 \times 10^6$ s shows clear sharp diffraction lines but a broad peak is rarely recognized. All the sharp diffraction peaks can be indexed to b.c.t.-Zr$_2$Cu crystalline phase. No other diffraction peaks such as f.c.c.-Zr$_2$Ni, Zr$_6$Al$_2$Ni and quasicrystalline phase are observed. The quantity of the b.c.t.-Zr$_2$Cu crystalline phase increased with annealing time, while no change in constituent crystalline phases was not observed at 613 K.

Fig. 4 shows change in TEM microstructures of the amorphous phase in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy during thermal crystallization at 613 K. In the melt-spin specimen
featureless contrast image is seen and the corresponding SAD pattern shows only broad halo rings. Specimens annealed for $9 \times 10^5$ s (Fig. 4(b)) shows a typical two-phase structure composed of crystalline precipitates and an amorphous matrix, indicating that thermal crystallization progresses with the nucleation and growth process. Crystalline precipitates was identified as b.c.t.-Zr$_2$Cu phase by SAD pattern and the phase selection is in agreement with the XRD result. The b.c.t.-Zr$_2$Cu crystalline precipitates grow in a dendritic mode. The quantity of crystalline precipitates increases with increasing annealing time, while no significant change in morphology of precipitates is observed. There is a difference in the morphology of the amorphous–crystalline interface between Zr$_{66.7}$Cu$_{33.3}$ alloy and Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy, i.e. the existence of ruggedness at the growth interface. A smooth interface between the crystalline precipitates and the amorphous matrix was observed in Zr$_{66.7}$Cu$_{33.3}$ alloy [30], while significant ruggedness of the interface was observed in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy. The formation of nanocrystalline structures was not confirmed at any stage during thermal crystallization. Thus, it was very difficult to obtain nanocrystalline structure in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ metallic glass by thermal annealing of the amorphous phase.

3.2. Electron irradiation induced crystallization behavior

The amorphous phase was not stable in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy under electron irradiation at 298 K at the acceleration voltage of 2 MV, and the crystallization of this phase occurred at a significantly lower temperature than the usual annealing temperature. Kiritani et al. derived the model of temperature increase in irradiation area by solving the equation of heat conduction, and proposed that the expected temperature increase was not applicable in the case of electron irradiation to the metallic specimens because the most part of the heat transferred from electrons escapes from metallic specimen by the heat conduction.
With further electron irradiation, no significant change in granular contrast image is observed in BF image, but the intensity of Debye rings increases together with decrease in that of the halo rings in SAD pattern. The quantity of nanocrystalline precipitates increases with total dose, although there is no significant coursing of these precipitates during electron irradiation occurs. This result indicates that electron irradiation induced crystallization occurs with a nucleation and growth mode similar to thermal crystallization. But nucleation frequency and growth ratio of electron irradiation induced crystallization are quite distinct from these of thermal crystallization, resulting in the formation of nanocrystalline structure by the former in any stage.

To obtain more detailed information on electron irradiation induced crystallization, the electron diffraction intensity profiles at different total doses were investigated; the results are shown in Fig. 6. The intensity profile of the melt-spun specimen shows only broad peaks corresponding to an amorphous single phase. At the total dose of $4.3 \times 10^{26} \text{ m}^{-2}$, two sharp peaks appear; these cannot be indexed to b.c.t.-Zr$_2$Cu, f.c.c.-Zr$_2$Ni and Zr$_6$Al$_2$Ni which often precipitate from an amorphous phase or supercooled liquid through thermal crystallization. At the total dose of $1.1 \times 10^{27} \text{ m}^{-2}$, the intensity of the two peaks increases and new diffraction peaks appear. All peaks fit to the positions...
corresponding to the metastable f.c.c.-\(\text{Zr}_2\text{Cu}\) phase. With further electron irradiation, the intensity of diffraction peaks for the f.c.c.-\(\text{Zr}_2\text{Cu}\) phase becomes stronger together with weakening a broad peak corresponding to an amorphous phase. No other diffraction peaks other than amorphous and f.c.c.-\(\text{Zr}_2\text{Cu}\) phases are observed during electron irradiation.

Fig. 7 shows typical example of a HREM image of nanocrystalline precipitate formed by electron irradiation induced crystallization of the amorphous phase in \(\text{Zr}_{65.0}\)-\(\text{Al}_{17.5}\)-\(\text{Ni}_{10.0}\)-\(\text{Cu}_{17.5}\) alloy. The crystalline lattice image with nanoscale grain size of about 10 nm is embedded in maze-like contrast corresponding to an amorphous phase. The crystalline precipitate has a threefold symmetry and lattice fringe with a distance of about 0.24 nm corresponding to the plane spacing of (111) in f.c.c.-\(\text{Zr}_2\text{Cu}\) crystalline phase. This image provides positive experimental evidence of the formation of f.c.c.-\(\text{Zr}_2\text{Cu}\) nanocrystalline precipitates from an atomistic viewpoint. The electron irradiation induced crystallization progresses with precipitation of the f.c.c.-\(\text{Zr}_2\text{Cu}\) phase. A duplex structure was formed consisting of mostly f.c.c.-\(\text{Zr}_2\text{Cu}\) crystalline precipitates with nanoscale grain sizes and a small amount of an amorphous matrix. The thermally equilibrium b.c.t.-\(\text{Zr}_2\text{Cu}\) crystalline phase did not appear under electron irradiation. Although many studies have been made on thermal crystallization in Zr–Cu based metallic glasses [26–28], there has been no report of the formation of f.c.c.-\(\text{Zr}_2\text{Cu}\) phase during thermal annealing of these alloys. Electron irradiation to the amorphous phase is effective in obtaining nanocrystalline structure in metallic glasses.

### 3.3. Effect of irradiation temperature and acceleration voltage on electron irradiation induced crystallization

It is known that structure change in crystalline phases by electron irradiation is very sensitive to irradiation temperature and an acceleration voltage [32,33]. Thus, irradiation conditions may have a great effect on electron irradiation induced crystallization behavior of an amorphous phase. We therefore performed electron irradiation to the amorphous phase under various irradiation conditions: room temperature of 298 and 103 K using liquid N\(_2\) with an acceleration voltage of 1 and 2 MV.

Fig. 8 shows TEM microstructures and corresponding SAD patterns of the amorphous phase at a total dose of \(8.5 \times 10^{27} \text{m}^{-2}\), where the irradiation conditions are as follows: (a and d) 2 MV at 103 K; (b and e) 1 MV at 298 K; (c and f) 1 MV at 103 K. TEM microstructures show not a featureless contrast image but dark and bright granular contrast. Uncontinuous Debye rings and/or sharp diffraction spots together with broad halo rings are seen. These features confirm that the amorphous phase was unstable under electron irradiation and that there was an electron irradiation induced crystallization of this phase. The crystalline phase was identified as f.c.c.-\(\text{Zr}_2\text{Cu}\) phase from SAD patterns in all specimens, indicating that there is no difference in phase selection of electron irradiation induced crystallization independent of the irradiation conditions. One can note that the quantity and grain size of f.c.c.-\(\text{Zr}_2\text{Cu}\) crystalline phase are greatly affected by irradiation conditions. The quantity of crystalline precipitates varied depending on the total dose. The phase stability of the amorphous phase against electron irradiation in Zr–Cu based metallic glasses can be evaluated by the total dose required for precipitation of f.c.c.-\(\text{Zr}_2\text{Cu}\) crystalline phase [24].
In the present study, the critical total dose is defined as the total dose which Debye rings and/or diffraction spots corresponding to f.c.c.-Zr$_2$Cu crystalline phase appear in the SAD pattern during electron irradiation. Fig. 9 shows the effect of irradiation temperature and acceleration voltage on the total dose required for the electron irradiation induced crystallization in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy: there is a clear tendency for the total dose to decrease with increase in these two factors. The total dose at 103 K at 1 MV is about eight times as large as that at 298 K at 2 MV.

Fig. 10 shows changes in the average grain size of f.c.c.-Zr$_2$Cu precipitates formed by electron irradiation induced crystallization as a function of the total dose. Two significant characteristics can be recognized:

1. Nanocrystalline precipitates are formed under any irradiation conditions and the average grain size did not exceed 25 nm. Irradiation condition dependence on the average grain size is observed but the nanocrystalline structure can be obtained under all conditions.

2. No significant coarsening of f.c.c.-Zr$_2$Cu precipitates occurs during electron irradiation, although the crystallization of the amorphous phase is greatly promoted by this irradiation.

In contrast, the b.c.t.-Zr$_2$Cu precipitate grows rapidly after nucleation in the amorphous phase during thermal crystallization in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy. After the full crystallization, the grain size of the b.c.t.-Zr$_2$Cu phase increases with annealing time. As a result, nanocrystalline precipitates could not be obtained by thermal annealing of the amorphous phase.

4. Discussion

4.1. Thermal crystallization behavior

It was confirmed that thermal crystallization of the amorphous phase progresses with the precipitation of b.c.t.-Zr$_2$Cu crystalline phase in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy. The composition of this crystalline phase is different from that of the amorphous phase, indicating there is a redistribution of solute elements during thermal crystallization. The redistribution of solute elements at the amorphous–crystalline interface affects the growth behavior of crystalline precipitates in an amorphous phase, such as the morphology and kinetics of crystal growth of b.c.t.-Zr$_2$Cu crystalline phase.

The constitutional undercooling is due to the redistribution of the solute elements which influences the interface stability [34]. In an amorphous phase whose crystallization progresses not with eutectoid-like reaction mode but with single-phase nucleation and growth mode, the undercooling enhances the perturbation of the shape at the growth interface. A smooth growth interface can hardly be obtained when the constitutional undercooling contributes to the growth of single-phase crystalline precipitates embedded in an amorphous phase. When the constituent supercooling increases and the perturbation of the interface greatly develops, dendritic growth mode of precipitates is often observed. The redistribution of solute elements is believed to induce the unstable morphology of the growth interface and the formation of dendrites of b.c.t.-Zr$_2$Cu crystalline phase in Zr$_{66.7}$Cu$_{33.3}$ alloy.

A change in the average grain size of b.c.t.-Zr$_2$Cu crystalline phase during thermal crystallization of the amorphous phase at 593 K, which is lower than $T_g$ by 20 K in Zr$_{66.7}$Cu$_{33.3}$ alloy, was reported in previous papers [23,30]. B.c.t.-Zr$_2$Cu crystalline precipitates with micrometer order grain size were formed in Zr$_{66.7}$Cu$_{33.3}$ alloy whose crystallization proceeded in the polymorphic mode without the redistribution of solute elements, while the formation of b.c.t.-Zr$_2$Cu dendrites with the grain size of about 100 nm during thermal crystallization was
observed in the present study. Redistribution of the solute elements in crystal growth indicates the atomic rearrangement of the constituent elements on a long-range scale in the amorphous phase at the growth interface. The long-range atomic diffusion for crystallization leads to difficulties in atomic rearrangement from the glassy to crystalline structure, resulting in retardation of the crystal growth rate in Zr–Cu based metallic glasses. Since the redistribution of solute elements is necessary, the grain size of b.c.t.-Zr$_2$Cu phase in Zr$_{65.0}$Al$_{17.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy is one order of magnitude smaller than that in Zr$_{66.7}$Cu$_{33.3}$ alloy.

4.2. Electron irradiation induced crystallization

We suggested that there are two important factors in the occurrence of electron irradiation induced crystallization of an amorphous phase: (1) the promotion of atomic diffusion by electron irradiation in an amorphous phase to change the glassy structure and (2) the high phase stability of crystalline phases against electron irradiation to maintain the crystalline structure [17,22]. Electron irradiation induced crystallization of the amorphous phase occurs when the two factors are satisfied simultaneously.

The promotion of atomic diffusion in an amorphous phase is necessary for crystallization. Under electron irradiation, the elastic collision between irradiation electrons and constituent atoms occurs in an amorphous phase. The energy of irradiation electrons is proportional to the acceleration voltage. When high energy electrons whose acceleration voltage is above the threshold value are irradiated, the dynamic displacement of the constituent atoms by the elastic collision occurs. This phenomenon is called the electron knock-on effect and it promotes atomic diffusion. But there are no reports about the threshold acceleration voltage of the amorphous phase in Zr–Al–Ni–Cu metallic glasses. In contrast, the threshold acceleration voltage of electron irradiation in several crystalline metals has been reported: 140 kV [35–37] and 170 kV [38] for Al atom, 420 kV [39–41] and 440 kV [42] for Ni and 400 kV for Cu [38,43,44]. The acceleration voltage of 400 kV is believed to be sufficient for direct displacement of Zr atoms in crystalline alloys [45]. Taking these data into consideration, the applied acceleration voltage of 1 or 2 MV is believed to be enough to induce the electron knock-on effect in the amorphous phase.

Two mechanisms promoting atomic diffusion in an amorphous phase under electron irradiation were reported [46,47]:

1. The direct atomic movement of constituent atoms occurs by the electron knock-on effect.
2. A free volume is induced through the displacement of constituent atoms by electron knock-on effect, and atomic diffusion via the free volume in an amorphous phase is accelerated under electron irradiation.

In the present study, the promotion of atomic diffusion in an amorphous phase was believed to be achieved by a combination of these two mechanisms. The electron knock-on effect occurred not only in the amorphous phase but also in crystalline phases. If a crystalline phase could not maintain the original crystal structure against the displacement of constituent atoms by the electron knock-on effect, the crystalline structure was destroyed resulting in the transformation to other crystalline or amorphous phases with more stable structure under electron irradiation. Only crystalline phases which maintain their original structure under electron irradiation precipitate from an amorphous phase. Our previous work revealed the phase stability of crystalline phase against electron irradiation [23]:

1. b.c.t.-Zr$_2$Cu crystalline phase cannot maintain its original structure under electron irradiation and electron irradiation induced amorphization occurs.
2. f.c.c.-Zr$_2$Cu crystalline phase has high phase stability against electron knock-on effect and can exist stably under electron irradiation.

The electron irradiation induced crystallization of the amorphous phase in Zr$_{65.0}$Al$_{17.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy is caused by the simultaneous satisfaction of the following two factors: the high phase stability of f.c.c.-Zr$_2$Cu crystalline phase against electron knock-on effect, and the promotion of atomic diffusion in the amorphous phase.

4.3. Difference in crystallization behavior between thermal annealing and electron irradiation

There are two significant differences in crystallization behavior of the amorphous phase between thermal annealing and electron irradiation: one is phase selection and the other is the grain size of the crystalline precipitates. The thermal equilibrium b.c.t.-Zr$_2$Cu crystalline phase did not precipitate from the amorphous phase under electron irradiation even if atomic diffusion was promoted enough to change the glassy structure. Only f.c.c.-Zr$_2$Cu crystalline phase formed from the amorphous phase through electron irradiation induced crystallization in Zr$_{65.0}$Al$_{17.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy. It is reported that the f.c.c.-Zr$_2$Cu crystalline phase was formed in Zr$_{67}$Cu$_{33}$ alloy during high energy ball milling [48]. Not only electron irradiation but also mechanical milling can introduce a great number of lattice defects in crystalline phases. This report offers positive experimental evidence that f.c.c.-Zr$_2$Cu crystalline phase shows high stability against the introduction of enough lattice defects to maintain the original structure under electron irradiation. The applied acceleration voltage of 1 and 2 MV can easily induce the direct displacement of constituent atoms in the amorphous and crystalline phases in the present study. Crystalline phases cannot maintain their original structure under electron irradiation if the replacement of atoms by the electron knock-on effect occurs more
frequently than recovery of the original positions of atomic sublattice by thermal diffusion. Taking into account the direction of the atomic movement, the phase stability of crystalline phases against electron irradiation is thought to decrease with increasing degree of complexity of crystalline structure. The degree of the complexity is closely related to the size of the unit cells of the crystalline phase. The larger the unit cell of the crystalline phase, the lower the phase stability of that phase becomes against electron irradiation. The volume of unit cell of thermal equilibria b.c.t.-Zr$_2$Cu and f.c.c.-Zr$_2$Cu crystalline phases are 0.1160 and 0.0936 nm$^3$, respectively. The difference in phase selection may be due to the difference in the order of relative phase stability among f.c.c.-Zr$_2$Cu, b.c.t.-Zr$_2$Cu and amorphous phases with and without electron irradiation.

4.4. Phase stability of the amorphous phase against electron irradiation

The promotion of the atomic diffusion under electron irradiation is caused by the electron knock-on effect. The elastic collision effect on the constituent atoms is very sensitive to energy of the collision particles, and the energy of the irradiation electrons is proportional to the acceleration voltage. The quantity of displacement of atoms is believed to increase with increasing in the acceleration voltage.

The direct atomic movement of constituent atoms by the electron knock-on effect shows no temperature dependence, while the movement of these atoms via free volume depends strongly on the irradiation temperature. Therefore, the atomic diffusion due to the electron irradiation increases with rise in the irradiation temperature. The irradiation temperature and acceleration voltage dependence of the promotion of atomic diffusion under electron irradiation contribute to the critical total dose for the electron irradiation induced crystallization in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ amorphous alloy.

4.5. Nanocrystalline structure formation by electron irradiation induced crystallization

In amorphous alloys whose crystallization proceeds with nucleation and growth mode, simultaneous achievement of highly frequent homogeneous nucleation rate and extremely low crystal growth rate is necessary for formation of the nanocrystalline structure. The nanoscale crystalline clusters and/or the developed medium range ordered structure proposed by Hirotsu et al. [49] may be quenched-in embryos and act as nucleation sites for primary crystalline precipitates. When the quenched-in embryos were homogeneously and highly frequently dispersed in an amorphous phase, there was the strong possibility that highly frequent homogeneous nucleation to obtain nanocrystalline structure would be realized. However, no significant nanocrystalline clusters or MRO domains were confirmed in melt-spun amorphous phase of Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ alloy from HREM image. TEM microstructures in Fig. 4 show that the subsequent crystal growth is not effectively suppressed by the redistribution of solute elements during thermal annealing and a nanocrystalline structures cannot be obtained in this amorphous alloy.

The nucleation and subsequent crystal growth rate during electron irradiation induced crystallization is greatly different from these during thermal crystallization. An elastic collision between the electrons and constituent atoms occurs under electron irradiation and atoms in the amorphous phase are dynamically displaced by the electron knock-on effect. From the viewpoints of atomic species and direction of the atomic movement, highly frequent and homogeneous atomic movement in the amorphous phase is believed to be induced by electron irradiation more than by thermal annealing at low temperature. The highly frequent homogeneous nucleation for the nanocrystalline structure may be achieved by electron irradiation.

The crystal growth during electron irradiation can be discussed from the viewpoint of the attachment and detachment of the atoms at the crystal–amorphous interface, where the attachment and detachment of atoms indicate the atomic migration from the amorphous phase to crystal phase and the opposite direction, respectively. The rates of attachment and detachment depend on the frequency of atomic movement and the number of favorable sites which are closely related to the number of receiving atomic sites, the bonding nature among constituent atoms and symmetry of the structure. Frequency of atomic movement from amorphous to crystal phase and that from crystal to amorphous phase based on the direct atomic displacement are thought to be almost the same since the applied acceleration voltage of 1 or 2 MV was an extremely high. In contrast, the number of favorable sites for attachment may be smaller than that for detachment because the attachment sites are occupied by the fixed atomic sublattices in the crystalline phase. The direct atomic displacement between the crystal–amorphous phases by electron knock-on effect decreases the grain size of crystalline precipitates in the amorphous phase at low temperature. We call this process the dynamic amorphization effect and believe it may contribute to achieving the extremely low growth rate which obtains the nanocrystalline structure. A more detailed discussion is presented in the other paper [30].

5. Conclusions

The electron irradiation induced crystallization behavior of an amorphous phase in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ metallic glass was examined focusing on the difference in this behavior during thermal annealing and electron irradiation, and the following conclusions were reached:

1. The amorphous phase was not stable under electron irradiation at 103 and 298 K at an acceleration voltage of 1 and 2 MV in Zr$_{65.0}$Al$_{7.5}$Ni$_{10.0}$Cu$_{17.5}$ metallic glass.
Electron irradiation induced crystallization of the amorphous phase occurred. High thermal stability of metallic glasses is not always effective in suppressing the electron irradiation induced crystallization of an amorphous phase.

(2) B.c.t.-Zr$_2$Cu, f.c.c.-Zr$_2$Ni and Zr$_6$Al$_2$Ni crystalline phases precipitated from the glassy phase by thermal annealing. In contrast, only f.c.c.-Zr$_2$Cu phase precipitated from the amorphous phase under electron irradiation. The difference phase selection between thermal crystallization and electron irradiation induced crystallization is due to the difference between thermodynamical phase stability and the phase stability of crystalline phases against electron irradiation.

(3) The quantity of f.c.c.-Zr$_2$Cu crystalline phase with an average grain size of 10 nm order increased with total dose and nanocrystalline structure was maintained, while the nanostructure could rarely be obtained by thermal annealing. Electron irradiation is effective in obtaining unique nanocrystalline structures for Zr-based metallic glasses.

(4) The phase stability of an amorphous phase against electron irradiation dependent on the irradiation temperature and acceleration voltage. The nanocrystalline structure can be controlled by the electron irradiation conditions.

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