Electron Irradiation Induced Crystallization Behavior in $\text{Zr}_{66.7}\text{M}_{33.3}$ ($\text{M} = \text{Cu}, \text{Ni}, \text{Pd}$) Metallic Glasses

Yukichi Umakoshi*, Takeshi Nagase and Takashi Hosokawa

Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

The difference in electron irradiation induced crystallization behavior of melt-spun amorphous phase among $\text{Zr}_{66.7}\text{M}_{33.3}$ ($\text{M} = \text{Cu}, \text{Ni}$ and Pd) alloys was investigated. An amorphous phase was unstable under electron irradiation and the irradiation induced crystallization of the amorphous phase occurred in the three alloys. The phase selection of electron irradiation induced crystallization in $\text{Zr}_{66.7}\text{Pd}_{33.3}$ was obviously different from that in $\text{Zr}_{66.7}\text{Cu}_{33.3}$ and $\text{Zr}_{66.7}\text{Ni}_{33.3}$, while there was no significant difference between the latter two. The origin of the unique phase selection in $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloy was discussed based on the database of electron irradiation induced crystallization in Zr-based alloys. [doi:10.2320/matertrans.MJ200703]

(Received October 18, 2006; Accepted January 9, 2007; Published June 25, 2007)

Keywords: metallic glass, amorphous, quasi-crystal, nano crystal, crystallization, electron irradiation

1. Introduction

A metallic amorphous phase can be obtained by liquid quenching (LQ) with liquid-to-glass (L-G) transition or solid-state amorphization (SSA) with crystal-to-glass (C-G) transition. The SSA technique shows higher glass forming ability (GFA) than the LQ technique; electron irradiation can achieve SSA even in metallic materials whose amorphous phase is rarely realized by LQ.^{1,2)} From the viewpoint of the phase diagram, the free energy of liquid in an alloy system with a deep eutectic is lowered to a large extent by alloying with a glass-forming element and high GFA can be obtained by both LQ and SSA techniques.¹⁻⁴⁾ Binary Zr-based alloys in which electron irradiation induced SSA was observed are summarized in Fig. 1. The amorphous phase obtained in binary Zr-Cu, Zr-Co, Zr-Fe, Zr-Ni, Zr-Pd and Zr-Pt alloys has been obtained by the LQ method, while electron irradiation induced SSA was reported in Zr-Al, Zr-Cu, Zr-Cr, Zr-Fe, Zr-Ni and Zr-Pd alloys. These binary Zr-M ($\text{M} = \text{Al}, \text{Co}, \text{Cr}, \text{Cu}, \text{Fe}, \text{Ni}, \text{Pd}$ and Pt) alloys have a tendency to show a deep eutectic type phase diagram.

Recently, new metallic amorphous alloys called metallic glasses were found in many numerous alloy systems. They exhibit extremely high thermal stability which is enough to undergo the glass transition in conventional DSC measurement and the amorphous phase can be obtained in bulk-shape by the conventional casting method; therefore, they are called Bulk Metallic Glass (BMG). Several Zr-based BMGs have been developed and typical examples are also shown in Fig. 1. One can notice that binary Zr-Cu and Zr-Ni alloys are the prototype of typical multi-component BMG-type Zr-based alloys such as $\text{Zr}_{65}\text{Al}_{15}\text{Ni}_{25}$ etc.), $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ etc.), $\text{Zr}_{65}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{17.5}$, $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_{5}\text{Cu}_{30}$ etc.), $\text{Zr}_{57}\text{Nb}_{5}\text{Al}_{10}\text{Ni}_{12.6}\text{Cu}_{15.4}$ of Vitreloy-106 etc.) and $\text{Zr}_{52.5}\text{Ti}_{5}\text{Al}_{10}\text{Ni}_{14.6}\text{Cu}_{17.9}$ of Vitreloy-105/BAM-11 etc.) and so on.

More recently, it was reported that Zr-based metallic glass can be transformed to nano-crystalline or nano-quasicrystalline structure by thermal annealing, and both of these nano-

Fig. 1 Typical example of Zr-based binary metallic amorphous alloys and metallic glasses focusing on alloys in which electron irradiation induced amorphization and/or crystallization have been investigated to date. Open circle (○) and open square (□) mean alloys which showed electron irradiation induced amorphization and electron irradiation induced crystallization, respectively.

crystal-dispersed metallic glasses show superior mechanical properties.⁷⁻¹⁰⁾ However, the high phase stability of the glassy phase against thermal crystallization increases the crystallization temperature and/or changes the crystallization mode to an eutectoid-like reaction. These phenomena make it difficult to achieve nano-crystallization and formation of nano-quasicrystal. As a result, the nano-crystalline and/or nano-quasicrystalline structures have been obtained only in some limited Zr-based metallic glass by thermal annealing; nano-quasicrystalline structure formation has been reported in alloys including precious metal (Ag, Au, Pd, Pt) and oxygen as shown in Fig. 1.¹¹⁻²²⁾ The crystallization of an amorphous phase was induced not only by thermal annealing but also by other processes such as electron irradiation,^{23,24)}

*Corresponding author, E-mail: umakoshi@mat.eng.osaka-u.ac.jp

focused ion beam (FIB)²⁵⁾ and electro-pulsing^{26,27)} techniques. We found that high-energy electron irradiation with 2 MeV and high dose electrons ($\sim 10^{27}/\text{m}^2$) can induce nano-crystallization of an amorphous phase even in metallic glasses in which the nanostructure is not easily realized by thermal annealing.^{24,28)} The metastable nano-crystalline structure was also formed from an amorphous phase by electron irradiation.^{24,29–33)} Thus, electron irradiation to an amorphous phase is recognized as a new method to obtain the controlled nano-crystalline structure in metallic glass. In Fig. 1, Zr-based alloys in which electron irradiation induced crystallization and electron irradiation induced amorphization are marked by open square ($\square$) and the open circle ($\circ$), respectively. Both electron irradiation induced crystallization and amorphization behavior together have been investigated only in binary Zr-Cu ,^{1,5,30,31,35)} Zr-Ni ,^{1,2,32)} Zr-Pd ^{33,34,36)} and ternary Zr-Al-Cu ^{24,30,31)} alloys.

In the present study, high energy electron irradiation induced crystallization of an amorphous phase in $\text{Zr}_{66.7}\text{Cu}_{33.3}$ (prototype of BMG), $\text{Zr}_{66.7}\text{Ni}_{33.3}$ (prototype of BMG) and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ (prototype of QC-former) was investigated focusing on the difference in the irradiation induced crystallization behavior between BMG-type and QC-former type Zr-based alloys.

2. Experimental Procedure

Master ingots of $\text{Zr}_{66.7}\text{Cu}_{33.3}$, $\text{Zr}_{66.7}\text{Ni}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ (at%) alloys were prepared by arc melting raw materials of pure Zr, Cu, Ni and Pd in purified Ar atmosphere. Rapidly quenched ribbon with a cross section of about $2.0\text{ mm} \times 0.02\text{ mm}$ was produced from the ingots at a rotation speed of 42 ms^{-1} by a single roller melt-spinning method in this atmosphere. Thermal properties and crystallization behavior of the melt-spun ribbon were examined by differential scanning calorimeter (DSC) and differential thermal analysis (DTA) in the atmosphere at heating rates of 0.67 and 0.33 Ks^{-1} , respectively. The kinetic map was obtained by DSC measurement with various heating rates from 0.083 to 0.83 Ks^{-1} for $\text{Zr}_{66.7}\text{Cu}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloys. Thin foils for electron irradiation were prepared from the ribbon by twin jet polishing in a solution of 30% nitric acid and 70% methanol at about 243 K for $\text{Zr}_{66.7}\text{Cu}_{33.3}$ and $\text{Zr}_{66.7}\text{Ni}_{33.3}$ alloys, and by ion milling for $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloy. The foils were electron irradiated using an ultra-high voltage electron microscope (UHVEM) H-3000 in Osaka University. The irradiation was performed at the acceleration voltage of 2.0 MV at the irradiation temperature of 298 K . The applied dose rate was between 1.6×10^{24} and $1.1 \times 10^{25}\text{ m}^{-2}\text{s}^{-1}$, with the maximum total dose density of $3.0 \times 10^{28}\text{ m}^{-2}$. Changes in the bright field (BF) images and selected area diffraction (SAD) patterns during electron irradiation were observed in situ by UHVEM at 2.0 MV . Additional electron irradiation during in situ TEM observation was neglected because of the low dose rate. Structure of the ribbon was also examined by X-ray diffractometry using $\text{Cu-K}\alpha$ radiation, transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HREM). The intensity profile of the SAD pattern was analyzed using a PICTRO STAT DIGITAL 400 image analyzer.

Fig. 2 X-ray diffraction patterns of melt-spun binary $\text{Zr}_{66.7}\text{Cu}_{33.3}$, $\text{Zr}_{66.7}\text{Ni}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloys.

3. Results

3.1 Thermal properties and thermal crystallization behavior

Figure 2 shows X-ray diffraction patterns of melt-spun specimens of binary $\text{Zr}_{66.7}\text{Cu}_{33.3}$, $\text{Zr}_{66.7}\text{Ni}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloys. All specimens show only a typical broad halo peak at around $2\theta = 36$ degrees. No sharp diffraction peaks corresponding to a crystalline structure are observed, nor is there any significant difference in the half-value width of the peak or in peak position in the broad peaks. The difference in amorphous structure among the three alloys cannot be detected by conventional XRD analysis.

Figure 3 shows thermal analysis of melt-spun specimens of binary $\text{Zr}_{66.7}\text{Cu}_{33.3}$, $\text{Zr}_{66.7}\text{Ni}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloys. In DTA analysis (a), all curves show exothermic peaks corresponding to thermal crystallization at T_x before a sharp endothermic peak for thermal melting (crystal-to-liquid transition) at T_m . $\text{Zr}_{66.7}\text{Cu}_{33.3}$ and $\text{Zr}_{66.7}\text{Ni}_{33.3}$ alloys show a single exothermic peak, while double exothermic peaks appear in $\text{Zr}_{66.7}\text{Pd}_{33.3}$. The thermal crystallization mode in $\text{Zr}_{66.7}\text{Pd}_{33.3}$ differs from that in $\text{Zr}_{66.7}\text{Cu}_{33.3}$ and $\text{Zr}_{66.7}\text{Ni}_{33.3}$ alloys. The T_x and T_m in the former are slightly higher than those in the latter two. The thermal properties of melt-spun amorphous phase can be evaluated by DSC in detail, and the results of DSC at a heating rate of 0.67 Ks^{-1} are shown in Fig. 3(b). It should be noticed that an anomalous endothermic reaction corresponding to glass-to-supercooled liquid transition occurs at T_g in $\text{Zr}_{66.7}\text{Cu}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloys before thermal crystallization, while such an endothermic anomaly is rarely observed in $\text{Zr}_{66.7}\text{Ni}_{33.3}$ alloy. In $\text{Zr}_{66.7}\text{Cu}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloys, the supercooled liquid state is maintained over a wide temperature range ($\Delta T_x = T_x - T_g$), and then thermal crystallization starts at T_x . The T_g and T_x are sensitive to the heating rate, (ϕ , Ks^{-1}); a typical example is shown in Fig. 3(c) of the kinetic map in

Fig. 3 Thermal analysis of melt-spun specimens in binary $\text{Zr}_{66.7}\text{Cu}_{33.3}$, $\text{Zr}_{66.7}\text{Ni}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloys. (a) DTA analysis at a heating rate of 0.33 K s^{-1} , (b) Kinetic map of melt-spun $\text{Zr}_{66.7}\text{Cu}_{33.3}$ alloy obtained by DSC measurement with various heating rates, (c) DSC analysis at a heating rate of 0.67 K s^{-1} .

Fig. 4 XRD patterns of thermal annealed specimen quenched in water from the temperature just after exothermic reaction during DTA measurement at a heating rate of 0.33 K s^{-1} . The quenched temperatures are 703 K for $\text{Zr}_{66.7}\text{Cu}_{33.3}$, 713 K for $\text{Zr}_{66.7}\text{Ni}_{33.3}$, and 753 K and 803 K for $\text{Zr}_{66.7}\text{Pd}_{33.3}$.

melt-spun $\text{Zr}_{66.7}\text{Cu}_{33.3}$ alloy. Both T_x and T_g decrease with decreasing heating rate. The degree of decrease in T_x is larger than that in T_g , resulting in the intersection of two extrapolated curves of the least-squares fit lines at the critical heating rate. The intersection temperatures (T_c) in $\text{Zr}_{66.7}\text{Cu}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ are about 574 K and 692 K, respectively. Recently, Ichitsubo *et al.* reported that T_c of $\text{Zr}_{70}\text{Ni}_{30}$ alloy was about 643 K.^{37,38)} According to previous papers,^{2,39)} the intersection temperature (T_c) corresponds to the ideal glass transition temperature (T_K). This ideal glass transition temperature, namely, Kauzmann temperature is thermodynamically defined as the temperature at which the entropy of liquid equals that of crystal. Although the kinetic glass transition T_g in $\text{Zr}_{66.7}\text{Ni}_{33.3}$ cannot be observed in the conventional DSC measurement, the thermodynamical glass transition temperature T_K for the three alloys may be near T_c .

To examine the structure change, specimens were quenched in water at the temperature just after exothermic reaction during DTA measurement at a heating rate of 0.33 K s^{-1} . The quenching temperatures were 703 K for $\text{Zr}_{66.7}\text{Cu}_{33.3}$, 713 K for $\text{Zr}_{66.7}\text{Ni}_{33.3}$, and 753 K and 803 K for $\text{Zr}_{66.7}\text{Pd}_{33.3}$, respectively. Figure 4 shows XRD patterns of the thermal annealed specimens. The annealed $\text{Zr}_{66.7}\text{Cu}_{33.3}$ specimen consists of the thermal equilibrium C11_b- Zr_2Cu crystalline phase. The XRD pattern of the $\text{Zr}_{66.7}\text{Ni}_{33.3}$ specimen show diffraction peaks corresponding to the thermal equilibrium C16- Zr_2Ni phase, while the formation of the metastable Zr_2Ni crystalline phase with f.c.c. structure called Big-Cube was not confirmed.⁴⁰⁾ The $\text{Zr}_{66.7}\text{Pd}_{33.3}$ specimen quenched from 803 K shows the thermal equi-

Fig. 5 BF images and corresponding SAD patterns of nano-crystalline structure obtained by electron irradiation induced crystallization at 298 K at the acceleration voltage of 2.0 MV in binary $\text{Zr}_{66.7}\text{Cu}_{33.3}$, $\text{Zr}_{66.7}\text{Ni}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloys. (a) $\text{Zr}_{66.7}\text{Cu}_{33.3}$ at the total dose of $3.3 \times 10^{27} \text{ m}^{-2}$, (b) $\text{Zr}_{66.7}\text{Ni}_{33.3}$ at the total dose of $5.4 \times 10^{27} \text{ m}^{-2}$, (c) $\text{Zr}_{66.7}\text{Pd}_{33.3}$ at the total dose of $4.9 \times 10^{27} \text{ m}^{-2}$.

librium $\text{C11}_b\text{-Zr}_2\text{Pd}$ crystalline phase, while diffraction peaks corresponding not only to this phase but also to the QC phase can be seen by quenching from 753 K. Metastable QC phase precipitated preferentially from the supercooled liquid phase during thermal crystallization and then thermal equilibrium $\text{C11}_b\text{-Zr}_2\text{Pd}$ crystalline phase was formed in $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloy.³²⁾ From the viewpoint of metastable QC formation in the thermal crystallization, $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloy is different from $\text{Zr}_{66.7}\text{Cu}_{33.3}$ and $\text{Zr}_{66.7}\text{Ni}_{33.3}$ alloys.

3.2 Electron irradiation induced crystallization of melt-spun amorphous phase

In situ TEM observation was performed by UHVEM at 2.0 MV. Figure 5 shows BF images and corresponding SAD patterns of nano-crystalline structure obtained by 2.0 MV electron irradiation induced crystallization at 298 K in the binary $\text{Zr}_{66.7}\text{Cu}_{33.3}$, $\text{Zr}_{66.7}\text{Ni}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloys. The total dose was applied at $3.3 \times 10^{27} \text{ m}^{-2}$ for $\text{Zr}_{66.7}\text{Cu}_{33.3}$, at $5.4 \times 10^{27} \text{ m}^{-2}$ for $\text{Zr}_{66.7}\text{Ni}_{33.3}$ and at $4.9 \times 10^{27} \text{ m}^{-2}$ for $\text{Zr}_{66.7}\text{Pd}_{33.3}$, respectively. All specimens show a dark and bright granular contrast with a size of about 10 nm in the BF image. Discontinuous Debye rings can be seen together with broad halo rings in the SAD pattern. Melt-spun amorphous phase could not maintain the original structure under electron irradiation at 298 K and electron irradiation induced crystallization occurred, resulting in the formation of nano-crystalline structure composed of nano-crystalline precipitates and residual amorphous matrix. One can notice that the shape of these precipitates in $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloy is slightly different from that in the other two alloys. The grain boundary of nano-crystalline precipitates in the these two is sharper than that of $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloy; in contrast, no significant difference in BF image between $\text{Zr}_{66.7}\text{Cu}_{33.3}$ and $\text{Zr}_{66.7}\text{Ni}_{33.3}$ alloys is seen. In the diffraction patterns, the number of discontinuous Debye rings for $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloy is

Fig. 6 Electron diffraction intensity profiles of nano-crystalline structure obtained by electron irradiation induced crystallization at 298 K at the acceleration voltage of 2.0 MV in binary $\text{Zr}_{66.7}\text{Cu}_{33.3}$, $\text{Zr}_{66.7}\text{Ni}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloys. The total dose is $3.3 \times 10^{27} \text{ m}^{-2}$ for $\text{Zr}_{66.7}\text{Cu}_{33.3}$, $5.4 \times 10^{27} \text{ m}^{-2}$ for $\text{Zr}_{66.7}\text{Ni}_{33.3}$ and $4.9 \times 10^{27} \text{ m}^{-2}$ for $\text{Zr}_{66.7}\text{Pd}_{33.3}$.

larger than that in $\text{Zr}_{66.7}\text{Cu}_{33.3}$ and $\text{Zr}_{66.7}\text{Ni}_{33.3}$ alloys, while the latter two seems similar.

To examine electron irradiation induced crystallization behavior focusing on the phase formation, the intensity profiles of SAD patterns during the irradiation were analyzed. Figure 6 shows the intensity profiles of nano-crystalline structure obtained from the binary $\text{Zr}_{66.7}\text{Cu}_{33.3}$, $\text{Zr}_{66.7}\text{Ni}_{33.3}$ and $\text{Zr}_{66.7}\text{Pd}_{33.3}$ alloys by 2.0 MeV electron irradiation

Fig. 7 Onset total dose of electron irradiation induced crystallization of melt-spun $Zr_{66.7}Cu_{33.3}$, $Zr_{66.7}Ni_{33.3}$ and $Zr_{66.7}Pd_{33.3}$ alloys. The onset total dose was defined as the total dose at which Debye rings and/or diffraction spots corresponding to crystalline phases appeared in the SAD pattern during electron irradiation.

induced nano-crystallization at 298 K; the profiles are obtained from the electron diffraction patterns shown in Fig. 5. In $Zr_{66.7}Cu_{33.3}$ and $Zr_{66.7}Ni_{33.3}$ alloys, the precipitates were identified as f.c.c.-solid solution (f.c.c.-SS) from the position of those diffraction peaks. The precipitation of thermal equilibrium $C11_b$ - Zr_2Cu , $C16$ - Zr_2Ni or big-cube phase was not confirmed. The constituent crystalline phases in $Zr_{66.7}Pd_{33.3}$ alloy were different from those in $Zr_{66.7}Cu_{33.3}$ and $Zr_{66.7}Ni_{33.3}$ alloys. Two types of f.c.c. solid solution with different lattice constants, namely, f.c.c.-SS 1 and f.c.c.-SS 2 were formed in $Zr_{66.7}Pd_{33.3}$ alloy. Existence of these nano-crystalline f.c.c. phases was confirmed by HREM microscope observation on the basis of the fringe spacing and geometry of the cross-fringe image, and Fourier Transfer patterns in a separated paper.³⁶⁾ The difference in phase selection between $Zr_{66.7}Pd_{33.3}$ alloy and $Zr_{66.7}M_{33.3}$ ($M = Cu$ and Ni) may correspond to that in the nano-crystalline structure in the BF image shown in Fig. 5.

Phase stability of an amorphous phase against electron irradiation can be evaluated by the onset total dose at which electron irradiation induced crystallization begins.^{24,30)} In the present study, the onset total dose was defined as the critical total dose at which Debye rings and/or diffraction spots corresponding to crystalline phases appeared in the SAD pattern during electron irradiation. The way onset total dose was determined was the same as that in Zr-Cu based metallic glasses reported in previous papers.^{24,30)}

Figure 7 shows the onset total dose of electron irradiation induced crystallization of melt-spun amorphous phase of binary $Zr_{66.7}Cu_{33.3}$, $Zr_{66.7}Ni_{33.3}$ and $Zr_{66.7}Pd_{33.3}$ alloys. There is no significant difference in the onset total dose between $Zr_{66.7}Cu_{33.3}$ and $Zr_{66.7}Ni_{33.3}$ alloys from the viewpoint of the absolute value and temperature dependence of this dose. One can notice that the onset total dose of $Zr_{66.7}Pd_{33.3}$ alloy at the irradiation temperature of 103 K is much higher than that in $Zr_{66.7}Cu_{33.3}$ and $Zr_{66.7}Ni_{33.3}$ alloys at the same temperature; the degree of temperature dependence of this dose in the former is obviously larger than that in the other alloys. The kinetics of electron irradiation induced crystallization in $Zr_{66.7}Pd_{33.3}$ alloy is different from that in $Zr_{66.7}Cu_{33.3}$ and

$Zr_{66.7}Ni_{33.3}$ alloy in the temperature range between 103 K and 298 K.

4. Discussion

In the electron irradiation induced crystallization behavior in $Zr_{66.7}M_{33.3}$ ($M = Cu, Ni, Pd$) alloy, $Zr_{66.7}Pd_{33.3}$ alloy shows a difference in nano-crystalline structure, phase formation and kinetics from those of $Zr_{66.7}Cu_{33.3}$ and $Zr_{66.7}Ni_{33.3}$ alloys, while there is no significant difference in the behavior between these latter two. The thermal properties and thermal crystallization behavior in $Zr_{66.7}M_{33.3}$ ($M = Cu, Ni, Pd$) alloy can be summarized as follows;

(1) phase formation: the metastable QC phase is formed in $Zr_{66.7}Pd_{33.3}$ alloy during thermal annealing while it cannot be observed in $Zr_{66.7}Cu_{33.3}$ and $Zr_{66.7}Ni_{33.3}$ alloys. (2) crystallization mode: $Zr_{66.7}Pd_{33.3}$ shows double step thermal crystallization, while crystallization in $Zr_{66.7}Cu_{33.3}$ and $Zr_{66.7}Ni_{33.3}$ occurs in a single step. The double step crystallization is closely related to the formation of the metastable QC phase in $Zr_{66.7}Pd_{33.3}$ alloy. In $Zr_{66.7}Cu_{33.3}$ and $Zr_{66.7}Ni_{33.3}$ alloys, the thermal equilibrium crystalline phase directly precipitates from an amorphous or supercooled liquid phase. (3) the thermal equilibrium crystalline phase is the $C11_b$ structure in $Zr_{66.7}Cu_{33.3}$ and $Zr_{66.7}Pd_{33.3}$ alloys, while the $C16$ structure is the thermal equilibrium crystalline phase in $Zr_{66.7}Ni_{33.3}$ alloy. (4) kinetic glass transition T_g : the glass-to-supercooled liquid transition can be seen in $Zr_{66.7}Cu_{33.3}$ and $Zr_{66.7}Pd_{33.3}$ alloys, while it is rarely observed in $Zr_{66.7}Ni_{33.3}$ alloy during conventional DSC measurement at a heating rate of $0.67 Ks^{-1}$, (5) thermodynamic glass transition T_K : all three alloys may have ideal glass transition temperature T_K near T_C .

Formation of the QC phase during thermal crystallization is considered to be the most important factor affecting the mode of crystallization among thermal properties, thermal crystallization and electron irradiation induced crystallization behavior. To date, electron irradiation induced crystallization has been investigated in binary-type, QC-former type and BMG-type alloys as shown in Fig. 1. The electron irradiation induced crystallization behavior in Zr-based metallic amorphous alloys and metallic glasses is summarized in Table 1.^{5,34,36)} The hatched area indicates the irradiation condition corresponding to the present study at acceleration voltage of 2.0 MV and at the irradiation temperature of 298 K. One can notice that formation of two types of f.c.c.-SS at 298 K can be observed only in QC former type $Zr_{66.7}Pd_{33.3}$ and $Zr_{80}Pt_{20}$ alloys. Single f.c.c.-SS was formed not only in binary $Zr_{66.7}Cu_{33.3}$ and $Zr_{66.7}Ni_{33.3}$ alloys but also in BMG-type $Zr_{65}Al_{7.5}Cu_{27.5}$, $Zr_{60}Al_{15}Ni_{25}$ and $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloys. The database also supports the idea that QC formation during thermal crystallization is the most important factor affecting the mode of electron irradiation induced crystallization in Zr-based binary metallic amorphous alloys and metallic glasses.

5. Conclusion

In the present study, the difference in electron irradiation induced crystallization behavior among binary $Zr_{66.7}M_{33.3}$

Table 1 Occurrence of electron irradiation induced crystallization and difference of phase selection in crystallization between thermal annealing and electron irradiation in Zr-based binary metallic amorphous alloys and metallic glasses.

Composition [at%]	Conditions		A-C transition	Phase selection in crystallization				Lattice constant [nm]	Ref.
	A.V. [MV]	Temp. [K]		Thermal annealing	Electron irradiation				
Zr _{66.7} Cu _{33.3}	2.0	602	Yes	C11 _b -Zr ₂ Cu	C11 _b			—	5,35)
	2.0	552	Yes		C11 _b			—	5,35)
	2.0	298	Yes		F.c.c.-I			0.52	24,30,31)
	2.0	103	Yes		F.c.c.-I			0.51	24,30)
	1.0	298	Yes		F.c.c.-I			0.51	24,30)
	1.0	103	Yes		F.c.c.-I			0.51	24,30)
Zr _{66.7} Ni _{33.3}	2.0	298	Yes	C16-Zr ₂ Ni	F.c.c.-I			0.51	32)
	2.0	103	Yes		F.c.c.-I			0.51	32)
Zr _{66.7} Pd _{33.3}	2.0	298	Yes	Quasi-crystal	F.c.c.-I	+ F.c.c-2		0.52,0.48	33,34,36)
	2.0	103	Yes		F.c.c.-2	+B.c.c.		0.48,0.36	36,36)
	2.0	20	Yes		B.c.c.			0.36	36)
Zr ₈₀ Pt ₂₀	2.0	298	Yes	Quasi-crystal	F.c.c.-I	+ F.c.c-2		0.51,0.48	**
Zr ₆₅ Al _{7.5} Cu _{27.5}	2.0	298	Yes	C11 _b -Zr ₂ Cu	F.c.c.-I			0.52	24,30,31)
	2.0	103	Yes		F.c.c.-I			0.51	31)
	1.0	298	Yes		F.c.c.-I			0.51	31)
	1.0	103	Yes		F.c.c.-I			0.51	31)
Zr ₆₀ Al ₁₅ Ni ₂₅	2.0	298	Yes	Zr ₆ Al ₂ Ni	F.c.c.-I			0.51	32)
	2.0	103	No		—	—	—	—	32)
Zr ₆₅ Al _{7.5} Ni ₁₀ Cu _{17.5}	2.0	298	Yes	C11 _b -Zr ₂ Cu	F.c.c.-I			0.52	30,31,41)
	2.0	103	Yes		F.c.c.-I			0.52	30,41)
	1.0	298	Yes		F.c.c.-I			0.51	30,41)
	1.0	103	Yes		F.c.c.-I			0.51	30,41)

Temp.: Temperature A.V.: Acceleration voltage A-C: Amorphous-to-Crystal (Crystallization) **: Unpublished work

($M = Cu, Ni$ and Pd) alloy was investigated. The results were summarized and the following conclusions were reached:

(1) The melt-spun amorphous phase cannot retain its original glassy structure under electron irradiation, and electron irradiation induced crystallization of this phase occurred in all three alloys.

(2) A nano-crystalline structure composed of nano-crystalline f.c.c.-solid solution and residual amorphous matrix was formed in the three alloys through the electron irradiation induced nano-crystallization.

(3) There was a difference in phase selection of crystallization between QC-former type of Zr-Pd and BMG prototype of Zr-Cu and Zr-Ni alloys. In the case of thermal crystallization, thermal equilibrium C11_b-Zr₂Cu and C16-Zr₂Ni directly precipitated from melt-spun amorphous phase in Zr-Cu and Zr-Ni alloys, while metastable QC phase was formed in Zr-Pd alloy. Under electron irradiation, a single f.c.c.-solid solution was formed in Zr-Cu and Zr-Ni alloys in spite of there being two-type f.c.c. solid solution formation in Zr-Pd alloy. QC formation through thermal crystallization was viewed as the most important factor for electron irradiation induced crystallization behaviors in Zr-based metallic amorphous alloys and metallic glasses.

Acknowledgements

Electron irradiation was carried out using a facility in the Research Center for Ultrahigh Voltage Electron Microscopy,

Osaka University. The authors are grateful to Prof. H. Mori and Dr. T. Sakata of that Research Center for operating the H-3000 UHVEM. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area A, "Materials Science of Metallic Glasses" from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Part of this work was also supported by the same Ministry's "Priority Assistance of the Formation of Worldwide Renowned Centers of Research-The 21st Century COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design)".

REFERENCES

- 1) H. Mori: *Current Topics in Amorphous Materials: Physics and Technology*, eds. by Y. Sakurai, Y. Hamakawa, T. Masumoto, K. Shirac and K. Suzuki (Elsevier Science Publishers, Amsterdam 1997), pp. 120–126.
- 2) P. R. Okamoto, N. Q. Lam and L. E. Rein: *Physics of Crystal-to-glass transformations, in: solid state physics*, vol. 52, eds. H. Ehrenreich and F. Spaepen (Academic Press, San Diego, 1999).
- 3) T. Masumoto: *Materials Science of Amorphous Metals*, (Ohm Publication, Tokyo 1982).
- 4) A. Inoue: *Acta Mater.* **48** (2000) 279–306.
- 5) T. Nagase and Y. Umakoshi: *Mater. Trans.* **47** (2006) 1469–1479.
- 6) H. Kakiuchi, A. Inoue, M. Onuki, Y. Takano and T. Yamaguchi: *Mater. Trans. JIM* **42** (2001) 678–681.
- 7) C. Fan and A. Inoue: *Mater. Trans. JIM* **38** (1997) 1040–1046.
- 8) C. Fan, A. Takeuchi and A. Inoue: *Mater. Trans. JIM* **40** (1999) 42–51.
- 9) A. Inoue, T. Zhang, J. Saida, M. Matsushita, M. W. Chen and T.

- Sakurai: *Mater. Trans., JIM* **40** (1999) 1137–1143.
- 10) A. Inoue, T. Zhang, M. W. Chen and T. Sakurai: *Appl. Phys. Lett.* **76** (2000) 967–969.
 - 11) U. Koster, J. Meinhardt, S. Roos and H. Liebertz: *Appl. Phys. Lett.* **69** (1996) 179–181.
 - 12) J. Eckert, N. Mattern, M. Zinkevich and M. Seidei: *Mater. Trans., JIM* **39** (1998) 623–632.
 - 13) B. S. Murty, D. H. Ping, K. Hono and A. Inoue: *Acta Mater.* **48** (2000) 3985–3996.
 - 14) A. Inoue, T. Zhang, M. Matsubara, M. W. Chen and T. Sakurai: *Mater. Trans., JIM* **40** (1999) 1181–1184.
 - 15) J. Saida, M. Matsushita and A. Inoue: *Intermetallics* **10** (2002) 1089–1098.
 - 16) M. W. Chen, T. Zhang, A. Inoue, A. Sakai and T. Sakurai: *Appl. Phys. Lett.* **75** (1999) 1697–1699.
 - 17) A. Inoue, J. Saida, M. Matsushita and T. Sakurai: *Mater. Trans.* **41** (2000) 362–365.
 - 18) J. Saida, M. Matsushita and C. Li: *Appl. Phys. Lett.* **76** (2000) 3558–3560.
 - 19) M. Matsushita, J. Saida, C. Li and A. Inoue: *J. Mater. Res.* **15** (2000) 1280–1283.
 - 20) J. Saida, M. Matsubara and A. Inoue: *Appl. Phys. Lett.* **77** (2000) 73–75.
 - 21) B. S. Murty, D. H. Ping and K. Hono: *Appl. Phys. Lett.* **77** (2000) 1102–1104.
 - 22) J. Saida, M. Matsushita and A. Inoue: *Phil. Mag. Lett.* **81** (2001) 39–44.
 - 23) T. Nagase, Y. Umakoshi and N. Sumida: *Mater. Sci. Eng. A* **323** (2002) 218–225.
 - 24) T. Nagase and Y. Umakoshi: *Mater. Sci. Eng.* **352** (2003) 251–260.
 - 25) R. Tarumi, K. Takashima and Y. Higo: *Appl. Phys. Lett.* **81** (2002) 4610–4612.
 - 26) R. S. Qin, S. X. Su, J. D. Guo, G. H. He and B. L. Zhou: *Nanostructured Mater.* **10** (1998) 71–76.
 - 27) H. Mizubayashi, N. Kameyama, T. Hao and H. Tanimoto: *Phys. Rev. B* **64** (2001) 054201-1-054201-10.
 - 28) T. Nagase, Y. Umakoshi and N. Sumida: *Sci. Tech. Adv. Mater.* **3** (2002) 119–128.
 - 29) T. Nagase and Y. Umakoshi: *Scripta Mater.* **48** (2003) 1237–1242.
 - 30) T. Nagase and Y. Umakoshi: *J. Appl. Phys.* **93** (2003) 912–918.
 - 31) T. Nagase and Y. Umakoshi: *Mater. Trans.* **45** (2004) 13–23.
 - 32) T. Nagase, M. Nakamura and Y. Umakoshi: *Intermetallics* **15** (2007) 211–224.
 - 33) T. Nagase, T. Hosokawa and Y. Umakoshi: *Scripta Mater.* **53** (2005) 1401–1405.
 - 34) T. Nagase, T. Hosokawa and Y. Umakoshi: *Intermetallics* **14** (2006) 1027–1032.
 - 35) Y. Umakoshi and T. Nagase: *Mater. Sci. Eng., A* **449–451** (2007) 605–608.
 - 36) T. Nagase, T. Hosokawa and Y. Umakoshi: *Metal. Mater. Trans. A* **38** (2007) 223–235.
 - 37) T. Ichitsubo, E. Matsubara, H. Numakura, K. Tanaka, N. Nishiyama and R. Tarumi: *Phys. Rev. B* **72** (2005) 052201-1-052201-4.
 - 38) T. Ichitsubo, E. Matsubara, J. Saida and H. S. Chen: *Mater. Trans.* **46** (2005) 2282–2286.
 - 39) R. Busch, Y. J. Kim and W. L. Johnson: *J. Appl. Phys.* **77** (1995) 4039–4043.
 - 40) Z. Altounian, E. Batalla, J. O. Strom-Olsen and J. L. Walter: *J. Appl. Phys.* **61** (1987) 149–155.
 - 41) T. Nagase and Y. Umakoshi: *Sci. Tech. Adv. Mater.* **5** (2004) 57–67.