Electron Irradiation Induced Crystal-to-Amorphous-to-Crystal Transition in Some Metallic Glasses

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Electron irradiation induced crystal-to-amorphous-to-crystal (C-A-C) transition in metallic glasses was investigated in various metallic glasses among binary Zr-based, ternary Fe-Nd-B and Fe-Zr-B alloys. In situ observation of the TEM microstructures and corresponding SAD patterns was performed by ultra high-voltage electron microscope (UHREM). The origin of amorphization, crystallization and C-A-C transition was discussed based on the temperature-Gibbs free energy diagram.

Keywords: metallic glass, amorphous, quasi-crystal, solid-state amorphization, crystallization, electron irradiation

1. Introduction

Metallic amorphous formation can be achieved by two fundamentally different processes: the thermal process and the mechanical process. The thermal process refers to the thermal treatment of metallic glass alloys by mechanical atomic displacement was induced not only by thermal annealing but also electron irradiation, focused ion beam (FIB) and electro-pulsing techniques. We found that electron irradiation can induce nano-crystallization of an amorphous phase even in metallic glasses in which the nanostructure is not easily realized by thermal annealing. The metastable nano-crystalline structure was also formed from an amorphous phase by electron irradiation. Crystallographically oriented nanocrystals formed by FIB irradiation were reported. These results imply that electron irradiation to an amorphous phase is a new method for obtaining a controlled nano-crystalline structure in a metallic glass.

Recently a unique disordering-ordering phase transition in metallic glass alloys by mechanical atomic displacement was induced by mechanical milling and electron irradiation techniques: cyclic crystalline-amorphous (Cyclic-CA) transition during mechanical milling, electron irradiation induced crystal-to-amorphous-to-crystal (C-A-C) transitions, and electron irradiation induced quasicrystal-to-amorphous-to-crystal (Q-A-C) transition.

In the present study, the electron irradiation induced C-A-C and Q-A-C transition in metallic glasses were reviewed in various metallic glasses among binary Zr-based, ternary Fe-Nd-B and Fe-Zr-B alloys. The origin of C-A, A-C and C-A-C transition was discussed based on the temperature-Gibbs free energy diagram.

2. Experimental Procedure

Master ingots of Zr₆₆.₇Cu₃₃.₃, Zr₆₆.₇Pd₃₃.₃, Fe₈₉.₅Nd₁₀.₅, Fe₈₂.₄Nd₁₁.₁B₉.₉, Fe₈₂.₁Nd₇.₁B₁₀.₇ and Fe₈₁Zr₁₀ (at%) alloys were prepared by arc melting raw materials of pure Zr, Cu, Pd, Fe, Nd metals, B(crystal-boron) and Fe-B(ferro-boron) alloy in a purified Ar atmosphere. Rapidly quenched ribbon with a thickness of between 0.02 mm to 0.04 mm was produced from the ingots at a rotation speed of 42 ms⁻¹ by a single roller melt-spinning method in this atmosphere. An amorphous single phase was formed in Zr-based Zr₆₆.₇Cu₃₃.₃ and Zr₆₆.₇Pd₃₃.₃ alloys, and Fe-Zr-B based Fe₈₁Zr₁₀ alloy. The melt-spin Fe-Nd-B based Fe₈₀.₅Nd₁₀.₅, Fe₈₂.₄Nd₁₁.₁B₉.₉ and Fe₈₂.₁Nd₇.₁B₁₀.₇ alloys were not an amorphous single phase but they contained crystalline phases. Melt-spin ribbon of Zr-based and Fe-Zr-B alloys showed good ductility adequate for 180 degree bending, while Fe-Nd-B based alloys of Fe₈₉.₅Nd₁₀.₅, Fe₈₂.₄Nd₁₁.₁B₉.₉ and Fe₈₂.₁Nd₇.₁B₁₀.₇ were brittle. Thermal properties and crystallization behavior of the melt-spin ribbon were examined by differential scanning calorimeter (DSC) in Ar atmosphere at the heating rate of 0.67 Ks⁻¹. The anomalous endothermic reaction corresponding to glass transition and sharp exothermic reaction corresponding to thermal crystallization were observed in melt-spin ribbon of Zr-based and Fe-Zr-B alloys. The glass transition temperature (Tg), crystallization temperature (Tc) and temperature interval of the supercooled liquid region (ΔTg = Tg − Tc) for Zr₆₆.₇Cu₃₃.₃ alloy (5,9,11) 710 K, 754 K and 44 K for Zr₆₆.₇Pd₃₃.₃ alloy (13,18) and 847 K, 876 K and 29 K for Fe₈₁-
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 $\text{Zr}_{66}^{\text{Cu}}_{33}$, and a solution of 10% perchloric and 90% acetic acid at room temperature for $\text{Fe}_{81}^{\text{Zr}}_{9}^{\text{B}}_{10}$ alloy. Thin foils of $\text{Zr}_{66}^{\text{Pd}}_{33}$ and $\text{Fe-Nd-B}$ alloys for electron irradiation were prepared by ion milling technique. The foils were electron irradiated by 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 temperatures of 103 K and 298 K. The applied dose rate was between $1.6 \times 10^{24}$ and $1.1 \times 10^{25}$ m$^{-2}$ s$^{-1}$. 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. The size of selected area (SA) aperture of UHVEM H-3000 was about 1 μm in the present study. Effect of additional electron irradiation during in situ TEM observation can be neglected because of the low dose rate. Structure of melt-spun, annealed and irradiated ribbons was also examined by X-ray diffractometry using Cu-Kα 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.

3. Results

3.1 Crystal-to-amorphous-to-crystal (C-A-C) transition in binary $\text{Zr}_{66}^{\text{M}}_{33}$ (M = Cu, Pd) alloys

The electron irradiation induced C-A-C transition in metallic materials was firstly reported in $\text{Zr}_{66}^{\text{Cu}}_{33}$ alloy.$^9$ A typical example of C-A-C transition is seen in Fig. 1 where a change in TEM microstructures and corresponding SAD patterns of the crystalline phase of $\text{C}_{11b}-\text{Zr}_{2}^{\text{Cu}}$ intermetallic compound during 2.0 MeV electron irradiation at 298 K are shown. The specimen (Fig. 1(a)) irradiated at the total dose of $4.4 \times 10^{26}$ m$^{-2}$ shows a crystalline contrast in the BF image and electron diffraction spot in the SAD pattern. At the total dose of $1.7 \times 10^{27}$ m$^{-2}$ (Fig. 1(b)), the crystalline contrast disappeared in the BF image. Concurrently, electron diffraction spots corresponding to the $\text{C}_{11b}$ crystalline phase vanished and a halo ring corresponding to an amorphous phase newly appeared in the SAD pattern. This indicates that the phase stability of $\text{C}_{11b}$ crystalline phase under electron irradiation is not high enough to maintain the original structure against electron irradiation so that amorphization of this phase occurs. In other words, crystal-to-amorphous (C-A) transition occurs under electron irradiation. In SAD pattern of Fig. 1(b), some electron diffraction spots are observed together with broad halo ring corresponding to an amorphous phase newly appeared in the SAD pattern. In order to examine the electron diffraction spots corresponding to the $\text{C}_{11b}$ crystalline phase vanished and a halo ring corresponding to an amorphous phase newly appeared in the SAD pattern. In other words, crystal-to-amorphous (C-A) transition occurs under electron irradiation. In SAD pattern of Fig. 1(b), some electron diffraction spots are observed together with broad halo ring corresponding to an amorphous phase. The diffraction spots may be due to the crystalline phase in the peripheral area of electron irradiation because the size of SA aperture in the present study is about 1 μm. At the total dose of $1.1 \times 10^{28}$ m$^{-2}$ (Fig. 1(c)), dark and bright granular contrast about 10 nm order in size appeared again from a featureless contrast at the central part of the irradiated area in the BF image. In the SAD pattern, Debye rings appeared for the first time. The crystalline phase was identified not as the $\text{C}_{11b}$ phase with b.c.t.-structure but as f.c.c.-solid solution. In order to examine the electron
irradiation induced C-A-C transition in C11\textsubscript{b}-Zr\textsubscript{2}Cu crystalline phase in detail, HREM observation was made of the specimens electron irradiated at the dose density of 1.7 \times 10^{27} \text{m}^{-2} and 1.1 \times 10^{28} \text{m}^{-2}. These irradiation conditions create the structures just after the first and second phase transformations, namely, just after amorphization and crystallization.

At the total dose of 1.7 \times 10^{27} \text{m}^{-2}, a typical isotropic salt-pepper pattern contrast image can be seen in Fig. 2(a). This supports the fact that the amorphization occurs by electron irradiation in the C11\textsubscript{b}-Zr\textsubscript{2}Cu crystalline phase. In Fig. 2(b), crystalline lattice images with a nano-scale grain size of about 10 nm order are observed. The lattice image is randomly oriented in each region and hence each nano-crystalline precipitate appears with a random orientation. This indicates that f.c.c.-solid solution is not directly formed from C11\textsubscript{b}-Zr\textsubscript{2}Cu but by crystallization through the amorphous phase. The two-step phase transformation behavior and the formation of a nano-crystalline structure composed of f.c.c.-solid solution crystalline precipitates nano-scale in size and with a residual amorphous matrix were confirmed by the HREM observation. Thus, neither the C11\textsubscript{b} crystalline phase nor the amorphous phase can maintain its original structure under electron irradiation, and another crystalline phase of f.c.c.-solid solution appears. The C11\textsubscript{b} crystalline phase is transformed to an amorphous phase through SSA and then the amorphous phase is transformed to a nano-crystalline phase in spite of the same irradiation conditions. We named the amorphous phase formation the C-A-C transition.

After amorphous phase formation, the amorphous area spreads with increasing irradiation time. In the central area of electron irradiation as indicated by a white arrow, and the nano-crystalline area spreads with the difference in mechanical atomic displacement processes of plastic deformation in the mechanical milling and electron knock-on effect in the electron irradiation.

The C-A-C transition was observed not only in Zr\textsubscript{66.7}Cu\textsubscript{33.3} alloy but also in other Zr-based alloys. Figures 3 and 4 show a typical example of C-A-C transition in Zr\textsubscript{66.7}Pd\textsubscript{33.3} alloy under 2.0 MV electron irradiation at 103 K. Electron irradiation induced amorphization of C11\textsubscript{b}-Zr\textsubscript{2}Pd was confirmed by TEM observation (Fig. 3(b)) and HREM image (Fig. 4(a)). After C-A-C transition, a nano-crystalline structure composed of f.c.c.-solid solution and residual amorphous phase was formed as shown in Fig. 3(c) and Fig. 4(b). In Zr\textsubscript{66.7}Pd\textsubscript{33.3} alloy, a similar type phase transition of quasicrystal-to-amorphous-to-crystal (Q-A-C) was reported.\textsuperscript{18}

3.2 Crystal-to-amorphous-to-crystal transition in ternary Fe-M-B (M=Nd, Zr) alloys

C-A-C transition can be observed in a metal-metalloid alloy system as well as a metal-metal alloy system such as Zr-Cu and Zr-Pd. A typical example of C-A-C transition of Nd\textsubscript{2}Fe\textsubscript{14}B polycrystalline compound in a metal-metalloid type of Fe\textsubscript{82.4}Nd\textsubscript{11.5}B\textsubscript{5.9} alloy under 2.0 MeV electron irradiation at 298 K is shown in Fig. 5, where changes in BF images and SAD patterns of the Nd\textsubscript{2}Fe\textsubscript{14}B compound can be detected in detail by \textit{in situ} UHVEM observation. Such systematic investigation of mechanical atomic displacement induced phase transformation between amorphous and crystalline phases is rarely realized by severe plastic deformation and mechanical milling techniques. The specimen before irradiation shows a typical poly-crystalline structure with a grain size of about 50 nm (a). The Nd\textsubscript{2}Fe\textsubscript{14}B compound can not maintain its original structure under 2.0 MeV electron irradiation, solid-state amorphization occurs at 15 s by electron irradiation as shown in Fig. 6(b). After amorphous phase formation, the amorphous area spreads with increasing irradiation time. In the central area of electron irradiation, an amorphous phase can maintain a glassy structure until the irradiation time reaches 180 s (g). At this time, nano-crystallization of the amorphous phase occurs in the central area of electron irradiation as indicated by a white arrow, and the nano-crystalline area spreads with

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Change in HREM image of C11\textsubscript{b}-Zr\textsubscript{2}Cu crystalline phase during electron irradiation induced crystal-to-amorphous-to-crystal transition. (a) 450 s at the total dose of 1.7 \times 10^{27} \text{m}^{-2}, (b) 3.0 \times 10^{5} \text{s at the total dose of 1.1 \times 10^{28} \text{m}^{-2}.}
\end{figure}
increasing irradiation time. The nano-crystalline structure composed of b.c.c.-solid solution, defective crystalline compounds and residual amorphous matrix is formed through C-A-C transition. A electron irradiation induced C-A-C transition has been found to date not only in Nd$_2$Fe$_{14}$B compound$^{16}$ but also in Nd$_2$Fe$_{23}$B$_3$, Fe$_{17}$Nd$_2$ and Fe-Zr-B based $\alpha$-Mn type crystalline phase.$^{17}$ In Fig. 5(c)–(f), diffuse diffraction rings inside the first halo ring corresponding to an amorphous phase are observed. The position of the diffuse diffraction rings is similar to that of metallic compounds obtained by electron irradiation induced C-A-C transition. The formation of nano-crystalline precipitates or medium range order (MRO) corresponding to metallic compounds near the electron irradiated area may be the origin of the diffuse diffraction rings.

4. Discussion

The alloys and/or compounds in which electron irradiation induced C-A-C transition has so far been confirmed summarized in Table 1(a), together with the data of Q-A-C transition (b). Table 1 indicates that C-A-C and Q-A-C transition is not a unique phase transition in extremely limited alloys but a conventional phase transition in metallic materials. In this section, the origin of electron irradiation induced C-A-C transition is discussed based on a temper-
Fig. 5 Change in TEM microstructure and corresponding SAD patterns of quasi-crystalline phase during 2.0 MV electron irradiation at 298 K in Zr$_{66}$Pd$_{33}$ alloy. Quasi-crystalline phase was obtained by thermal annealing of melt-spun amorphous ribbon at 743 K for 600 s in vacuum. (a) before electron irradiation, (b) 30 s at the total dose of $2.8 \times 10^{26}$ m$^{-2}$, (c) $1.2 \times 10^3$ s at the total dose of $1.1 \times 10^{28}$ m$^{-2}$.

Change in TEM microstructure and corresponding SAD patterns of Nd$_2$Fe$_{14}$B crystalline phase during 2.0 MV electron irradiation at 298 K at the dose rate of $1.0 \times 10^{25}$ m$^{-2}$ s$^{-1}$. Nd$_2$Fe$_{14}$B crystalline phase was obtained by melt-spinning method in Fe$_{82}$Nd$_{11}$B$_{5.9}$ alloy. (a) before electron irradiation, (b) 15 s, (c) 30 s, (d) 45 s, (e) 60 s, (f) 120 s, (g) 180 s, (h) 300 s, (i) 450 s, (j) 600 s, (k) $1.2 \times 10^3$ s, (l) $1.8 \times 10^3$ s.
defective crystal. In Fig. 6, not only conventional glass
the temperature-entropy diagram. In the present study, a
illustration of the temperature-Gibbs free energy diagram and
energy by electron irradiation. Figure 6 shows a schematic
increase in the entropy, resulting in phase transition.
tron irradiation causes the introduction of lattice defects and
talline materials, mechanical atomic displacement by elec-
trons under electron-irradiation. In metallic crystals, atoms in a material are dynamically displaced by an electron
collision energy transformed from the electrons is sufficient
to produce only a single or at most double atom displace-
ments.1,2,21) Electron-irradiation can induce the phase trans-
formation of crystalline and amorphous phases because
 constituent atoms in the material. At 2.0 MV irradiation the
mean glass transition temperature, ideal glass transition temperature, namely, Kauzmann tempera-
ture is thermodynamically defined as the temperature at
which the entropy of liquid equals that of crystal. The Gibbs
free energy of defective crystal is higher than that of perfect
crystal because of excess energy of introduced lattice defects.
The tangent of the Gibbs free energy of the defective crystal,
which the entropy of liquid equals that of crystal. The Gibbs
free energy diagram focusing on defective crystal. (a)
(a) Crystal-to-amorphous-to-crystal (C-A-C) transition
(b) Quasicrystal-to-amorphous-to-crystal (Q-A-C) transition
(a) Crystal-to-amorphous-to-crystal (C-A-C) transition
(b) Quasicrystal-to-amorphous-to-crystal (Q-A-C) transition

Table 1 Occurrence of electron irradiation induced crystal-to-amorphous-
to-crystal (C-A-C) transition (a) and quasicrystal-to-amorphous-to-crystal
(Q-A-C) transition (b).

<table>
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<td>Temp. [K]</td>
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<td>Yes</td>
<td>9)</td>
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Temp.: Temperature A.V.: Acceleration voltage **: Unpublished Work

When a material is irradiated with high energy electrons,
an elastic collision occurs between those electrons and constituent atoms in the material. At 2.0 MV irradiation the
collision energy transformed from the electrons is sufficient to produce only a single or at most double atom displace-
ments.1,2,21) Electron-irradiation can induce the phase trans-
formation of crystalline and amorphous phases because
atoms in a material are dynamically displaced by an electron
knock-on effect under electron-irradiation. In metallic crys-
talline materials, mechanical atomic displacement by elec-
tron irradiation causes the introduction of lattice defects and increase in the entropy, resulting in phase transition.
The cause of electron irradiation induced phase transition is considered based on change in entropy and Gibbs free
energy by electron irradiation. Figure 6 shows a schematic illustration of the temperature-Gibbs free energy diagram and
the temperature-entropy diagram. In the present study, a
crystal with irradiation induced lattice defects is called
defective crystal. In Fig. 6, not only conventional glass
transition temperature ($T_g$) but also ideal glass transition temperature ($T_K$) is indicated in the temperature axis. This ideal
glass transition temperature, namely, Kauzmann tempera-
ture is thermodynamically defined as the temperature at
which the entropy of liquid equals that of crystal. The Gibbs
free energy of defective crystal is higher than that of perfect
crystal because of excess energy of introduced lattice defects.
The phase boundary ($S_{Ideal
glass}$) becomes the same as that of crystal ($S_{Crystal}$) because
$S_{Ideal
glass}$ cannot be lower than $S_{Crystal}$.

Fig. 6 Schematic illustration of temperature-Gibbs free energy diagram and
temperature-entropy diagram focusing on defective crystal. (a) temperature-Gibbs free energy diagram of crystal, liquid, amorphous, ideal glass and defective crystal. (b) temperature-entropy diagram of crystal, liquid, amorphous and ideal glass. In the Figures, $T_d$, $T_K$, $T_m$, $T_m^d$, $T_m^d$ mean glass transition temperature, ideal glass transition temperature, melting temperature of perfect crystal and melting temperature of defective crystal, respectively.
energy range where an amorphous phase exists. The free energy of this amorphous phase is very sensitive to the $T_g$.

The two different un-relaxed amorphous phases $G_{\text{Amorphous}(1)}$ and $G_{\text{Amorphous}(2)}$ can be defined by the kinetic glass-to-liquid transition temperature of $T_g(1)$ and $T_g(2)$. If the liquid state were quenched at the temperature $T_K$, the ideal glass phase would be formed. In Fig. 7(b), the gray hatched-area (B) shows the free energy range where crystalline phase can occupy. Electron irradiation raises the energy of the crystalline phase due to lattice defects created by the electron knock-on effect. The difference in free energy between defective crystal $G_{\text{Defective crystal}(1)}$ and $G_{\text{Defective crystal}(2)}$ is caused by the difference in the concentration of atomic defects. One should notice that the hatched area (A) in Fig. 7(a) overlaps with the gray hatched-area (B) in Fig. 7(b), and the overlapping area (C) is shown in Fig. 7(c). In the overlapped area (C) in Fig. 7(c), both defective crystal and an amorphous phase can exist. The overlap zone between defective crystal and an amorphous phase can exist not only in entropy as shown in Fig. 6(b) but also in Gibbs free energy as shown in Fig. 7(c). Electron irradiation induced C-A-C transition occurs with the combination of the C-A transition pass of (A) and crystallization pass of (B) in the overlapping zone as shown in Fig. 7(d). The electron irradiation induced C-A-C transition can be explained by the temperature-Gibbs free energy diagram of Fig. 7 without any contradiction. Phase stability of metallic materials under electron irradiation cannot be discussed based on the simple temperature-free energy diagram because they are not in a thermal equilibrium state due to adequate additional energy provided by electron irradiation. Another model was proposed in other papers.20,26) However, Fig. 7 clearly shows that there is an overlapping zone where both defective crystal and an amorphous phase can exist, and the concept of the overlapping zone is very important for electron irradiation induced C-A-C transition. The idea of this overlapping zone is also applied for cyclic C-A transition during mechanical milling14,15) and electron irradiation induced Q-A-C transition.18)

5. Conclusion

In the present study, electron irradiation induced crystal-to-amorphous-to-crystal (C-A-C) and quasicrystal-to-amorphous-to-crystal (Q-A-C) transitions were reviewed and discussed based on the temperature-Gibbs free energy diagram. The results have been summarized and the following conclusions reached:
C-A-C transition was observed not only in Zr$_{66.7}$Cu$_{33.3}$ alloy but also other Zr-based and Fe-based metallic materials. In Zr$_{66.7}$Pd$_{33.3}$ alloy, both C-A-C and Q-A-C transitions occurred under electron irradiation.

Occurrence of C-A-C transition can be explained by the concept of an overlapping zone where both an amorphous phase and defective crystalline phases exist. Solid-state amorphization of crystal-to-amorphous (C-A) transition, crystallization of amorphous-to-crystal (A-C) transition, and C-A-C transition can be discussed by the overlapping zone in the temperature-Gibbs free energy diagram.

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