Amorphization and subsequent crystallization in Zr$_{66.7}$Ni$_{33.3}$ alloy under MeV electron irradiation

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Abstract. MeV electron irradiation introduces Frenkel pairs in a crystalline phase and free volume in a glassy phase, resulting in solid-state amorphization of metallic crystals and crystallization of metallic glasses, respectively, in some alloy systems. C16-Zr$_2$Ni intermetallic compound transformed to a f.c.c.-type nano-crystalline phase through an amorphous state under electron irradiation. Namely, a metastable nano-crystalline structure was formed by a Crystal-to-Amorphous-to-Crystal (C-A-C) transition in the C16-Zr$_2$Ni thermal equilibrium phase. An overlap of amorphization and crystallization was observed at 298K, while such an overlap could not be observed at 103K. This behavior can be explained by the difference in the temperature dependence of electron dose required for amorphization and crystallization.

1. Introduction

MeV electron irradiation introduces Frenkel pairs in a crystalline phase and free volume in a glassy phase. Figure 1 shows a schematic illustration of Frenkel pair and free volume formation by the electron knock-on effect. It is reported that in some alloy systems, solid-state amorphization of metallic crystals [1-3] and crystallization of metallic glasses [4-6] occurs by the accumulation of atomic defects under the irradiation. Various unfavourable factors such as temperature rise, contamination, oxidation, change in chemical composition and cascade effect can be neglected in the case of electron irradiation, while these factors must be taken into account in other mechanical processes such as mechanical milling, severe plastic deformation, shot peening, ion and neutron irradiation. Furthermore, in-situ observation during MeV electron irradiation by a high voltage electron microscope (HVEM) makes it possible to carry out a real-time analysis of changes in microstructure. HVEM offers therefore a unique opportunity to investigate the phase stability of a crystalline phase against excess Frenkel pairs and of a glass phase against excess free volume.

Recently unique disordering-ordering phase transitions in metallic alloys were induced by mechanical milling and electron irradiation techniques: namely, cyclic crystalline-amorphous (Cyclic-CA) transformation during mechanical milling [7,8], electron irradiation induced crystal-to-amorphous-to-crystal (C-A-C) transitions [9,10], and electron irradiation induced quasicrystal-to-amorphous-to-crystal (Q-A-C) transition [11]. In the present study, a C-A-C transition in Zr$_{66.7}$Ni$_{33.3}$ alloy was investigated by high voltage electron microscopy, with emphasis placed on the temperature dependence of the transition.
2. Experimental procedures

A master ingot of Zr_{66.7}Ni_{33.3} alloy was prepared by arc melting of raw materials of pure Zr (purity, >99.9 at.%) and Ni (purity, >99.9 at.%) metals in a purified Ar atmosphere. Rapidly quenched ribbons with thickness between 0.02mm and 0.04mm were produced from the ingot at a rotation speed of 42 ms\(^{-1}\) by a single roller melt-spinning method in the same atmosphere. Thermal properties of the melt-spun amorphous phase were evaluated by differential scanning calorimetry (DSC) measurements in Ar atmosphere. C16-Zr_{2}Ni intermetallic compound was obtained by isothermal annealing at 1273 K for 1.8x10^{3} s in Ar atmosphere and vacuum. Thin foils for electron irradiation were prepared from the ribbons by twin-jet polishing in a solution of 30 % nitric acid and 70 % methanol kept at about 243 K. Electron irradiation was performed with the H-3000 ultrahigh voltage electron microscope (UHVEM) at Osaka University. The acceleration voltage was 2.0 MV and the dose rate was in the range between 3.3x10^{24} and 9.2x10^{25} m\(^{-2}\)s\(^{-1}\). Changes in the bright field (BF) images and selected area diffraction (SAD) patterns during electron irradiation were monitored in situ by UHVEM.

3. Results

3.1. Thermal crystallization and electron irradiation induced crystallization of amorphous phase

Figure 2(a) shows a DSC curve of melt-spun specimens measured at a heating rate of 0.67 Ks\(^{-1}\). An exothermic peak corresponding to the thermal crystallization of the melt-spun amorphous phase is seen at \(T_x\). The temperature of \(T_x\) is evaluated to be 673K. Fig. 2(b) shows isothermal DSC curves of melt-spun amorphous specimens. Isothermal annealing in a DSC furnace began just after the rapid heating of the alloy sample up to the required temperature at a constant heating rate of 0.83 Ks\(^{-1}\). Time-temperature transformation (TTT) diagram of thermal crystallization of melt-spun amorphous can be constructed based upon isothermal DSC measurements shown in Fig.2 (b). The TTT diagram obtained is shown in Fig. 2 (c). The onset time of an exothermic peak increases with decreasing annealing temperature. The solid and dotted lines, corresponding to onset and offset time of thermal crystallization, respectively, can be fitted to the following equation [12],

\[
\tau = \tau_0 \cdot \exp\left(\frac{-E}{RT}\right)
\]

where \(\tau\) is the onset time or offset time, \(E\) is the activation energy, \(R\) is the gas constant and \(T\) is temperature, respectively. Based on equation (1), the onset time of thermal crystallization at 103K and 298K is estimated to be of the order of 10^{12} s and 10^{10} s, respectively. It seems then reasonable to consider that the metastable amorphous phase maintains the glassy state stably and devitrification of this phase through thermal crystallization can be ignored at room temperature.
Figure 3 shows a typical example of electron irradiation induced crystallization of the amorphous phase in a Zr66.7Ni33.3 alloy [13]. Changes in BF images and corresponding SAD patterns of the melt-spun amorphous phase in a Zr66.7Ni33.3 alloy during 2.0 MV electron irradiation at 298K, are illustrated. Before irradiation (a), the amorphous phase shows only featureless contrast over the entire BF image and only broad halo rings in SAD pattern. Grains with nano-granular contrast appear in the BF image and the Debye rings appear together with decrease in the intensity of the halo ring after irradiation for 600s (b). It is evident that the amorphous phase is not stable under electron irradiation at 298K in spite of the high phase stability against thermal crystallization, resulting in the formation of a nanocrystalline structure. The phase selection of irradiation induced crystallization was investigated in the previous study; not the thermal equilibrium C16-Zr2Ni but a metastable f.c.c.-type nanocrystalline phase appeared from the amorphous phase under electron irradiation [13].

Electron irradiation induced C-A-C transition

3.2. Electron irradiation induced C-A-C transition

Figure 4 shows changes in BF images and corresponding SAD patterns of C16-Zr2Ni intermetallic compound during 2.0MV electron irradiation at 103K. In situ TEM observation was performed by UHVEM at 2.0 MV. The specimen before electron irradiation shows bend contours in the BF image and electron diffraction spots in the SAD pattern (a). After 30s electron irradiation (b), the contrast of bend contours disappeared at the central area of the irradiation in the
BF image. Concurrently, halo rings corresponding to an amorphous phase appeared in the SAD pattern. Further electron irradiation brought about an increase in the intensity of the halo rings at the expense of that of the diffraction spots. In the specimen irradiated for 60s (d), the crystalline contrast (i.e., contrast of bend contours) vanished in the BF image. In the SAD pattern, electron diffraction spots vanished and only halo rings can be seen. The phase stability of intermetallic compound under electron irradiation is not high enough to maintain the original structure against electron irradiation, and an amorphous single phase was obtained through a crystal-to-amorphous (C-A) transition. In the specimen irradiated for 600s (e), grains with dark and bright granular contrast, with about 10 nm in size, appeared at the central part of the irradiated area in the BF image. In the SAD pattern, Debye
Rings appeared in addition to the halo rings. Nano-crystalline grains were formed through electron irradiation induced crystallization of an amorphous phase that had been obtained through the C-A transition by the irradiation. Namely, an electron irradiation induced C-A-C transition was observed in C16-Zr2Ni intermetallic compound. The nanocrystalline grains obtained by the C-A-C transition are considered to be a f.c.c.-type phase which is similar to that obtained by electron irradiation induced crystallization of melt-spun amorphous phase in Zr66.7Ni33.3 alloy.

Figure 5 shows the C-A-C transition in C16-Zr2Ni intermetallic compound at 298K. Nanocrystalline f.c.c. phase was formed under electron irradiation. One can notice that the C-A-C transition behavior at 298K is different from that at 103K. An amorphous single state cannot be observed during the C-A-C transition. After electron irradiation for 30s (b), not only halo rings but also Debye rings appeared in the SAD pattern. Further electron irradiation brought about an increase in the intensities of halo rings and Debye rings at the expense of those of the diffraction spots. In the specimen irradiated for 180s (c), not featureless contrast typical of an amorphous phase but nano granular contrast was observed in the BF image. After irradiation for 900s (e), both electron diffraction spots in the SAD pattern and typical crystalline contrast (i.e., bend contours) in the BF image vanished. Instead, nano granular contrast can be seen in the BF image, and a mixture of halo rings and Debye rings corresponding to the f.c.c.-type phase can be observed in the SAD pattern. The amorphous-to-crystal (A-C) transition in this amorphous phase seems to be overlapped with the C-A transition of the original C16-Zr2Ni intermetallic compound. The authors believe such an overlap behavior of C-A and A-C transitions during the C-A-C transition in intermetallic compounds under MeV electron irradiation has been observed here for the first time.

4. Discussion

An overlap behavior was observed at 298K, while such a behavior could not be observed at 103K during electron irradiation induced C-A-C transition in C16-Zr2Ni intermetallic compound. It is well known that the temperature dependence of electron irradiation induced crystallization shows the opposite tendency to that of amorphization [14]. Higher the irradiation temperature is, smaller the total dose required to induce the crystallization is. In contrast, the total dose for amorphization increases with increasing irradiation temperature. The overlap effect can be explained by the difference in the temperature dependence of required electron dose between amorphization and crystallization. Figure 6 shows a schematic illustration of the temperature dependence of the doses in a Zr66.7Ni33.3 alloy. At temperature indicated by A in Fig. 6, a C-A transition occurs under electron irradiation. At this temperature, the incubation time of the crystallization of an amorphous phase to the f.c.c.-type phase is long enough for amorphization to complete. Then, the crystallization starts after complete amorphization of the intermetallic compound. This case corresponds to the present experimental result at 103K. The incubation time of crystallization decreases with increasing irradiation temperature, while that of amorphization increases with increasing temperature. At temperature indicated by B, the amorphous phase obtained by the C-A transition of the intermetallic compound can immediately transform to the f.c.c.-type phase. The crystallization starts before complete amorphization under electron irradiation. Overlap effect during C-A-C transition at 298K in the present study may correspond to the condition indicated by B in Fig. 6.
5. Conclusion

(1) Overlap of amorphization (C-A) and crystallization (A-C) was observed in the C-A-C transition of C16-Zr2Ni intermetallic compound under 2.0MeV electron irradiation.

(2) The overlap behavior can be explained by the difference in the temperature dependence of electron dose required for amorphization and crystallization.

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