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In situ HVEM studies on the effects of electron-irradiation on the thermal stability of Ni-based amorphous alloys

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In situ high voltage electron microscope (HVEM) studies on the thermal stability of splat-cooled Ni-based amorphous alloys were made and three kinds of accelerated crystallization modes were observed during bombardment by focused 1000 keV electrons. In one case the crystalline grains induced by irradiation were coarser near the edge of the irradiated region (IR) than in other parts. This type of crystallization was observed in $Ni_{75}B_{17}Si_8$ and $Ni_{75}B_{15}Si_8C_2$ amorphous alloys subjected to a continuous increase in temperature of irradiation. The second case was one where there was no appreciable difference in size distribution of the crystalline grains throughout the IR. This type was observed in a $Ni_{80}P_{10}B_{10}$ amorphous alloy which again was subjected to a continuous increase in irradiation temperature and also observed in $Ni_{75}B_{17}Si_8$ amorphous alloy irradiated during isothermal annealing. In these two cases, the crystalline grains induced during irradiation did not cover the whole of the IR before crystallization started in the unirradiated region. In the third case, however, the amorphous phase completely disappeared from the IR before crystallization in the unirradiated region occurred. This type of crystallization was observed in $Ni_{80}P_{20}$ amorphous alloy whilst the temperature was being increased continuously during irradiation.

1. Introduction

As is well known, splat-cooling, i.e. rapid quenching from the melt, can produce various kinds of binary, ternary and multicomponent alloys without forming crystalline grains [1]. These so-called amorphous alloys exhibit some interesting physical, chemical and mechanical properties which are not observed in ordinary crystalline metallic materials. Since these properties are a result of the atomic arrangement, the thermal stability of the amorphous structure is very important for the practical use of amorphous materials. From this point of view, a large number of experimental studies have already been made on the crystallization of amorphous alloys of various kinds [2]. However, only a few dynamic observations have been performed using *in situ* high voltage electron microscopy to study the crystallization, and in particular, the effect of electron-irradiation on the crystallization [3–7].

The author's group [3–5] made experimental studies on the thermal stability of Fe–P, Fe–P–C, Ni–B–Si, Ni–P–C and Fe–B–Si amorphous alloys by using the *in situ* heating technique in a high voltage electron microscope (HVEM). Two types of irradiation effects from 400 keV electrons were found. One is the acceleration of crystallization, i.e. a deterioration in the thermal stability of the amorphous phase, and the other is the retardation of crystallization, i.e. an improvement in thermal stability due to electron-irradiation. These irradiation effects are considered to be closely related to the species of metal (Fe, Ni)–metalloid (B, C, Si, P) atom combination; in the case of Ni–B–Si and Fe–B–Si amorphous alloys an acceleration was observed, whereas in the case of Fe–P and Fe–P–C amorphous alloys a retardation was observed. Therefore, in the present experimental studies, the effects of electron-irradiation on the thermal stability of several kinds of splat-

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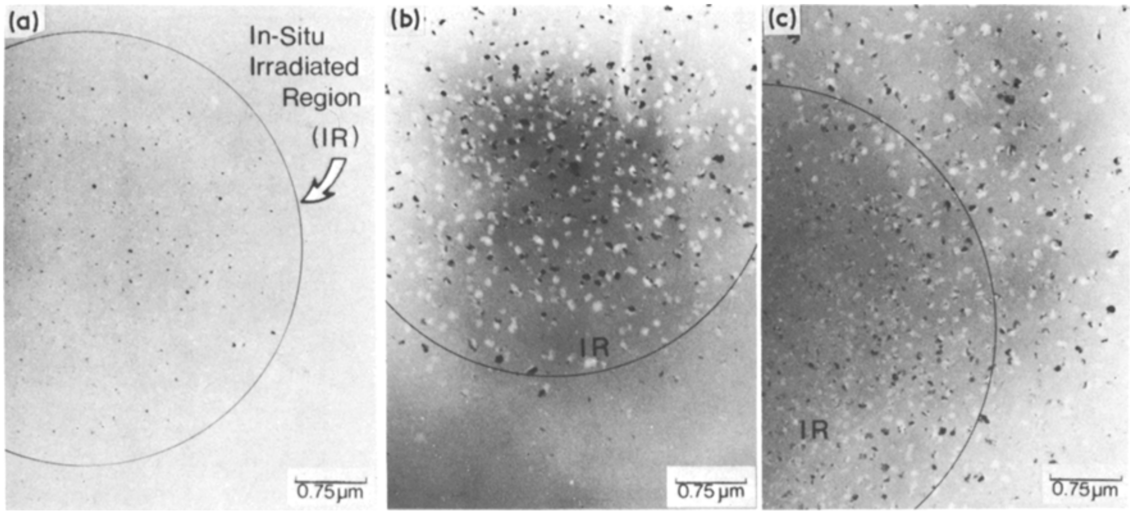

Figure 1 Crystallization processes of $Ni_{75}B_{17}Si_8$ amorphous alloy in the irradiated region (IR) marked by the circles: (a) crystalline grains appeared in the IR at 623 K, when the foil specimen was heated *in situ* at the rate of 0.1 K sec^{-1}; (b) irradiation during isothermal annealing at 663 K caused accelerated crystallization; (c) after further annealing at 663 K, crystalline grains appeared also in the unirradiated region, i.e. outside the region (IR) irradiated during *in situ* heating from room temperature to 663 K at the rate of 0.1 K sec^{-1}.

cooled Ni-based binary, ternary and multicomponent amorphous alloys have been investigated in detail by means of *in situ* high voltage electron microscopy.

2. Experimental procedures

$Ni_{75}B_{17}Si_8$, $Ni_{75}B_{15}Si_8C_2$, $Ni_{80}P_{10}B_{10}$ and $Ni_{80}P_{20}$ alloys* were rapidly quenched from the melt (splat-cooled) in argon at atmospheric pressure by using a roller-quenching technique (twin-roll method). The rotation speed of the twin rollers of 50 mm diameter which were made of carbon tool steel, was either 4500 or 4950 rpm. The amorphous ribbon samples thus obtained were between 1 and 1.5 mm in breadth and between 0.015 and 0.030 mm in thickness. Thin foil specimens used for HVEM observations were prepared by electropolishing the splat-cooled ribbon samples either in a solution of H_3PO_4 saturated with CrO_3 at room temperature or in a solution of $HClO_4$ (1 part) and C_2H_5OH (9 parts) at about 240 K.

As regards electron-irradiation, the irradiation of focused 1000 keV electrons was performed during either of two different *in situ* heat treatments in the HVEM as follows; in one case, the temperature was continuously increased from room temperature at the rate of 0.1 K sec^{-1}, and in the other case the temperature was kept constant at a certain value. The temperature at which crystalline grains appeared in the unirradiated region during the former heat treatment is designated as the crystallization temperature T_c. However, during isothermal annealing (the latter case) at a temperature which was not as high as T_c, crystalline grains appeared in the unirradiated region when the annealing time exceeded a certain value t_c, although t_c depended on the annealing temperature.

The dose rates were 2.6×10^{23} or 2.7×10^{23} e m^{-2} sec^{-1} throughout the above-mentioned irradiations. HVEM observations and photographs were also made at an accelerating voltage of 1000 kV but the dose rate was reduced to less than one third (about 0.7×10^{23} e m^{-2} sec^{-1}) of the aforementioned value.

3. Experimental results

3.1. Ni–B–Si amorphous alloy

When a foil specimen of $Ni_{75}B_{17}Si_8$ amorphous alloy was heated *in situ* at 0.1 K sec^{-1} in the HVEM during irradiation by focused 1000 keV electrons, fine crystalline grains appeared only in the irradiated region (IR) before the temperature reached 600 K. At 623 K, the nucleation and growth of the crystalline grains proceeded progressively in the IR, as indicated by the IR circle in Fig. 1a. Judging from the diffraction patterns and their appearance, the fine crystalline grains

*The subscripts of each element indicate the atomic percentage.

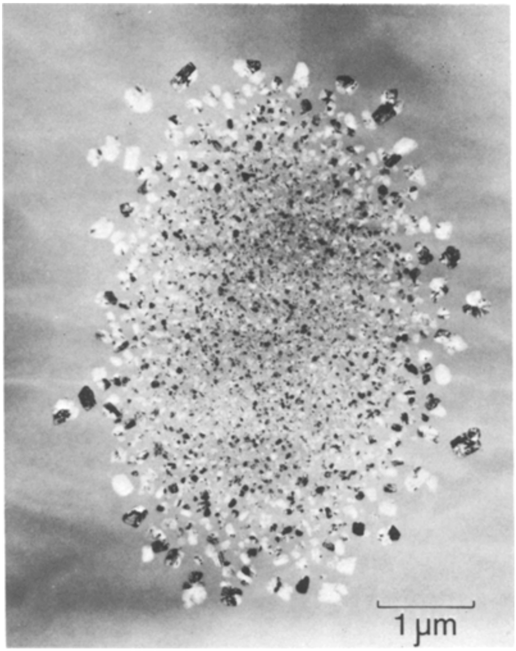

Figure 2 Transmission electron micrograph indicating the accelerated crystallization of $Ni_{75}B_{15}Si_8C_2$ amorphous alloy (this micrograph was taken at 633 K). When the temperature was increased from room temperature to 633 K during *in situ* electron-irradiation, crystalline grains appeared in the IR only. Grains near the centre of the IR were numerous and much finer than those near the edge.

had an fcc structure and corresponded to the metastable crystalline phase I (so-called MS–I reported by Masumoto, Inoue and Kimura [8]). This MS–I phase is considered to be a solid solution of metalloid atoms in crystalline Ni, i.e. Ni-base α solid solution, but the precise composition of the MS–I phase and the compositional change of this phase during growth were not determined in the present experiments*.

Fig. 1b illustrates the effect of electron-irradiation during the isothermal annealing of a $Ni_{75}B_{17}Si_8$ amorphous alloy at 663 K. In this case, crystalline grains (MS–I) appeared also in the region irradiated for 600 sec (which was less than t_c) by focused 1000 keV electrons. After annealing at 663 K for a longer period than t_c, the crystalline grains (MS–I) appeared also in the unirradiated region, as illustrated in Fig. 1c (in this figure, the IR circle denotes the region irradiated by electrons during the *in situ* heating from room temperature to 663 K at the rate of 0.1 K sec^{-1}). The grains which appeared in the unirradiated region (outside the IR) were coarser than those near the centre of the IR. Furthermore, obvious differences in size distributions were not recognized between the grains which were induced by the irradiation during isothermal annealing at 663 K and the grains which appeared in the unirradiated region during annealing at the same temperature (compare Fig. 1b with Fig. 1c).

Fig. 2 illustrates the effect of electron-irradiation on the crystallization process of a splat-cooled Ni–B–Si–C amorphous alloy in which a part of the boron content in the $Ni_{75}B_{17}Si_8$ alloy is substituted by carbon. When a foil specimen of this $Ni_{75}B_{15}Si_8C_2$ amorphous alloy was heated *in situ* at 0.1 K sec^{-1} in the HVEM during irradiation by focused 1000 keV electrons, crystalline phase (MS–I) appeared first in the IR below 573 K. Further heating was done in steps (20 K every 300 sec), and nucleation and growth of MS–I occurred only in the IR. At 633 K, the MS–I grains near the centre of the IR were numerous and much finer than those near the edge, as shown in Fig. 2.

Figs. 3, 4 and 5 illustrate the effect of electron-irradiation on the crystallization process of $Ni_{75}B_{17}Si_8$ amorphous alloy which was, at first, partially crystallized by *in situ* annealing at 663 K and then irradiated at 663 K (Figs. 3a and b), 703 K (Fig. 4) and 723 K (Fig. 5) so that MS–I grains were present before and after irradiation. At 663 K, fine crystalline grains of MS–I appeared in the amorphous matrix inside the IR as indicated by bold arrows in Fig. 3. At 703 K, the same process continued but the number and size of crystalline grains which appeared during irradiation were larger. The electron-irradiation at both temperatures (i.e. 663 and 703 K), however did not have any remarkable effect on the size of MS–I grains which appeared before irradiation.

The asterisk indicated by an arrow on each micrograph of Fig. 3 shows the same location in the foil. The number of detectable fine grains which appeared during irradiation and the isothermal annealing at 663 K, was not large (cf. Fig. 3b). In this irradiated region, however, a large

*Herold and Köster [9], and von Heimendahl and Maussner [10, 11] have shown that when some amorphous alloys transform to the stable crystalline state by passing through the intermediate stages where metastable crystalline phases appear, the compositional change of the metastable crystalline phase, e.g. the decrease in metalloid content of MS–I phase, occurs during growth.

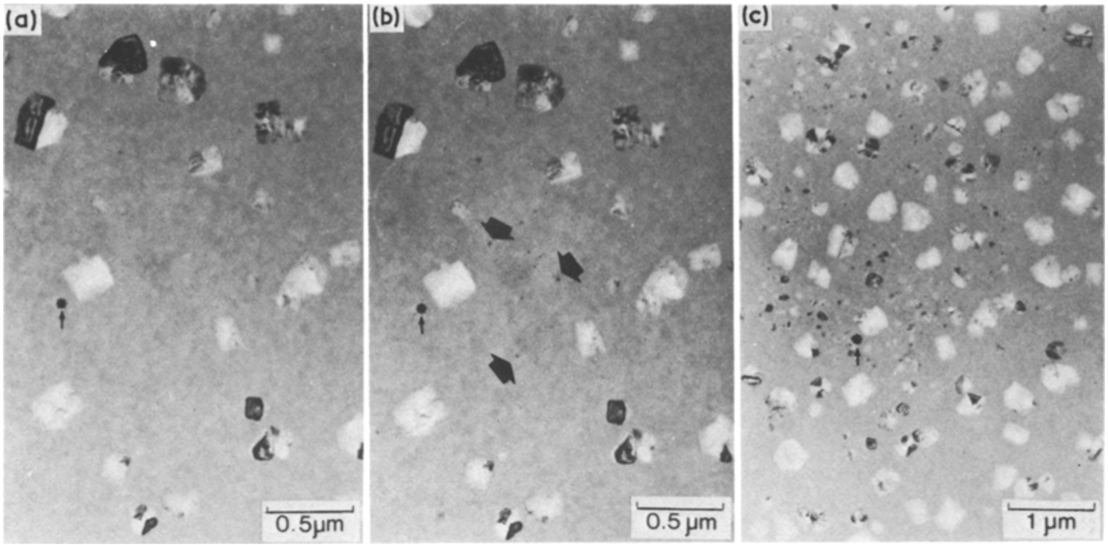

Figure 3 Crystallization stages of partially crystallized $Ni_{75}B_{17}Si_8$ amorphous alloy during irradiation at 663 K: (a) irradiated for 120 sec; (b) irradiated for 240 sec; (c) irradiated for 240 sec and annealed at 703 K for 980 sec. Small crystalline grains appeared in the irradiated region as indicated by bold arrows in (b). Many crystalline grains came into view during annealing (c). The asterisk pointed by an arrow on each micrograph indicates the same location.

number of grains appeared during annealing at a higher temperature without irradiation (i.e. 703 K), as illustrated in Fig. 3c.

At 723 K, the nucleation and growth of MS–I grains were no longer observed but a new type of crystalline phase appeared both in the IR and in the unirradiated region, as indicated by white arrows in Fig. 5b. This type of crystalline phase corresponds to the metastable crystalline phase II (so-called "MS–II" reported by Masumoto *et al.* [8]). An obvious difference between the nucleation and growth of MS–II grains in the IR and those in the unirradiated region was not observed. Even at such high temperatures where the MS–II phase appeared, the electron-irradiation induced nucleation of MS–I in the amorphous matrix inside the IR, as indicated by bold arrows in Fig. 5b.

3.2. Ni–P–B amorphous alloy

When *in situ* continuous heating of splat-cooled $Ni_{80}P_{10}B_{10}$ amorphous alloy was made under the irradiation of focused 1000 keV electrons, fine crystalline grains (hereinafter called the "F-grain")

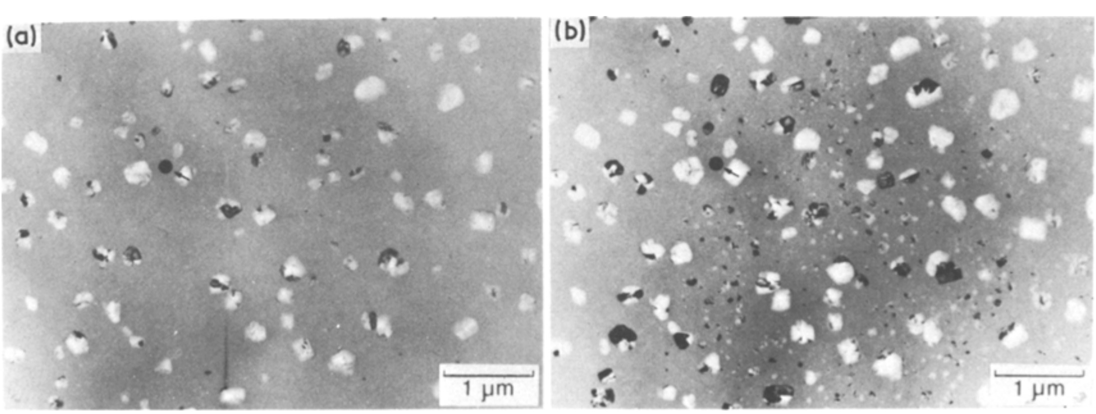

Figure 4 Crystallization stages of partially crystallized $Ni_{75}B_{17}Si_8$ amorphous alloy during irradiation at 703 K. Many crystalline grains appeared in the irradiated region. The full circle pointed by an arrow on each micrograph indicates the same location.

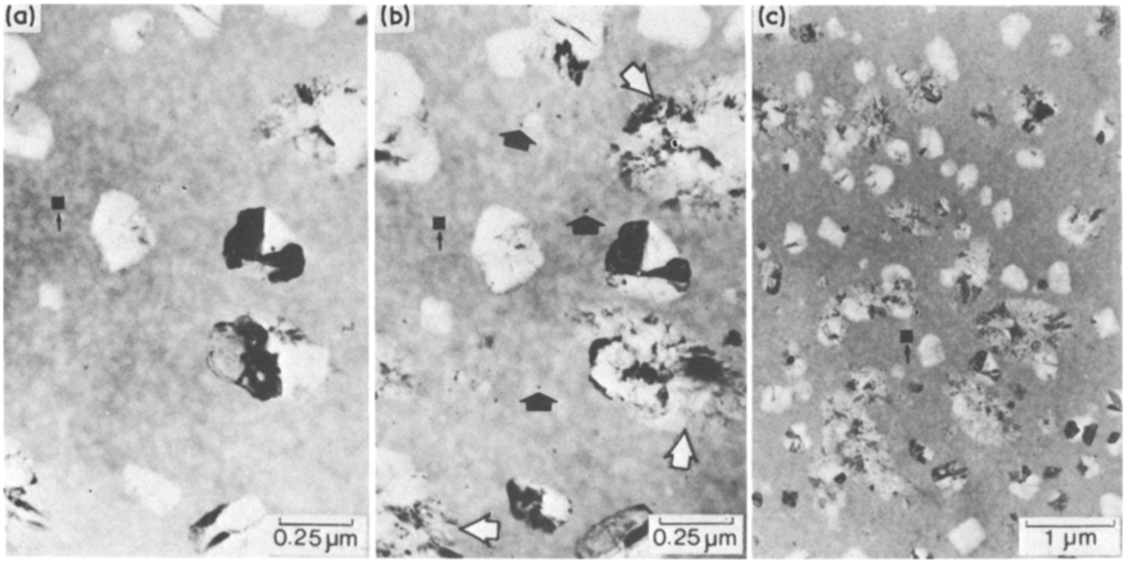

Figure 5 Nucleation of crystalline grains occurred in partially crystallized $Ni_{75}B_{17}Si_8$ amorphous alloy during irradiation at 723 K, as indicated by bold arrows. The second type of crystalline phase indicated by white arrows also appeared throughout the foil specimen at 723 K. The full square pointed by an arrow on each micrograph indicates the same location.

appeared first in the IR at a temperature of 623 K, as illustrated in Fig. 6a. According to the diffraction analysis, these F-grains had an f c c structure and were considered to be a solid solution of metalloid atoms in crystalline Ni. At 645 K, F-grains appeared also in the unirradiated region, as illustrated in Fig. 6b. The size of F-grains near the edge of the IR did not differ appreciably from that near the centre of the IR.

Whilst irradiating the foil during isothermal annealing at 668 K (in this case, the electron beam was focused on the same area as the irradiated area mentioned before), a change in the electron micrograph of the IR was seen, as shown in Fig. 6c, and new diffraction spots appeared in addition to those from F-grains.

In the unirradiated region, the second type of new crystalline grains (hereinafter called the "S-grain") appeared in places during further annealing at 668 K, as indicated by white arrows

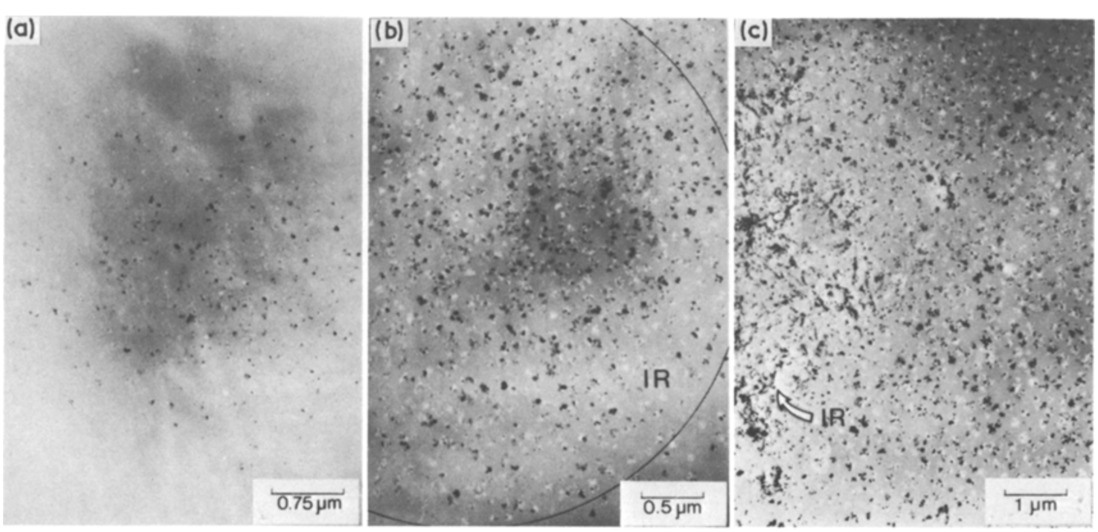

Figure 6 Crystallization stages of $Ni_{80}P_{10}B_{10}$ amorphous alloy: (a) 623 K; (b) 645 K; (c) 668 K. Crystallization was accelerated by electron-irradiation.

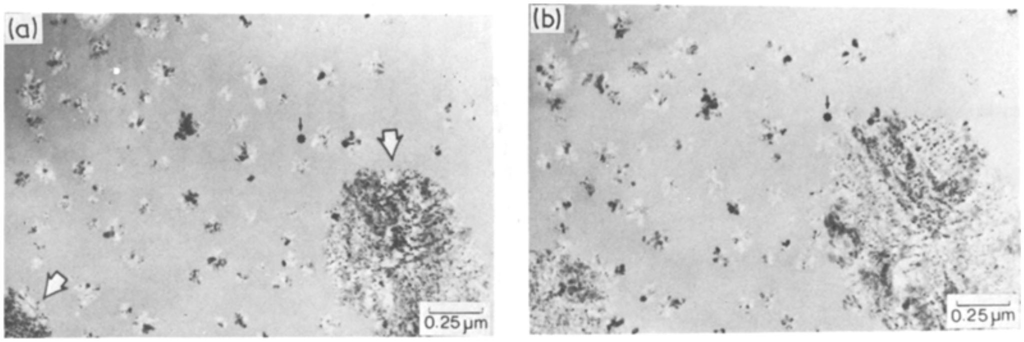

Figure 7 Crystallization stages of $Ni_{80}P_{10}B_{10}$ amorphous alloy during isothermal annealing at 668 K without irradiation. The difference in time between (a) and (b) was 600 sec. The asterisk pointed by an arrow on each micrograph indicates the same location.

in Fig. 7a. These S-grains grew faster and became much coarser than F-grains during isothermal annealing at 668 K without irradiation.

3.3. Ni–P amorphous alloy

When *in situ* continuous heating of splat-cooled $Ni_{80}P_{20}$ amorphous alloy was carried out at temperatures up to 645 K under the irradiation of focused 1000 keV electrons, crystallization occurred only in the IR, as shown in Fig. 8a. In this case, however, the crystalline grains which appeared during irradiation were not dispersed in the amorphous matrix, but were in contact with each other covering most parts of the IR. Therefore, the boundary between the crystallized region and the uncrystallized region was very clear as shown in Fig. 8b. Judging from the selected area diffraction patterns, the crystallized region consisted of an aggregate of Ni (maybe α solid solution of Ni) and Ni_3P phases.

4. Discussions

In all the splat-cooled Ni-based amorphous alloys used in the present experiments, irradiation by focused 1000 keV electrons caused accelerated crystallization. Detailed examination of the results, however, suggests that the accelerated crystallization process follows one of three modes, as illustrated in Fig. 9. Type 1 is the case in which crystalline grains near the edge of the IR are coarser than those near the centre of the IR. This type was observed in the Ni–B–Si and

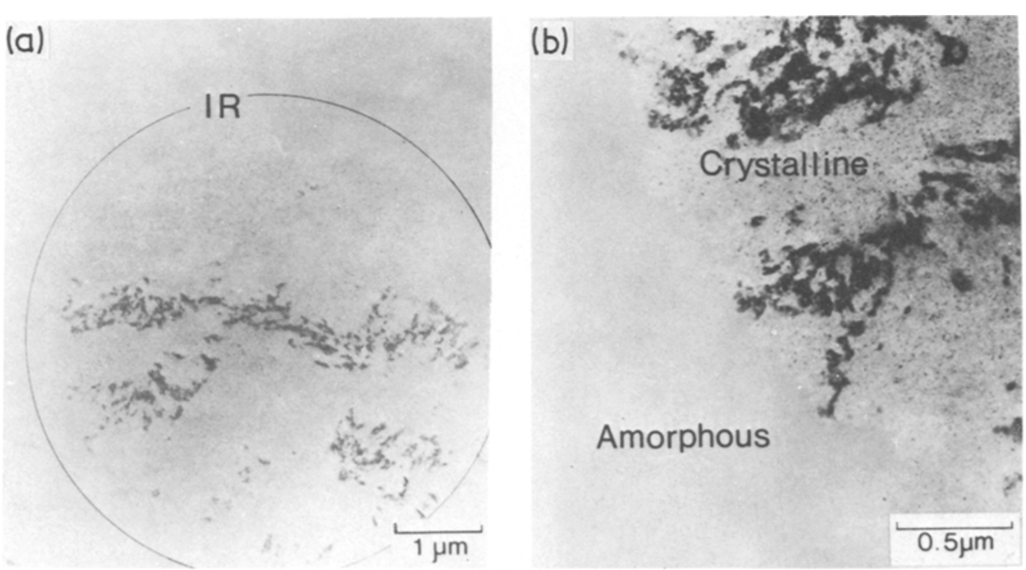

Figure 8 Accelerated crystallization by electron-irradiation as observed in $Ni_{80}P_{20}$ amorphous alloy during *in situ* heating to 645 K.

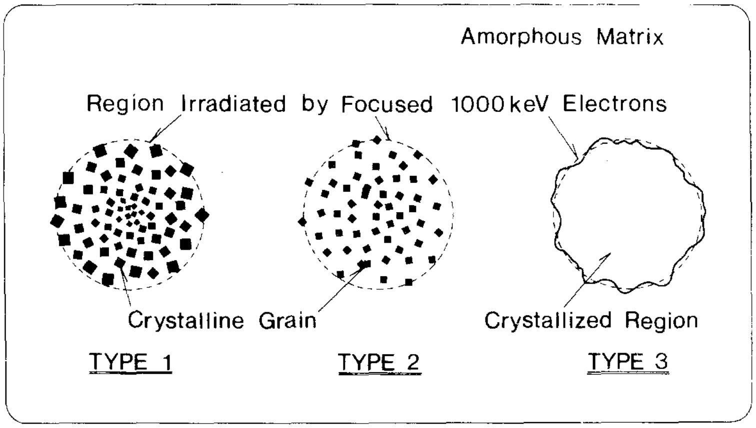

Figure 9 Schematic drawing showing the three types of accelerated crystallization observed in the present experimental studies.

Ni–B–Si–C amorphous alloys (e.g. Figs. 1c and 2). Whilst in the case of Type 2, the crystalline grains near the centre of the IR are not significantly different from those near the edge of the IR. This type was observed in the Ni–P–B amorphous alloy (cf. Fig. 6) and also in the Ni–B–Si amorphous alloy which had been irradiated during isothermal annealing slightly below T_c (cf. Fig. 1b).

In both cases mentioned above, i.e. Type 1 and Type 2, the crystalline grains induced by the electron-irradiation are dispersed in the amorphous matrix. In contrast with this, Type 3 is the case in which the crystalline grains induced by irradiation are in contact with each other. Hence, the whole of the IR transforms completely to the crystalline state before the crystalline phase appears in the unirradiated region. This type was observed in the Ni–P amorphous alloy (cf. Fig. 8).

As shown in Figs. 3 and 4, when a partially crystallized Ni–B–Si amorphous alloy is irradiated by electrons, MS–I grains which appear before irradiation do not grow appreciably but fine crystalline grains of MS–I appear at new sites in the amorphous matrix within the IR. This fact suggests that the electron-irradiation has a tendency to induce nucleation of a crystalline phase rather than promote growth of existing grains. In addition to this, even when the irradiation was made at high temperatures so that the nucleation and growth of MS–II took place, only MS–I grains appeared at new sites and nucleation of new MS–II grains did not occur, as illustrated in Fig. 5. Therefore, it is obvious that the electron-irradiation induces the nucleation of MS–I.

According to the electron micrographs of Figs. 1c and 2, it seems probable that the number of nuclei induced by the electron-irradiation near the centre of the IR is much larger than that near the edge and the former can grow only into much finer grains than the latter because of mutual interference (Type 1 accelerated crystallization). Compared with this result, it is interesting that the electron-irradiation of the Ni–B–Si amorphous alloy at a higher temperature caused Type 2 accelerated crystallization (cf. Fig. 1b). This fact suggests that because of an improvement in diffusivity due to the increased temperature, the growth of crystalline grains proceeds rapidly whilst the number of nuclei induced near the centre of the IR is not very large in the early stages of electron-irradiation.

In the case of Ni–P binary amorphous alloy, Type 3 accelerated crystallization occurred during irradiation. This $Ni_{80}P_{20}$ amorphous alloy has no intermediate stage of crystallization but directly transforms to a stable crystalline state, i.e. forming Ni (α solid solution of Ni) and Ni_3P phases (a similar observation was reported by other investigators [12]). Hence it is probable (see Fig. 8) that the nuclei of Ni_3P as well as those of Ni are formed at about the same time during irradiation as the nuclei of the Ni phase are formed. The excess P atoms must be emitted into the matrix and hence the area surrounding the Ni phase becomes a favourable region for forming the Ni_3P phase.

5. Conclusions

(1) In the case of all the splat-cooled Ni-based amorphous alloys used in the present experimental studies, the irradiation by focused 1000 keV electrons caused accelerated crystallization, i.e. a deterioration in the thermal stability of the amorphous state.

(2) When *in situ* heatings of $Ni_{75}B_{17}Si_8$ and $Ni_{75}B_{15}Si_8C_2$ amorphous alloys are made at the

rate of 0.1 K sec^{-1} under the irradiation of focused 1000 keV electrons, crystalline grains appear in the irradiated region (IR) first. The crystalline grains near the edge of the IR are coarser than those in other parts of the IR.

(3) When irradiation by focused 1000 keV electrons is made during isothermal annealing at a temperature slightly below the crystallization temperature (T_c) for the unirradiated amorphous matrix, crystalline grains appear first in the IR. There is no appreciable difference in the size distribution of crystalline grains induced by irradiation in the IR. A similar effect is observed also in the case of $Ni_{80}P_{10}B_{10}$ amorphous alloy being irradiated during *in situ* continuous heating at a rate of 0.1 K sec^{-1}.

(4) In the case of $Ni_{80}P_{20}$ amorphous alloy, the crystalline grains induced by irradiation grow to such a size that almost the whole of the IR transforms to the crystalline state before the unirradiated region transforms.

(5) Electron-irradiation is able to nucleate crystalline grains but has no appreciable effect on the growth of crystalline grains.

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