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Ar^{+}-ion-irradiation-induced phase transformation in an $Al_{62}Cu_{25.5}Fe_{12.5}$ icosahedral quasicrystal

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Abstract. In this paper, the 120 keV Ar^{+}-ion-irradiation-induced phase transformation from the $Al_{62}Cu_{25.5}Fe_{12.5}$ icosahedral quasicrystal (IQC) to B2(CsCl)-based phases has been studied by means of transmission electron microscopy. The dose dependence of the Ar^{+} ion irradiation effect and the subsequent *in-situ* heating and cooling behaviours after irradiation have been investigated. The experimental results show that the Ar^{+}-irradiation-enhanced diffusion can accelerate the transformation from the $Al_{62}Cu_{25.5}Fe_{12.5}$ IQC to a B2-type or B2-based phase at room temperature and that this B2 or B2-based phase transforms reversely to the IQC when the Ar^{+} dose is equal to or lower than 10^{14} Ar^{+} cm^{-2} and the temperature is increased to about 1000 K.

1. Introduction

Bradley and Goldschmidt (1939) studied the Al–Cu–Fe ternary system and found 'a complex phase with undetermined structure' close to the composition $Al_{65}Cu_{23}Fe_{12}$ which corresponds to the recently discovered Al–Cu–Fe icosahedral quasicrystal (IQC) (Tsai *et al* 1987). Faudot *et al* (1991), Bancel (1991) and Gratias *et al* (1993) studied systematically the Al–Cu–Fe ternary phase diagram around the IQC region. According to these studies, Bancel (1991) pointed out that the IQC is stable in the temperature range 500–870 °C. The IQC field is largest near the onset of peritectic melting at 740 °C. At lower temperatures the IQC field contracts. Extrapolating such a contraction to below 500 °C suggests that the IQC should completely disappear by 400 °C. Nevertheless, as reported by Gratias *et al* (1993), the IQC of a composition near the concentration line $Al_{62}Cu_{25.5}Fe_{12.5}$–$Al_{62.6}Cu_{24.4}Fe_{13}$ does not transform even after annealing for 5d at 400 °C. Because of the sluggish atomic diffusion at low temperatures, such a thermal annealing experiment cannot determine the stability of the IQC at lower temperatures.

It is well known (Gittus 1978, Nolfi 1983) that high-energy particle irradiation produces lattice vacancies and interstitial atoms and hence accelerates diffusion. The irradiation-enhanced diffusion can in turn accelerate phase transformations at low temperatures. Applying this idea to the quasicrystals, Wang *et al* (1992, 1993) studied phase transformations in $Al_{76}Si_4Mn_{20}$ IQCs induced by 120 keV Ar^{+} ion irradiation. Zhang and Urban (1992) studied the phase transformation of the decagonal quasicrystals (DQCs) to a B2(CsCl)-type crystalline phase induced by 400 keV electron irradiation.

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We have irradiated an $Al_{62}Cu_{25.5}Fe_{12.5}$ perfect IQC at room temperature with 120 keV Ar^+ ions to different doses to accelerate the possible phase transformations. The present paper reports the main results on the Ar^+-irradiation-induced transformation from the IQC to the B2-type phase and the subsequent transformation behaviour during *in-situ* heating and cooling in a transmission electron microscope.

2. Experimental details

The alloy of composition $Al_{62}Cu_{25.5}Fe_{12.5}$ was prepared by melting the high-purity elements in an induction furnace under an Ar atmosphere. The ingot was annealed at 1095 K for 47.2 h, cooled during a period of 30 h to room temperature and then cut into slices of 3 mm diameter. A synchrotron radiation topography study (Zou *et al* 1993) showed that these slices are perfect IQCs with very large grains ranging from 0.1 to 3 mm in diameter. Foils for transmission electron microscopy (TEM) were prepared by mechanical thinning and Ar^+ ion milling. Foils were examined first by TEM and then irradiated at room temperature with Ar^+ ions of 120 keV energy to doses of 10^{11}, 10^{12}, 10^{13}, 10^{14}, 10^{15}, 4×10^{15}, 10^{16} or 5×10^{16} Ar^+ cm^{-2}. The irradiated foils were observed by TEM systematically at room temperature and then *in situ* heated and observed by TEM.

TEM observations were carried out in Philips EM-420 and Jeol JEM 100CX(II) electron microscopes. An *in-situ* heating experiment was carried out in a 100CX(II) microscope equipped with a double-tilting heating stage. The applied acceleration voltage of these microscopes is 100 kV.

A theoretical calculation shows that the projected range is 74.8 nm with 29.6 nm longitudinal straggling and 30.0 nm lateral straggling when the $Al_{62}Cu_{25.5}Fe_{12.5}$ alloy is bombarded with 120 keV Ar^+ ions. The projected range of the Ar^+ ion is comparable with the observable thickness for electrons of 100 keV energy.

3. Results

3.1. Ar^+-irradiation-induced phase transformation from the icosahedral quasicrystal to the B2-based phase

An electron diffraction experiment showed that the original TEM foils were perfect IQCs with such large grains that the whole thin region of a foil belongs to a single grain. When irradiated with 120 keV Ar^+ ions to a sufficiently high dose, the IQC transformed to a B2-type crystalline phase. Figure 1 shows a series of electron diffraction patterns (EDPs) when both IQC and B2 phases coexist. Such EDPs reveal the orientational relationship between the IQC and the B2 phase to be as follows:

$$\begin{aligned} &\mathrm{A5(IQC)} \parallel [110]\mathrm{(B2)} \\ &\mathrm{A2(IQC)} \parallel [11\bar{1}]\mathrm{(B2)}. \end{aligned} \tag{1}$$

Figure 2 illustrates this relationship by means of two stereographic projection diagrams for the IQC (figure 2(*a*)) and the B2 phase (figure 2(*b*)) which are parallel to each other. All our experimental observations are consistent with such a relationship. For example, according to (1) and figure 2, the A5 axis of the IQC should also be parallel to the $\langle 113 \rangle$ axis of the B2 phase, the A3 (IQC) axis parallel to $\langle 111 \rangle$ (B2), $\langle 123 \rangle$ (B2) or $\langle 115 \rangle$ (B2), the A2 IQC

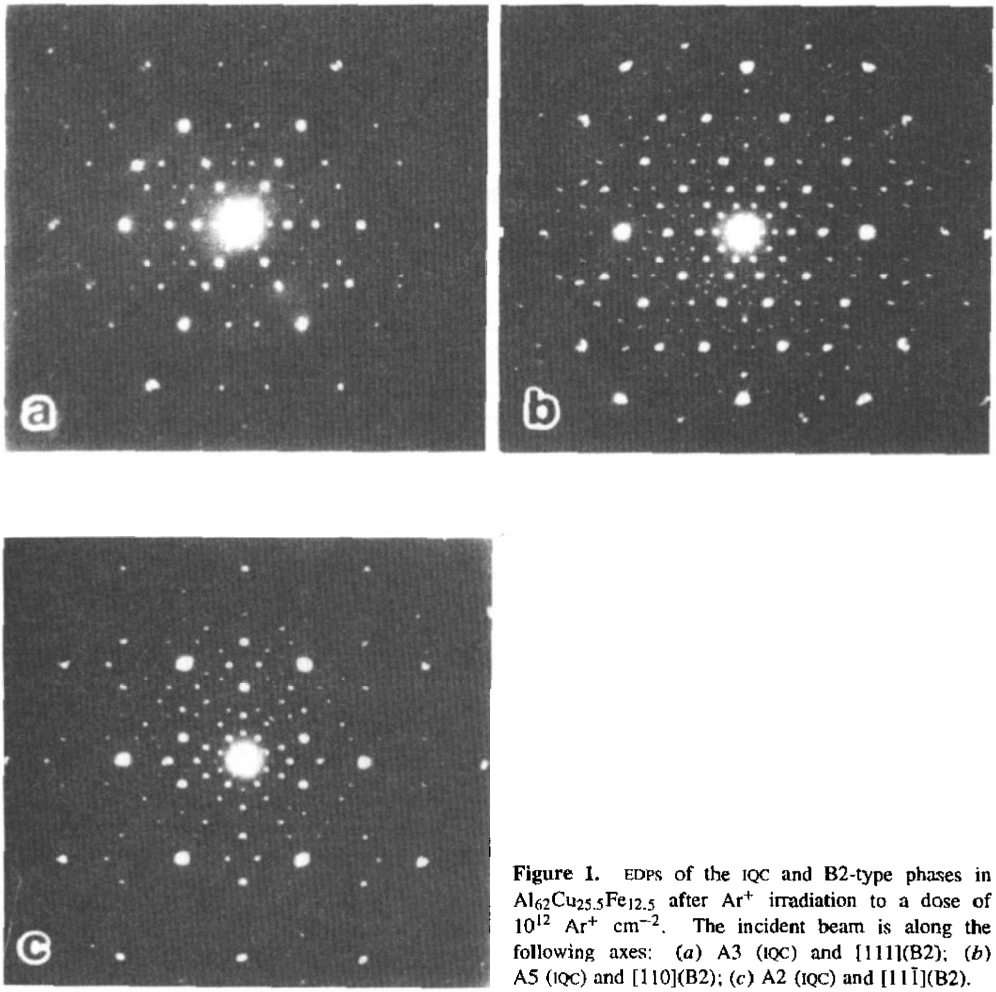

Figure 1. EDPs of the IQC and B2-type phases in $Al_{62}Cu_{25.5}Fe_{12.5}$ after Ar^+ irradiation to a dose of 10^{12} Ar^+ cm^{-2}. The incident beam is along the following axes: (*a*) A3 (IQC) and [111](B2); (*b*) A5 (IQC) and [110](B2); (*c*) A2 (IQC) and $[11\bar{1}]$(B2).

axis parallel to ⟨110⟩ (B2), ⟨112⟩ (B2) or ⟨113⟩ (B2) and the A2P axis of the IQC shown in figure 2(*a*) should be parallel to ⟨001⟩ (B2), ⟨112⟩ (B2) or ⟨221⟩ (B2). Figure 3 shows an example of this type consisting of five ⟨113⟩ (B2) EDPs with a fivefold symmetry.

In the Ar^+-irradiated TEM foils, in addition to the B2-type structure phase, there is another phase whose strong diffraction spots coincide with those of the B2 phase but with many more medium and weak superreflections. Following Zhang and Li (1990) we call it the B2-based phase.

3.2. Dose dependence of the Ar^+ ion irradiation effect

The Ar^+ ion irradiation effect is dose dependent. When the dose is very low (10^{12} Ar^+ cm^{-2}), only a small amount of the IQC transforms to the B2-based phase. On increase in the Ar^+ dose, the amount of B2-based phase transformed from the IQC increases. When the dose is equal to or higher than 10^{13} Ar^+ cm^{-2}, almost all the thin regions transparent to the electron beam of 100 keV energy transform to the B2-based and B2-type phases. This dose effect is shown in figure 4 where figure 4(*a*) is the EDP of the

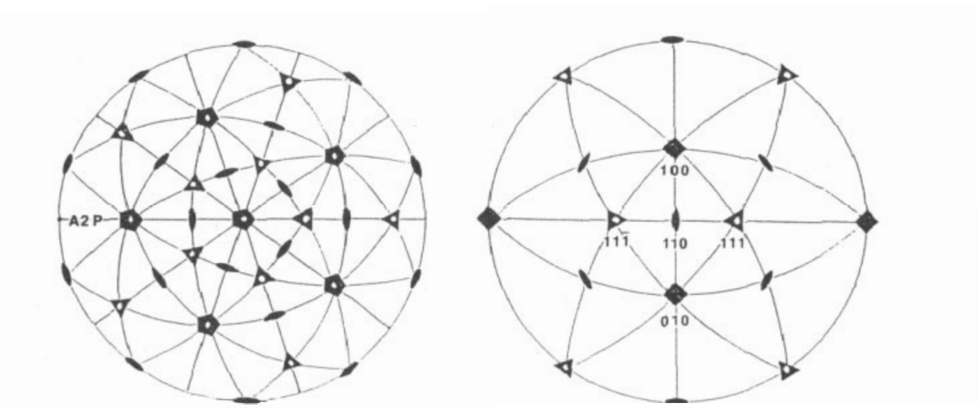

Figure 2. Stereographic projection diagram showing the orientational relationship between the IQC and B2-type phases.

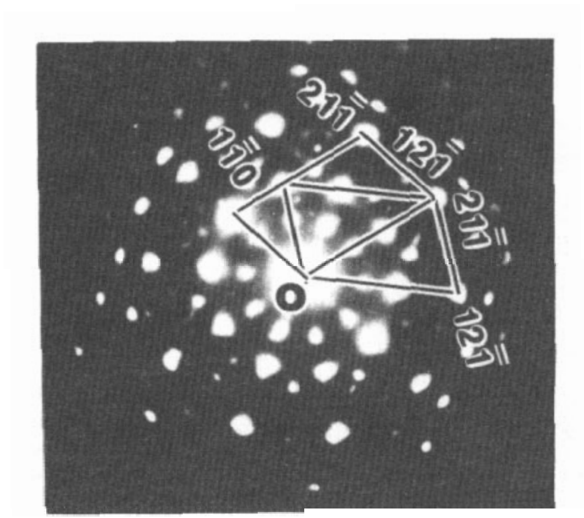

Figure 3. EDP of $Al_{62}Cu_{25.5}Fe_{12.5}$ along the A5 axis of the IQC. This EDP consists of five $\langle 113 \rangle$ (B2) EDPs distributed with fivefold symmetry.

A2P (IQC) axis for the lowest dose (10^{11} Ar^+ cm^{-2}). When the dose is equal to or higher than 10^{13} Ar^+ cm^{-2}, the characteristic diffraction spots for the A2P axis of the IQC disappear and are replaced by those of the [001](B2) EDP (see figures 4(*b*)–4(*d*)). Moreover, when the Ar^+ dose increases, the diffraction spots become increasingly broader along the tangential direction (figures 4(*c*) and 4(*d*)) and even some weak diffraction rings appear when the dose is rather high (10^{16} Ar^+ cm^{-2}). This indicates that the size of the coherent regions decreases and the misorientation of these regions increases with increasing Ar^+ dose.

3.3. In-situ heating observation

Figure 5 shows the main result of the *in-situ* heating experiment of the TEM foil irradiated to a dose of 10^{14} Ar^+ cm^{-2}. Figures 5(*a*), 5(*c*) and 5(*e*) are bright-field (BF) images of a typical region which may be divided into the following three parts with different thicknesses: part A is a thin region, part C a thick region and part B in between. When the temperature

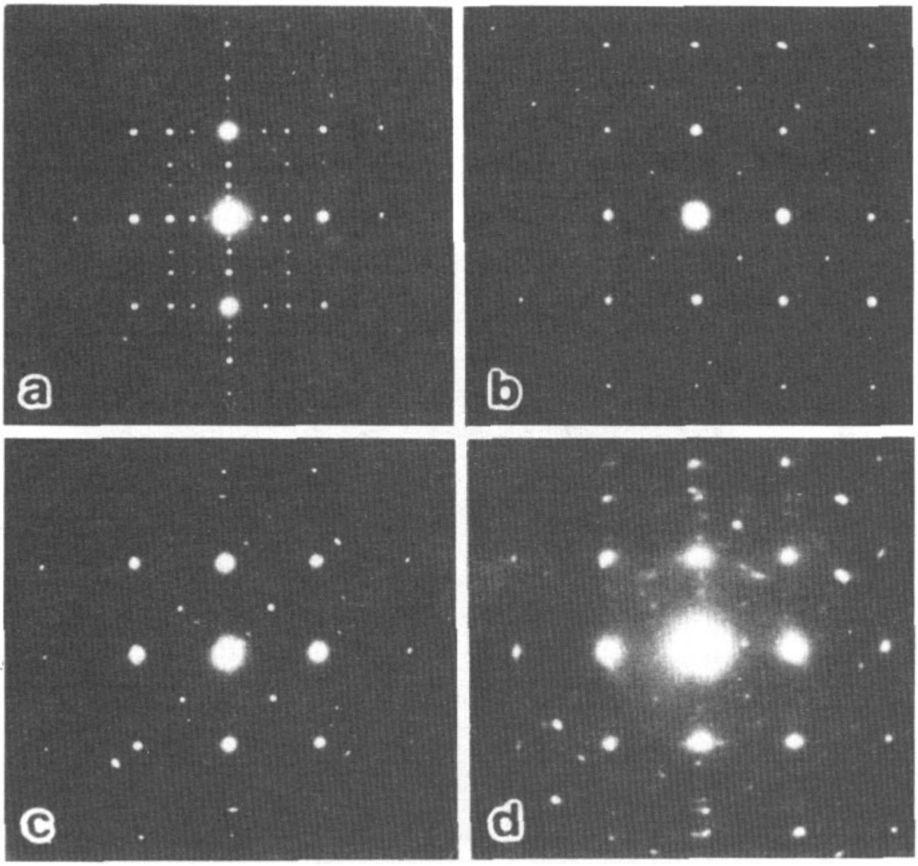

Figure 4. EDPS along the A2P (IQC) and [001](B2) axes of $Al_{62}Cu_{25.5}Fe_{12.5}$ irradiated to the following doses: (*a*) 10^{11} Ar^+ cm^{-2}; (*b*) 10^{13} Ar^+ cm^{-2}; (*c*) 10^{15} Ar^+ cm^{-2}; (*d*) 10^{16} Ar^+ cm^{-2}.

was lower than 880 K, the three regions were all B2 phase and had the same orientation. For example, figures 5(*a*) and 5(*b*) show their BF image and EDP along the $[11\bar{1}]$(B2) axis, respectively, before heating. When the foil was heated to 880 K, the whole thick region C and part of the region B transformed rapidly to an IQC with the orientation relationship (1).

After the transformation from a B2 phase to an IQC had been completed in the thick region C, the current of the heating stage was turned off and the foil cooled to room temperature. An electron diffraction experiment revealed that the thick region did not transform to the B2-type phase but remained an IQC.

Figures 5(*c*) and 5(*d*) show the BF image and EDP, respectively, when the foil was reheated to 1000 K at the same orientation as in figures 5(*a*) and 5(*b*). The EDP shown in figure 5(*d*) is along the A2 (IQC) axis.

When the foil was heated to 1080 K, the IQC transformed suddenly to a B2 phase as shown in figure 5(*e*) and 5(*f*) which are the BF image and corresponding EDP along the $[11\bar{1}]$(B2) axis. After heating to 1130 K, the foil was cooled slowly and held at 970 K for 30 min to observe the possible reverse B2→IQC transformation and then cooled to room temperature. During this cooling process the B2 phase did not transform to the IQC but

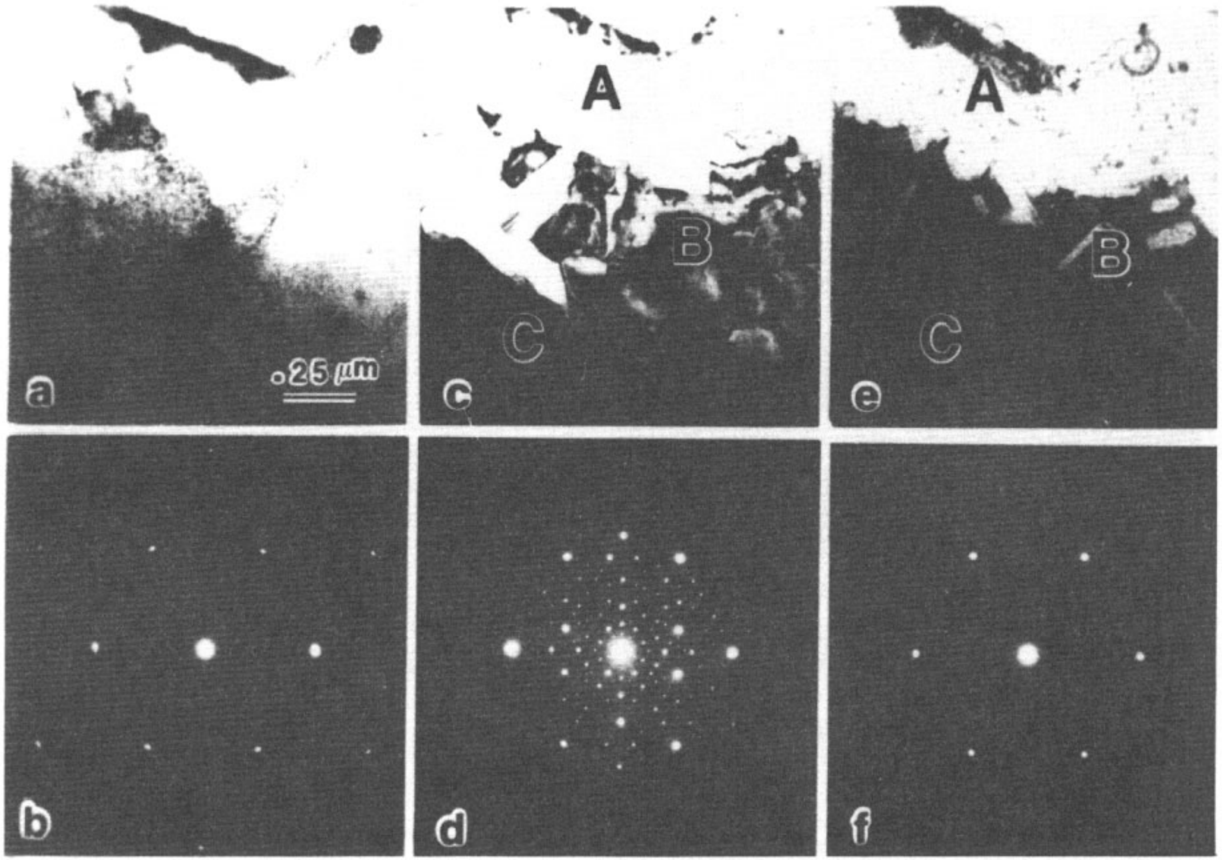

Figure 5. (*a*), (*c*), (*e*) BF images and (*b*), (*d*), (*f*) EDPs along the A2 (IQC) and [11$\bar{1}$](B2) axes showing the phase transformation during heating (*a*), (*b*) irradiated to a dose of 10^{14} Ar^+ cm^{-2}; (*c*), (*d*) as above, and then heated to 1000 K; (*e*), (*f*) as above, and then heated to 1080 K.

remained B2 phase.

During the heating process the thin region A and the other part of region B remained B2 phase irrespective of the phase transformation in the thick region.

We have heated other TEM foils irradiated with 120 keV Ar^+ ions to different doses. The B2-based phase in the foil irradiated with 10^{12} Ar^+ cm^{-2} transformed suddenly to an IQC when the temperature was raised to 930 K and then transformed to unidentified phases with very small grains (100 nm) and large misorientation when the temperature was increased further to 1120 K. When the dose is equal to or higher than 10^{15} Ar^+ cm^{-2}, the irradiation-induced B2 or B2-based phase did not transform to an IQC during heating.

4. Discussion

Zhang and Li (1990) determined the orientational relationship between the IQC and its surface B2-based phase. The orientational relationship (1) between the IQC and the B2-type phase, which is induced by 120 keV Ar^+ ion irradiation from the $Al_{62}Cu_{25.5}Fe_{12.5}$ IQC in the present work, is the same. As it is suggested that the surface B2-based phase is formed during TEM foil preparation by Ar^+ ion milling, this coincidence is not surprising. Zhang and Geng (1992) attributed the formation of the surface B2-type phase to the preferential etching of the Al atoms. According to the vertical section of the Al–Cu–Fe ternary phase diagram in the range of compositions between $Al_{70}Cu_{20}Fe_{10}$ and $Al_{58}Cu_{28}Fe_{14}$ as determined by Faudot *et al* (1991), a single-B2-phase region would occur when the Al content becomes less than 59 at.%. Such an effect of preferential etching of the Al atoms induced by Ar^+ ion irradiation leads to the experimental fact observed in the present work that the thin region of the TEM foil never transformed to an IQC and remained B2 phase during heating after 120 keV Ar^+ irradiation.

Although there exists a preferential sputtering effect of the Al atoms, it may be weaker in the interior of the TEM foils than at the surface. The fact that the thick region transforms to an IQC at temperatures ranging from 880 to 1080 K confirms that the composition in the interior of the foils has not changed very much, and the alloy composition still lies in the IQC single-phase region at 880 K.

Another effect of preferential evaporation of Al during heating may also induce a decrease in the Al content at the surface of the sample and hence promote the thickness dependence of the observed phase transformation.

It is well known (Gittus 1978, Russel 1984) that irradiation should alter the phase diagram. As discussed by Zhang and Urban (1992), in this respect the ratio of the rate at which damage is produced to the rate at which it is annealed by radiation-enhanced diffusion is important. According to the experimental fact (Wang *et al* 1992, 1993) that a dose of 4×10^{16} Ar^+ (120 keV) cm^{-2} is required at room temperature to induce a complete IQC-to-amorphous transformation for the $Al_{76}Si_4Mn_{20}$ IQC, we believe that the B2-type phase is a stable phase at room temperature for the $Al_{62}Cu_{25.5}Fe_{12.5}$ alloy and the effect of the 120 keV Ar^+ ion irradiation consists mainly of radiation-enhanced diffusion when the Ar^+ ion dose is 10^{14} Ar^+ cm^{-2} or less. When the dose is equal to or larger than 10^{15} Ar^+ cm^{-2}, the preferential sputtering effect of Al atoms and the damage amount caused by irradiation may be so strong that the B2-type structure cannot transform to an IQC during subsequent heating.

Acknowledgments

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