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LETTER TO THE EDITOR

Formation of a dodecagonal phase in an equilibrium immiscible Co–Cu system induced by ion irradiation and associated evolution

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Abstract

Abnormal structural changes were observed in the equilibrium immiscible $Co_{50}Cu_{50}$ multilayers induced by 200 keV xenon-ion irradiation at 77 K. First, a dodecagonal quasicrystal phase was formed at an irradiation dose of 1×10^{15} Xe^{+} cm^{-2}. Secondly, series of selected diffraction patterns taken later showed that the dodecagonal phase formed evolved to feature a high degree of ordering with increasing ion dose. Moreover, molecular dynamics simulations verified the possibility of formation of a metastable phase in the Co–Cu system. A mechanism possibly responsible for the observed structural changes upon ion irradiation is also discussed.

The quasicrystalline phases, as a new category of materials, have aroused enormous interest since the first discovery of an icosahedral Al–Mn phase in 1984 [1]. Many experimental and theoretical attempts have already been made to obtain insight into their anomalous structure and related properties [2]. Meanwhile, various methods, including liquid melt quenching [3], annealing of amorphous alloys [4], and ion-beam mixing (IM) [5], have been employed to produce quasicrystalline phases. Also, superlattice structures in quasicrystals have been suggested in view of the appearance of extra reflections in electron diffraction patterns of icosahedral and decagonal quasicrystals.

The Co–Cu system is equilibrium immiscible and characterized by a positive heat of formation of +10 kJ mol^{-1}, calculated from Miedema's model at an equiatomic stoichiometry [6]. Because of the immiscibility, the solubility between Co and Cu is very small. Nonetheless, there have also been some reports showing that some metastable Co–Cu alloys can be formed using diverse methods. For instance, mostly fcc-structured Co–Cu alloys have been obtained by mechanical milling [7], in epitaxial monolayers [8], and by solid-state reaction [9], etc. In this work, we report the evolution of a dodecagonal phase in this equilibrium immiscible system upon ion-beam mixing under increasing ion doses.

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It has been proven both by experiments [10] and by molecular dynamics simulation [11] that atomic diffusion is difficult at the interfaces of a metallic multilayer with close-packed atomic planes of both constituent metals parallel to the interfaces. In our experiment, to avoid close-packed atomic plane stacking at the interfaces of the Co–Cu multilayers, single-crystal NaCl(001) substrates were selected in order to obtain layers of (001)-textured polycrystalline Co and Cu in the multilayered films. Co–Cu multilayered films with an overall composition of $Co_{50}Cu_{50}$ were prepared by alternate deposition of pure Cu and Co. Copper was first deposited onto the NaCl substrate; this was followed by deposition of pure Co in an ultrahigh-vacuum (UHV) e-gun evaporation system with a background vacuum level of the order of 10^{-11} Torr. During deposition, the vacuum level was better than 1.6×10^{-8} Torr. The deposition rate was controlled at 0.5 Å s^{-1} and no special cooling was provided during deposition. Five Co and five Cu layers were alternately deposited and the overall composition of the multilayered films was adjusted by altering the relative thicknesses of the Co and Cu layers. After the deposition finished, the samples were preserved in a vacuum desiccator from contamination or oxidation until they were subjected to ion-beam irradiation; the time between deposition and irradiation was no longer than one day. The real compositions of the films were confirmed to be $Co_{50}Cu_{50}$ by energy-dispersive spectrum (EDS) analysis within an uncertainty of 3%. The total thickness of the films was about 40 nm, which was required to match the projected range plus projected range straggling of 200 keV xenon ions employed in the comparative ion irradiation experiment. Some as-deposited films were subjected to 200 keV xenon-ion irradiation in an implanter with a base vacuum level of the order of 10^{-6} Torr. The xenon-ion current density was controlled to be about 0.5 μA cm^{-2} and the sample holder was always cooled by liquid nitrogen (77 K). The as-deposited films and those that had been irradiated were removed from the NaCl substrates by de-ionized water and placed onto Mo grids. All the samples studied were analysed by TEM bright-field examination and selected-area electron diffraction (SAD).

Figures 1(a) and 1(b) show a typical morphology and a corresponding SAD pattern, respectively, for the as-deposited $Co_{50}Cu_{50}$ multilayered films. From the SAD pattern, one can see not only the diffraction rings but also strong diffraction spots, indicating a fcc (001) texture evident in the polycrystalline films. Figure 2(a) shows the SAD pattern of the multilayered films after irradiation to a dose of 1×10^{15} Xe^{+} cm^{-2}. From the pattern, it can be seen that

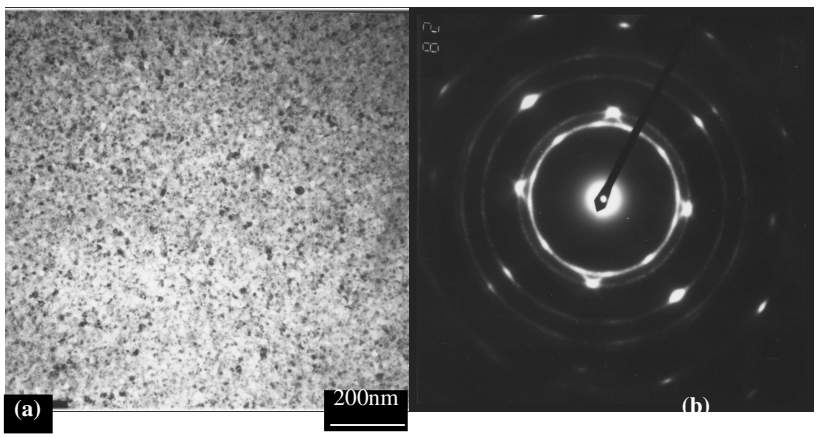

Figure 1. The bright-field image (a) and the corresponding SAD pattern (b) of the as-deposited $Co_{50}Cu_{50}$ multilayered films.

besides the bright spots, there are some diffraction rings, indicating formation of a new phase. Along with the increase of the irradiation dose, interesting structural change took place as evidenced by the evolution of the SAD pattern. For instance, figure 2(b) shows a SAD pattern of the films after irradiation to a dose of 3×10^{15} Xe^+ cm^{-2}. Comparing to figure 2(a), one can see that the diffraction rings of the new phase turn into diffraction spots and the spatial and intensity distributions of the spots are quite analogous to the cases of the identified twelvefold-rotational-symmetry quasicrystals, suggesting that a quasicrystal of dodecagonal phase was formed. Figures 2(c), 2(d), and 2(e) are the SAD patterns of the multilayered films after irradiation to doses of 5×10^{15} Xe^+ cm^{-2}, 7×10^{15} Xe^+ cm^{-2}, and 9×10^{15} Xe^+ cm^{-2}, respectively. Notably, figure 2(e) shows more than one set of spots featuring twelvefold rotational symmetry and, more interestingly, these sets of spots assembled themselves into a perfect fourfold rotational symmetry. These results seem to suggest that the dodecagonal phase formed tends to possess some long-range ordering as a result of increasing the irradiation doses. The above structural evolution can be summarized as follows:

crystalline Co + Cu in $Co_{50}Cu_{50}$ multilayered films

$\downarrow$ $\quad 1 \times 10^{15}$ Xe^+ cm^{-2}

dodecagonal quasicrystalline phase

$\downarrow$ $\quad 9 \times 10^{15}$ Xe^+ cm^{-2}

dodecagonal phase with the dodecagons assembled in fourfold rotational symmetry.

It is well known that ion mixing (IM) is a far-from-equilibrium process and can be divided into two steps [12]. The first step is the production of an atomic collision cascade and the second step is a process of relaxation. It is generally recognized that the structure of the newly formed alloy phase is determined in the relaxation period, but not in the first step of atomic collision, during which a large number of atoms are in violent motion. The atomic collision in the first step is responsible for the intermixing between the Co and Cu metal layers, as the Co and Cu atoms are excited by the impinging ions into motion and migrate, crossing the interfaces. To describe atomic displacements and defect creation induced by irradiation, a parameter 'dpa' (standing for the number of displacement events per atom) is defined [13], which can be calculated from

$$\mathrm{dpa} = \Phi\sigma_c \int_{E_d}^{E_2(\max)} \nu(E_2) \frac{\mathrm{d}\sigma}{\mathrm{d}E_2}\, \mathrm{d}E_2. \tag{1}$$

Φ is the ion flux. σ_c is the collision cross section. E_d and $E_2(\max)$ are the displacement threshold energy and the maximum energy received by the first knock-out atom, respectively. $\nu(E_2)$ is the number of displaced atoms created by the knock-out atom with an energy of E_2. $\mathrm{d}\sigma/\mathrm{d}E_2$ is the differential collision cross section at E_2. From equation (1), it is obvious that the dpa is in direct proportion to the ion flux Φ. This means that the irradiation dose will affect the amount of intermixing in the irradiated multilayers considerably. In the second step of relaxation, the highly energetic mixture should somehow relax towards equilibrium, during which process the thermodynamics suggests the possible states for the mixture to relax into. However, whether or not the mixture can reach an equilibrium state depends on the temperature and time available during the relaxation period. An alternative approach to viewing the IM process is to consider the energy deposition and its consequences. According to a thermal spike model, the relaxation time is estimated to be 10^{-10}–10^{-9} s, and the effective cooling speed available in IM could be as high as 10^{13}–10^{14} K s^{-1} [12]. Such a high cooling speed makes it possible to preserve most of the state that has been obtained during the atomic collision.

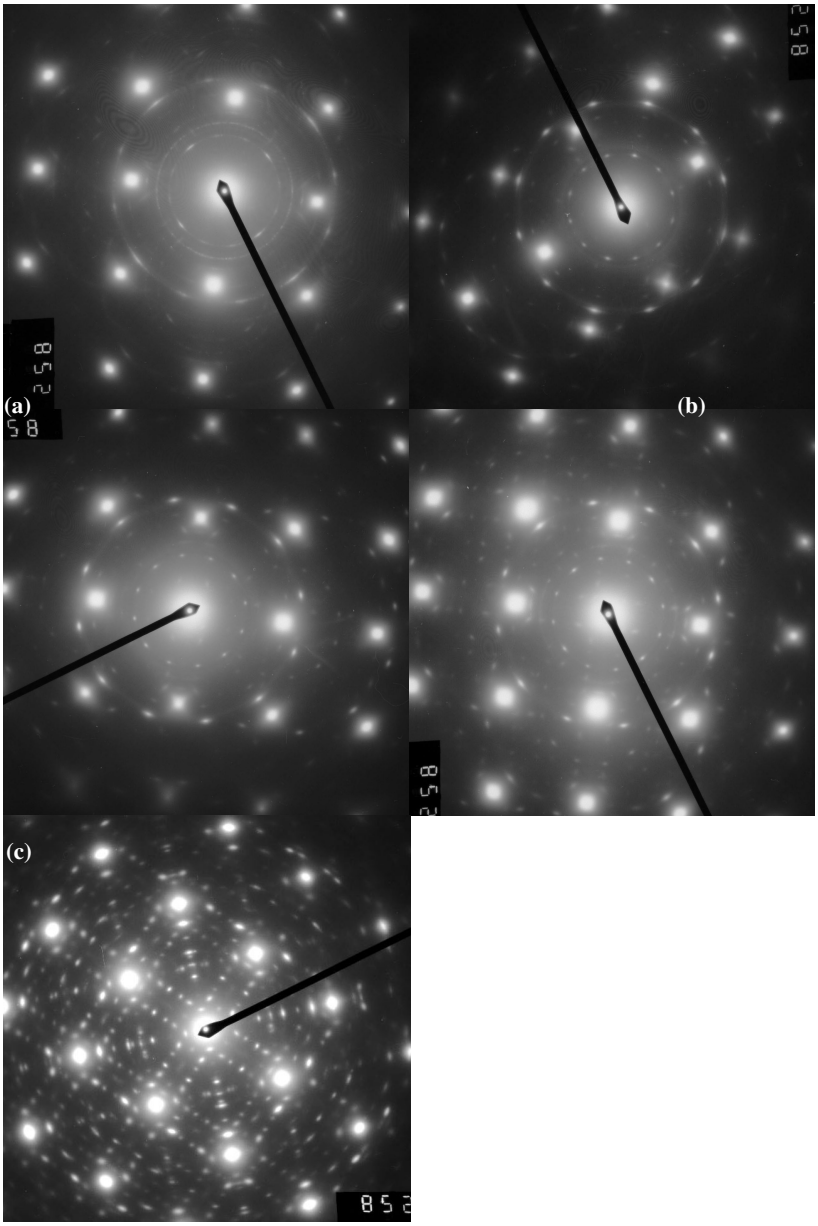

Figure 2. (a), (b), (c), (d), and (e) are the SAD patterns of $Co_{50}Cu_{50}$ multilayers after irradiation to doses of 1×10^{15} Xe^{+} cm^{-2}, 3×10^{15} Xe^{+} cm^{-2}, 5×10^{15} Xe^{+} cm^{-2}, 7×10^{15} Xe^{+} cm^{-2}, and 9×10^{15} Xe^{+} cm^{-2}, respectively.

We now turn to discussing the underlying physics of the above experimental observations in the Co–Cu system. First, according to our experimental observations, the dodecagonal phase has been formed upon all five different irradiations with the various doses, suggesting that for the Co–Cu system, the effective cooling speed available in ion irradiation is well suited to the

formation of the quasicrystal phase. In fact, using ion irradiation, some other quasicrystalline phases like the Fe–Cu icosahedral phase have also been reported [14], hinting that IM is a possible way to produce quasicrystal phases.

Secondly, in our case, a series of ion doses were applied to irradiate the multilayers as described above, and they would result in various amounts of mixing in the films. Generally, a higher irradiation dose will result in a larger amount of mixing than a lower dose does. Recalling the experimental observations, when the irradiation dose was at 1×10^{15} Xe^+ cm^{-2}, the SAD pattern showed mainly diffraction rings, while for an irradiation dose of 3×10^{15} Xe^+ cm^{-2}, the rings turned out to be distributed spots, suggesting that the dodecagonal phase formed in the early stage turned into a state like the single-crystalline one. Further increasing the irradiation dose from 5×10^{15} Xe^+ cm^{-2} to 9×10^{15} Xe^+ cm^{-2}, the diffraction spots gradually evolved to feature a fourfold rotational symmetry, corresponding to an assembling of the dodecagons. It is therefore deduced that a high dose, i.e. a large amount of mixing, leads to a strong tendency for the dodecagons to feature a long-range ordering.

In addition, we performed a constant-pressure molecular dynamics (MD) calculation with a many-body Co–Cu potential derived by Giorgio Mazzone *et al* [15] to investigate the atomic mixing between the Co and Cu metals and the stability of the metastable Co–Cu phase. In the simulation, we constructed a uniformly mixed Co–Cu solid solution of fcc structure in a composition range 10–80 at.% of Co. After the MD simulation of the solid-solution model had been run for several hundred picoseconds, all the related dynamic variables showed no secular variation, suggesting that the fcc solid solution could remain unchanged. In other words, the Co–Cu alloy of fcc structure is likely to be stable against spontaneous decay. These results could serve as indirect evidence that Co and Cu atoms could be uniformly mixed at an atomic scale.

In conclusion, a dodecagonal phase was obtained in the equilibrium immiscible Co–Cu system and it underwent a series of structural evolutions while increasing the irradiation dose. The higher the ion irradiation dose—corresponding to an increasing amount of mixing in the films—the more ordered the state into which the dodecagons assemble.

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