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LETTER TO THE EDITOR

A dodecagonal phase formed in an immiscible Co–Ag system by ion mixing of multilayers

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Abstract

In an immiscible Co–Ag system, a new Co–Ag dodecagonal phase is formed in the $Co_{50}Ag_{50}$ multilayers upon room temperature 200 keV xenon-ion irradiation to a dose of 5×10^{14} Xe^{+} cm^{-2}. The mechanism of formation of the quasicrystalline phase is also discussed in terms of the far-from-equilibrium process of ion mixing, as well as the role of the interfacial free energy, stresses caused by size mismatch and the radiation-enhanced diffusion.

In 1984, Shechtman *et al* obtained the first icosahedral Al–Mn quasicrystalline phase [1], which has since then attracted enormous attention as regards fundamental research in the field of condensed matter and materials physics [2]. In recent decades, various methods have been employed to produce quasicrystalline phases [3–5]. For instance, ion-beam mixing (IM) has been successfully employed to obtain nano-sized quasicrystals in the equilibrium immiscible Fe–Cu and Co–Cu thin films [6, 7]. In the present study, IM was employed to investigate the possibility of the formation of a quasicrystalline phase in another immiscible binary metal system, i.e. the Co–Ag system characterized by a large positive $H_f = +28$ kJ mol^{-1}. Also, the Co–Ag system has attracted attention in recent years, as its layered structure at the nano-scale may serve as a spin valve with giant magnetoresistances [8].

Two sets of Co–Ag multilayered samples with six and twelve layers were designed with a fixed total thickness of 40 nm, which was to match the projected range plus the projected range of straggling of the 200 keV xenon ions. The samples were prepared by alternately depositing pure Co and Ag on cleaved single NaCl crystals as substrates in an ultrahigh-vacuum electron-gun evaporation system with a deposition rate of 0.5 Å s^{-1}. The vacuum level was of the order of 10^{-11} Torr and was better than 1.6×10^{-8} Torr during evaporation. No special cooling was provided and the substrate temperature during evaporation was estimated to be below 200 °C. The real compositions of the as-deposited films were later confirmed to be about $Co_{50}Ag_{50}$ by energy-dispersive spectrum (EDS) analysis within an error of 2–3%. The multilayered films were irradiated by 200 keV xenon ions at room temperature, in an implanter with a vacuum level of the order of 10^{-6} Torr. The ion current density was controlled to be about 0.5 μA cm^{-2}

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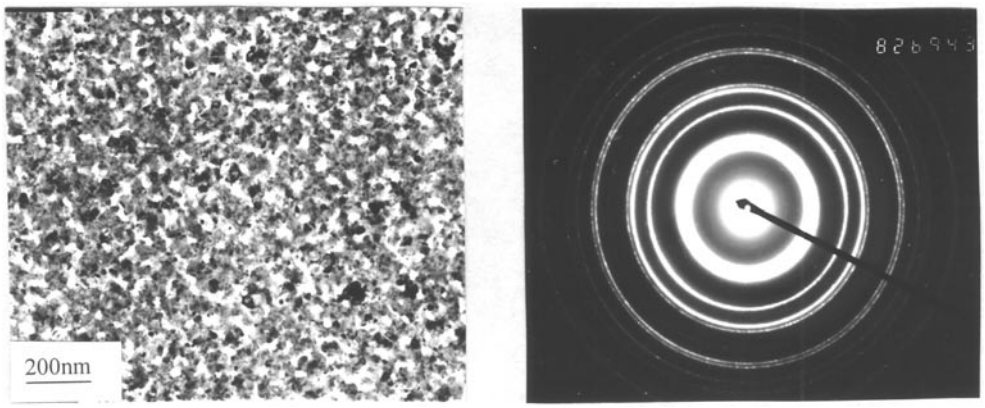
to minimize the beam heating effect and the temperature rise of the films was estimated to be well below 273 K under these conditions. All of the irradiated films were removed from the NaCl substrates by de-ionized water and put onto Mo grids, and then analysed by means of transmission electron microscopy (TEM) and selected-area electron diffraction (SAD). The vacuum level of the TEM was of the order of 10^{-7} Torr.

For the samples designed to consist of six layers, no new alloy phase was observed after the films were irradiated to doses ranging from 5×10^{14} Xe^+ cm^{-2} to 9×10^{15} Xe^+ cm^{-2}. In fact, the structures that emerged in the as-deposited and irradiated films were basically the same for both polycrystalline Co and Ag, as evidenced by the respective SAD patterns (not shown). In contrast, in the samples with twelve layers, an interesting structural change was observed after irradiation to a dose of 5×10^{14} Xe^+ cm^{-2}. Figures 1(a) and 1(b) show a typical morphology and a corresponding SAD pattern, respectively, for the as-deposited $Co_{50}Ag_{50}$ multilayered films consisting of twelve layers. From the SAD pattern, one can clearly see the sharp diffraction lines reflected from the polycrystalline Co and Ag of both fcc structures in the films. Figure 2(a) is a bright-field image showing some nano-sized bright grains embedded in a grey matrix. Figure 2(b) is a typical SAD pattern taken from one of the grains shown in figure 2(a). In the SAD pattern, one can clearly see the spots featuring a twelvefold rotational symmetry together with some diffraction lines from the remaining polycrystalline fcc Co and Ag. A careful inspection revealed that the spatial and intensity distributions of the diffraction spots were quite analogous to the cases of the well identified quasicrystalline phase with twelvefold rotational symmetry, indicating the formation of a dodecagonal phase embedded in the polycrystalline Co and Ag matrix at this irradiation stage. The composition of the dodecagonal grains was determined by EDS analysis to be close to $Co_{50}Cu_{50}$. To summarize, the above structural change can be expressed as follows:

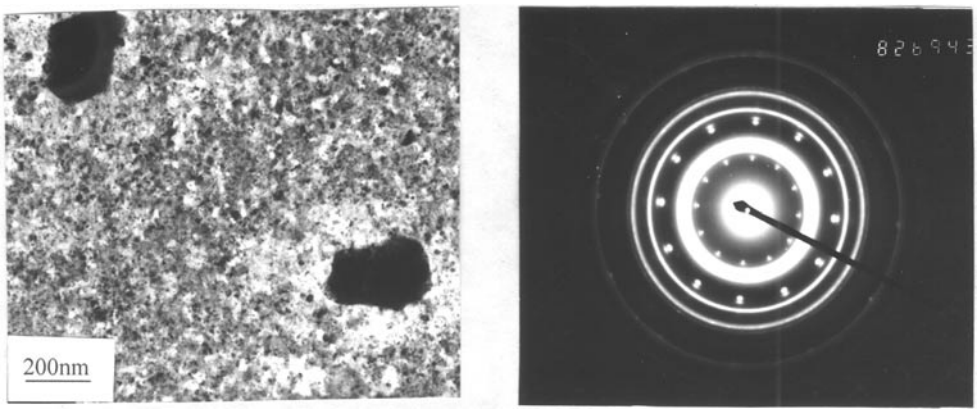
$$\text{crystalline Co} + \text{Ag} \xrightarrow{5\times10^{14}\ Xe^+\ cm^{-2}} (\text{crystalline Co} + \text{Ag}) + \text{dodecagonal}.$$



(a) (b)

Figure 1. (a) The morphology and (b) the corresponding SAD pattern of the as-deposited $Co_{50}Ag_{50}$ multilayered samples consisting of twelve layers.

We now discuss the mechanism of the observed structural change in the Co–Ag multilayered films upon ion irradiation. It is commonly known that IM can be divided into two steps, i.e. atomic collision and relaxation [9]. During atomic collision, irradiating ions of several 100 keV induce a series of atomic collisions, i.e. an atomic collision cascade, which is a far-from-equilibrium process and is responsible for atomic mixing between the Co and Ag



(a) (b)

Figure 2. (a) The morphology and (b) the corresponding SAD pattern of the $Co_{50}Ag_{50}$ multilayered samples consisting of twelve layers after irradiation to a dose of 5×10^{14} Xe^{+} cm^{-2}.

layers. After irradiation to an adequate dose, the discrete structure of the Co–Ag multilayers is smeared out and a uniform disordered mixture in a highly energetic state is thus obtained. In the relaxation period lasting only for 10^{-10}–10^{-9} s, the disordered mixture should somehow relax towards equilibrium, yet, in most cases, cannot go straightforwardly to an equilibrium state; instead, it frequently resides in some possible metastable states. In our case, one of the possible metastable states corresponded to the dodecagonal phase, which was obtained in this study by IM. Probably the dodecagonal phase has higher free energy in comparison with a ground state corresponding to a crystalline mixture of Co and Ag. To reach such an energetic level, some extra energy should be provided. In our case, it was from the interfacial free energy, which consisted of chemical and physical contributions. The physical contribution originated from a size mismatch between the Co and Ag lattices [10]. Naturally, the amount of interfacial free energy is in positive proportion to the number of layers in the samples [11]. For the samples consisting of six layers, the interfacial free energy is not high enough, whereas in the samples with twelve layers, the interfacial free energy is high enough to elevate the initial state of multilayered films to an energetic level, and therefore ion irradiation results in the formation of the observed dodecagonal phase. In addition, there were another two factors helping the formation of the metastable phase in the Co–Ag system, i.e. the mechanical stresses caused by the size mismatch and radiation-enhanced diffusion [12]. These two factors were of help in enhancing intermixing and metastable phase formation in the equilibrium Co–Ag multilayered films.

In conclusion, a new dodecagonal Co–Ag quasicrystalline phase featuring a twelvefold rotational symmetry was formed in the equilibrium immiscible Co–Ag system by IM with the important assistance of the excess interfacial free energy stored in the as-deposited Co–Ag multilayered films.

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References

[1] Shechtman D, Blech I, Gratias D and Cahn J W 1984 *Phys. Rev. Lett.* **53** 951
[2] Henley C L 1986 *Physica* A **140** 306
[3] Zhang Z, He H Q and Kuo K H 1985 *Phil. Mag.* A **52** L49
[4] Liu B X, Cheng G A and Shang C H 1987 *Phil. Mag.* **55** L265
[5] Shang C H, Li J and Liu B X 1988 *J. Phys. E: Sci. Instrum.* **18** L169
[6] Yang G W, Lai W S, Lin C and Liu B X 1999 *Appl. Phys. Lett.* **74** 3305
[7] Li Z F and Liu B X 2001 *Nucl. Instrum. Methods Phys. Res.* B to be published
[8] Tsang C, Fontana R E, Lin T Jr, Heim D E, Speriosu V S, Gurney B A and Williams M L 1994 *IEEE Trans. Magn.* **30** 3801
[9] Liu B X and Jin O 1997 *Phys. Status Solidi* a **161** 3
[10] de Boer F R, Boom R, Matter W C, Miedema A R and Niessen A K 1988 *Cohesion in Metals: Transition Metal Alloys* (Amsterdam: North-Holland)
[11] Zhang Z J, Jin O and Liu B X 1995 *Phys. Rev.* B **51** 8076
[12] Liu B X, Lai W S and Zhang Q 2000 *Mater. Sci. Eng.* R **29** 3