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Abstract
A dodecagonal quasicrystalline phase was grown in nano-sized Ag–Pt multilayers upon solid-state reaction and the existence of the respective metastable state in the Ag–Pt system was also confirmed by ion-beam mixing experiments. The major driving force for intermixing between the nano-sized Ag and Pt layers, as well as for the crystal-to-quasicrystal transition, was thought to be the interfacial free energy, which elevated the initial Ag–Pt multilayers up to an energetic state corresponding to the dodecagonal phase.

The quasicrystalline phase, as a new category of materials, has aroused enormous attention in fundamental research in the field of condensed matter and materials physics since the first discovery of an icosahedral Al–Mn phase in 1984 [1, 2]. Up to now, a number of experimental and theoretical attempts have been presented to give an insight into its anomalous structure and related properties [3]. Meanwhile, various methods, including liquid melt quenching [4], annealing of amorphous alloys [5] and ion-beam mixing (IM) [6], have been employed to produce quasicrystalline phases. Also, quasicrystals have some particular properties, e.g. interesting electrical and thermal transport properties [7, 8], high photon absorption [9], high hardness, unique corrosion resistance, and a low coefficient of friction, yet the single-phase quasicrystals are usually very brittle [10]. In this respect, some reports showed that nano-sized quasicrystals embedded in an amorphous or crystalline matrix may improve the mechanical properties. Very recently, some IM studies have demonstrated that, in a specific binary metal system, when the layer thickness was reduced to a couple of nanometres, the interfacial free energy in the multilayered films could be quite high and could drive the multilayers to some previously unknown energetic states, helping to explore new metastable phases, such as amorphous, metastable crystalline and quasicrystalline phases. For instance, IM has been successfully used to obtain nano-sized quasicrystals in the Fe–Cu [11], Co–Cu [12] and

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Co–Ag [13] thin films. In the present study, another method, i.e. solid-state reaction (SSR) together with comparative IM, was conducted to investigate the possibility of forming new quasicrystalline phases in the Ag–Pt system, which is characterized by a very small negative heat of formation ($H_f = -1$ kJ mol^{-1}) calculated by Miedema's model at an equiatomic stoichiometry [14].

Two sets of Ag–Pt multilayered samples, consisting of 6 and 12 layers, respectively, were prepared by depositing alternately Ag and Pt onto NaCl single crystals in an ultra-high vacuum (UHV) electron-gun deposition 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 to the substrates during deposition. The total thickness of the films was about 40 nm, which was required to match the projected range plus the projected range straggling of 200 keV xenon ions employed in IM experiment. The desired overall composition of the multilayered films, i.e. Ag$_{50}$Pt$_{50}$, was obtained by adjusting the relative thicknesses of the individual Ag and Pt layers. After deposition, the real composition of the films was confirmed to be Ag$_{52}$Pt$_{48}$ by energy-dispersive spectrum (EDS) analysis, for which the measuring error was around 3%. It should be noted that the thicknesses of the individual layers of the above designed multilayered samples were about 7 and 3 nm, respectively and therefore the length of atomic migration through interfaces for alloying upon SSR and IM was of the order of a couple of nanometres. Some as-deposited films were removed from the NaCl substrates by de-ionized water and placed onto the Mo grids for thermal annealing, which was conducted in a hot stage attached to the transmission electron microscopy (TEM) with a base vacuum level of the order of 10^{-7} Torr. The annealing procedure began at 100 °C, with incremental increases of 50 °C, and the staying time at each annealing temperature was 30 min. Meanwhile, some as-deposited Ag$_{52}$Pt$_{48}$ multilayered 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}. All the samples studied were analysed by TEM bright field examination and selection area electron diffraction (SAD).

We first checked the structure of the as-deposited Ag–Pt multilayered films consisting of either 6 or 12 layers. Take the Ag–Pt sample consisting of 6 layers as an example. Figures 1(a) and (b) show a bright field image and the corresponding SAD pattern, respectively, of the multilayered films in the deposited state. From the SAD pattern, one can see clearly the diffraction lines from the polycrystalline Ag and Pt. After annealing at 200 °C for about 30 min, an anomalous structural transition was observed in the Ag–Pt multilayered films consisting of 12 layers. Figure 2(a) shows a bright field image of the resultant structure after annealing. Figure 2(b) exhibits an interesting SAD pattern taken from the annealed sample and a dense set of sharp diffraction lines can be observed. From the SAD pattern, it can be deduced that the polycrystalline Ag and Pt have reacted to form a unique phase embedded in the polycrystalline Ag and Pt. According to the documented Joint Committee on Power Diffraction Standard (JCPDS) Cards, these diffraction lines can neither be indexed to those Ag–Pt intermetallic compounds nor any possible phase combining Ag, Pt and oxygen, which was taken into account because of possible contamination. Instead, the spatial and intensity distributions of these diffraction lines are quite analogous to the case of quasicrystals. Summarizing, the above structural change can be expressed by

$$\text{Crystalline Ag} + \text{Pt} \xrightarrow{\text{200 °C, 300 min}} (\text{Crystalline Ag} + \text{Pt}) + \text{quasicrystal}.$$
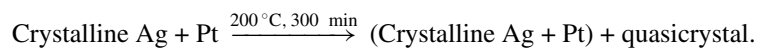
In order to prove the possibility of forming quasicrystals in the Ag–Pt system, an IM experiment was also conducted. It is well known that IM is capable of inducing intermixing between metal layers through dynamic atomic collision and driving the resultant mixture into a
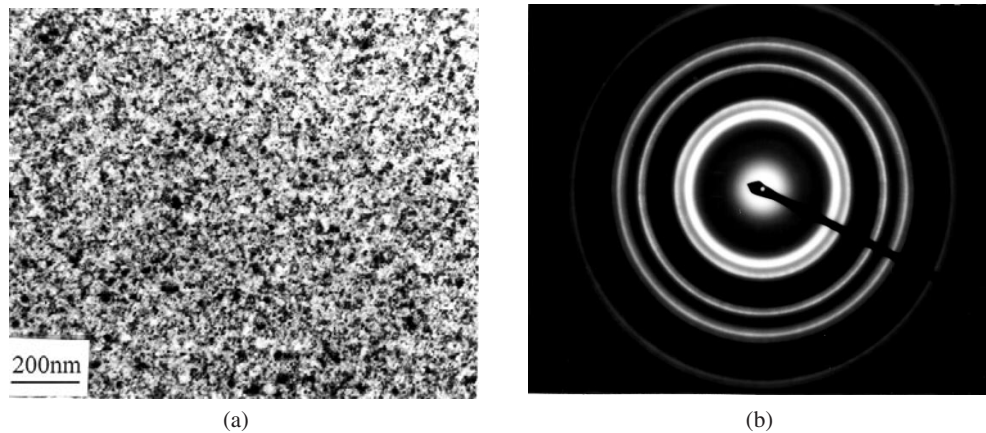
(a)　　　　　　　　　　　　(b)

Figure 1. (a) A bright-field image and (b) the corresponding SAD pattern of the Ag–Pt multilayered samples consisting of 6 layers.

highly energetic and disordered state. In the subsequent relaxation period, the highly energetic state would somehow relax towards equilibrium and reside in one of the possible metastable states in the system, thus producing the corresponding metastable phase [15]. In the present study, 200 keV xenon ion irradiation was performed with some Ag–Pt multilayered films to provide further evidence for the existence of the metastable state observed in SSR, and an interesting result was thus obtained. For the samples designed to consist of 6 layers, no new alloy phase was observed after the films were irradiated with doses ranging from 7×10^{14} $Xe^+ cm^{-2}$ to $9 \times 10^{15} Xe^+ cm^{-2}$. In fact, the structures produced in the as-deposited state and irradiated films were basically the same for both polycrystalline Ag and Pt, as shown by the respective SAD patterns (not shown). In contrast, in the Ag–Pt samples with 12 layers, an interesting structural change was observed after irradiation at a dose of $7 \times 10^{14} Xe^+ cm^{-2}$. Figure 3(a) is a bright field image showing some nano-sized grey grains embedded in a bright matrix. Figure 3(b) is a typical SAD pattern taken from one of the grains displayed in figure 3(a). In the SAD pattern, one can clearly see the spots featuring a twelve-fold rotational symmetry, together with some diffraction lines from the remaining polycrystalline Ag and Pt. 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 twelve-fold rotational symmetry, indicating the formation of a dodecagonal phase embedded in the polycrystalline Ag and Pt matrix at this irradiation stage. The composition of the dodecagonal grains was determined by EDS to be close to $Ag_{52}Pt_{48}$. To summarize, the above structural change can be expressed by

$$\text{Crystalline Ag + Pt} \xrightarrow{7 \times 10^{14}\,Xe^+cm^{-2}} \text{(Crystalline Ag + Pt) + dodecagonal.}$$
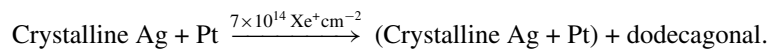
From the above characterization results, an Ag–Pt dodecagonal quasicrystal was formed, for the first time, by medium temperature annealing and IM of nano-sized Ag–Pt multilayered films.

We now discuss the formation mechanism of the metastable phases in the Ag–Pt system upon SSR and IM. Probably the dodecagonal phase has a higher free energy in comparison with a ground state corresponding to a mechanical mixture of crystalline Ag and Pt. To reach such an energetic level, some extra energy should be provided and, in the present case, it was from the interfacial free energy. According to the interfacial free energy calculation, at a fixed
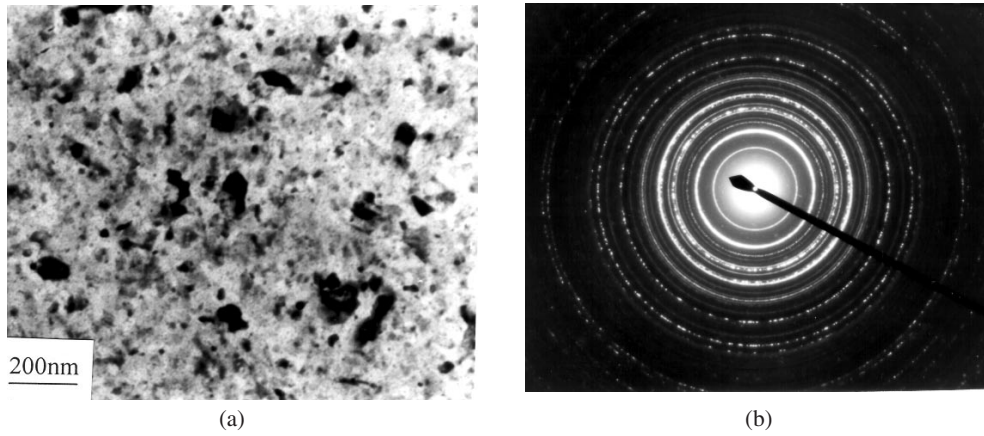
Figure 2. (a) A bright-field image and (b) the corresponding SAD pattern of the Ag–Pt multilayered samples consisting of 12 layers after thermal annealing at $200\,^{\circ}$C for 30 min.
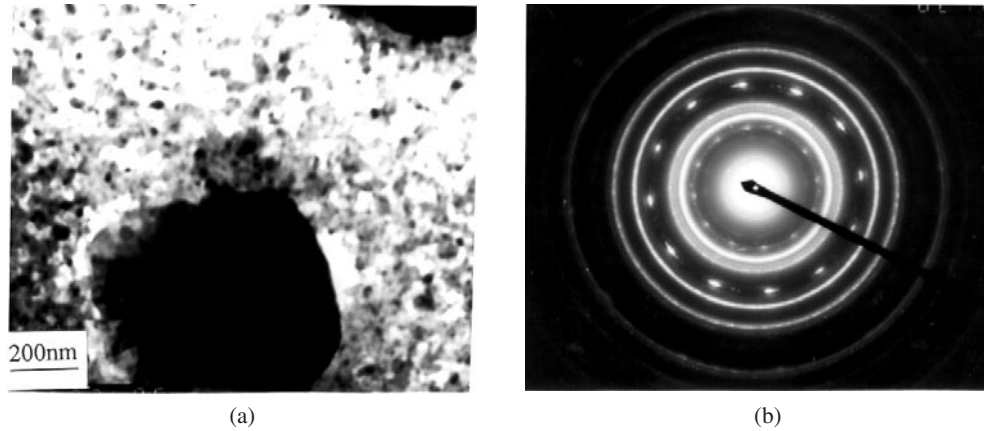

Figure 3. (a) A bright-field image and (b) the corresponding SAD pattern of the Ag–Pt multilayered samples consisting of 12 layers after 200 keV xenon ion irradiation at a dose of $7 \times 10^{14}\,\mathrm{Xe^+\,cm^{-2}}$.

total thickness, the amount of interfacial free energy is in positive proportion to the number of layers in the multilayered films [14–16], i.e. increasing the number of layers corresponds to increasing the interfacial free energy. For those samples consisting of 12 layers, the interfacial free energy is high enough to elevate the initial state of the multilayered films to an energetic level and therefore both annealing and ion irradiation result in the formation of the observed dodecagonal phase. For the sample consisting of 6 layers, no metastable phase was observed simply because of the lack of enough interfacial free energy.

In conclusion, with the important contribution from the excess interfacial free energy, properly designed Ag–Pt multilayered films were able to undergo a solid-state interfacial reaction at a moderate temperature for a relatively short time, which resulted in the formation of a dodecagonal quasicrystalline phase in the Ag–Pt system. The existence of the respective metastable state in the Ag–Pt system was confirmed by IM as well.

Acknowledgments

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