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Interface assisted formation of a metastable hcp phase by ion mixing in an immiscible Ag–Ni system

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Abstract. A metastable Ag–Ni phase was formed by 200 keV xenon ion mixing at 77 K in the Ag₈₀Ni₂₀ multilayered films, in which the excess interfacial free energy provided partial driving force for alloying in an equilibrium immiscible Ag–Ni system characterized by a large positive heat of formation. The metastable phase was identified to be of D0₁₉ hcp structure with a stoichiometry of Ag₃Ni and can therefore be considered as a Hume–Rothery 7/4 electron compound. A thermodynamic calculation showed that when the multilayers consisted of 8 or more bilayers, the interfacial free energy could elevate their initial energy levels up to a state higher than that of the hcp phase, and that while the multilayers composed of 6 or less bilayers, it was thermodynamically not favoured to form the hcp phase. Kinetically, the metastable hcp phase was grown from the fcc Ag lattice through a fast sliding mechanism. Furthermore, an *ab initio* calculation showed that a minimum total energy of the Ag₃Ni phase did correspond to the above observed metastable state, indicating that the stability of the metastable Ag–Ni hcp phase was correlated with its electronic structure.

Since the early 1980s, a scheme of ion-beam mixing (IM) of multilayers has been employed to study the formation of metastable alloys and a great number of amorphous and metastable crystalline (MX) alloys have so far been obtained by IM in a number of binary metal systems [1–4]. However, some issues still need further studies, e.g. the driving force for alloying in those systems with a positive heat of formation (H_f), the stability of MX phases in terms of their electronic structures, etc. In this paper, the Ag–Ni system was chosen to investigate the possibility of forming new metastable alloys by means of IM. Choosing the Ag–Ni system was based on the following considerations. Firstly, the system is characterized by a large positive $H_f = +23 \text{ kJ mol}^{-1}$, which is an unfavourable factor for alloying, and therefore the role of interfacial free energy in the multilayers in enhancing the alloying ability needs to be clarified. Secondly, the system has recently attracted much attention because the nanostructures of successive Ag and Ni layers have been shown as spin-valve systems with giant magnetoresistances (GMR) [5]. We report, in this paper, a new metastable Ag₃Ni hcp phase with a D0₁₉ structure formed by IM and its relative stability is discussed in terms of its electronic structure.

Four sets of Ag–Ni multilayered samples with various numbers of bilayers were designed to include various numbers of bilayers with a fixed total thickness of 40 nm, which was to match the projected range plus the projected range straggling of the 200 keV xenon ions used in IM experiments. The samples were prepared by alternately depositing the pure nickel and silver onto the freshly cleaved NaCl single crystals in an ultra-high vacuum e-gun evaporation

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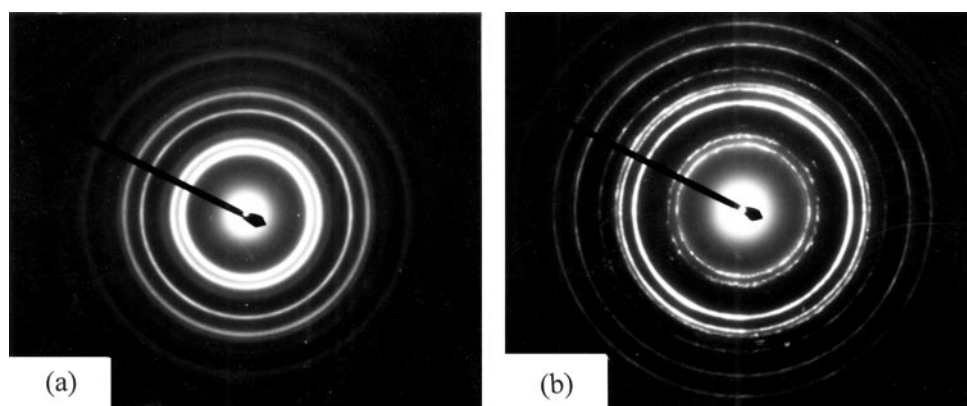


Figure 1. Selected area diffraction (SAD) images of the films consisted of six bilayers: (a) as deposited; (b) at an irradiation dose of $5 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$.

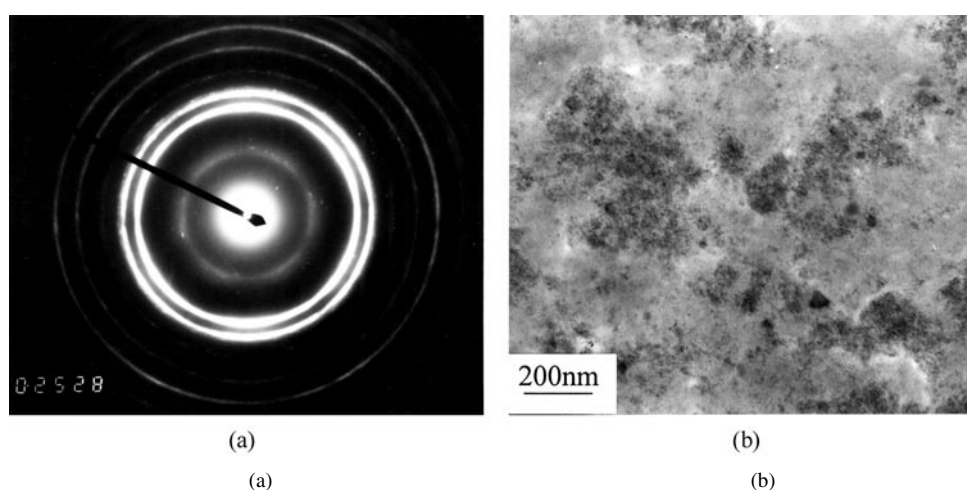


Figure 2. Selected area diffraction (SAD) and corresponding bright-field images of the films consisted of eight bilayers.

system with a background vacuum level of 10^{-11} Torr. The overall compositions of the samples were obtained by adjusting the relative thickness of Ag and Ni layers, which was monitored by an *in situ* quartz oscillator. Energy dispersive spectrum (EDS) analysis with an error of 3% was employed to confirm the overall compositions of the as-deposited samples and to determine the real compositions of the resultant phases after IM. IM experiments were carried out at 77 K by 200 keV Xe ions to various doses in an implanter with a vacuum level higher than 5×10^{-6} Torr. The ion current density was confined to be less than $1 \mu\text{A cm}^{-2}$ to minimize the beam heating effect. All the studied Ag–Ni films were removed from the NaCl substrates in the de-ionized water and put on Mo grids for transmission electron microscopy (TEM) examination and selected area diffraction (SAD) analysis for identifying the resultant structure.

We now discuss the effect of numbers of bilayers in the multilayered films on the structural change emerged in the Ag–Ni multilayered films upon 200 keV xenon ion-beam mixing at 77 K. For the samples designed to include 12 layers (6 bilayers) and less than 12 layers, no

Table 1. Indexing of the hcp phase formed in the Ag–Ni multilayered films induced by ion irradiation at a dose of $5 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$.

$D_{\text{exp}} (\text{Å})$	hkl	$D_{\text{cal}} (\text{Å})$
2.54	100	2.56
1.48	110	1.48
1.30	200	1.28
1.12	104	1.12
0.96	210	0.97
0.85	300	0.85
0.79	205	0.78
0.76	303	0.76
0.73	220	0.74

new alloy phase was observed after the films were irradiated by xenon ions in a dose range of $5\text{--}9 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$. Actually, the structures emerged in the as-deposited and the irradiated films were basically the same of both polycrystalline Ag and Ni, as shown by a typical SAD pattern exhibited in figure 1 for the sample consisting of 12 layers irradiated to a dose of $5 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$. Interestingly, with increasing the number of layers, i.e. in the samples designed to include 16 layers (8 bilayers), a structural change was observed after irradiation to a dose range of $5\text{--}9 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$. Figures 2(a) and 2(b) show a bright field image and the corresponding SAD pattern taken from the sample after xenon ion irradiation to the dose of $5 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$, respectively. From the SAD pattern in figure 2(b), a new metastable phase was apparently formed and identified to be of hcp ($D0_{19}$) structure. The indexing results are listed in table 1, from which the lattice parameters of the hcp phase were calculated to be $a = 2.96 \text{ Å}$, $c = 4.96 \text{ Å}$ and the c/a ratio approximately to be 1.67. The real composition of the metastable hcp phase was determined by EDS analysis to be 75 at.% of Ag. It should be noted that the same hcp phase was also obtained in the samples irradiated to other two doses. In short, an Ag_3Ni metastable phase with $D0_{19}$ structure was formed by IM in the equilibrium immiscible Ag–Ni system.

The formation of Ag_3Ni metastable phase may be attributed to the valence electron effect. For a close packed hexagonal structure, the maximum number of electron states per atom, n , filling up in the Jones' zone (including doubling for spin) can be calculated by the following equation [6]:

$$n = 2 - \frac{3}{4} \left(\frac{a}{c}\right)^2 \left[1 - \frac{1}{4} \left(\frac{a}{c}\right)^2\right] \quad (1)$$

where a and c are the lattice constants of the hcp structure. Accordingly, the n value of the Ag_3Ni hcp phase was calculated to be 1.756, which was quite close to the value of $7/4 = 1.75$, and therefore the Ag_3Ni hcp phase can be considered as a well-defined Hume–Rothery $7/4$ metastable electron compound [7].

It is commonly recognized that IM process can generally be divided into two consecutive steps, i.e. an atomic collision and a relaxation period [4]. During the first step, the irradiating ions of several 100 keV induce a series of atomic collisions, namely atomic collision cascade, which drives the multilayers to a far-from-equilibrium state and is responsible for atomic mixing between the Ag and Ni layers. After irradiation to an adequate dose inducing enough atomic mixing, the discrete structure in the Ag–Ni multilayers is smeared out and a uniform disordered mixture in a highly energetic state is obtained. At the moment of termination of atomic collision, the equilibrium thermodynamics comes into play and directs the disordered mixture to relax towards equilibrium. However, as the relaxation period is extremely short lasting only

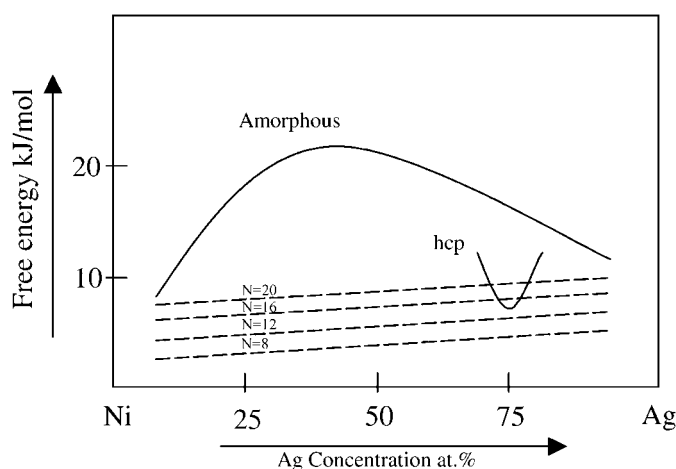


Figure 3. A calculated Gibbs free energy diagram of the Ag–Ni system as a function of the atomic concentration.

for 10^{-10} – 10^{-9} s, the disordered mixture cannot straightforwardly move to an equilibrium state in the most cases, instead, it frequently resides at one of the possible intermediate or metastable states. As IM begins with multilayered films, the excess interfacial free energy would certainly help in enhancing intermixing and alloying in the immiscible Ag–Ni system. Naturally, the amount of interfacial free energy depends on the fraction of the interfacial atoms versus the total atoms in the multilayered films, which can be designed intentionally in case of need [8]. Figure 3 shows the calculated free energy curves of the metastable hcp phase, the amorphous phase and the as-deposited films consisting of 4, 6, 8, and 10 bilayers, respectively, for the Ag–Ni system. The calculation was based on Miedema’s model and Alonso’s methods, which can be found in the well documented literature [9–11]. Obviously, for the multilayers including 12 or less layers, the interfacial free energy was not high enough to elevate the initial energetic state to a level higher than that of the metastable hcp phase. While for the samples with 16 layers or more, the extra interfacial free energy did elevate the multilayered films to an energetic state higher than that of the metastable hcp phase, which was indeed formed upon ion irradiation. Incidentally, the energetic state of all the multilayers were not higher than that of the amorphous state and therefore amorphization has not been observed so far in this study.

Concerning the growth kinetics, the Ag-enriched Ag_3Ni hcp phase was thought to grow from the fcc Ag lattice through a fcc–to–hcp transition, which is a fast transition mechanism able to complete during the relaxation period of IM. Since both fcc and hcp are close-packed structures, the atomic arrangements of the $(111)_{\text{fcc}}$ plane and the $(0001)_{\text{hcp}}$ are essentially the same, and the only difference is the stacking sequence of the atomic layers normal to these planes, i.e. ABCABC... for fcc, and ABAB... for hcp. Consequently, the lattice adjustment to transform fcc to hcp is geometrically simple, and a fast sliding of the atoms in $(11\bar{2})_{\text{fcc}}$ planes along various $\langle 11\bar{2} \rangle$ directions by a vector of $1/3(11\bar{2})$ can realize such a transition rapidly. The orientation relationship is $[1\bar{1}00]_{\text{hcp}} \parallel [11\bar{2}]_{\text{fcc}}$, which results in a lattice parameter relationship as $a_{\text{hcp}} = 1/\sqrt{2}a_{\text{fcc}}$ and $c_{\text{hcp}} = 2/\sqrt{3}a_{\text{fcc}}$. Accordingly, the parameters of the hcp phase were calculated to be $a = 2.95 \text{ \AA}$ and $c = 4.83 \text{ \AA}$, and the ratio of c/a was approximately to be 1.64, which were compatible with the experimental results.

Furthermore, the total energy of the Ag_3Ni phase with D0_{19} structure was calculated based on the Vienna *ab initio* simulation (VASP) [12], which has been described in detail

elsewhere [13]. Briefly, the establishment of the VASP code was based on the density functional theory within the local-density approximation. The electron–ion interaction is described by pseudopotentials. The method [14] used to build the pseudopotentials is derived from Vanderbilt’s recipe [15] previously employed for ultrasoft pseudopotentials. The pseudopotentials allow the use of a moderate cutoff for the construction of the plane-wave basis for the transition metals. The integration in the Brillouin zone was done on some special points in the reciprocal k -space determined by employing the Monkhorst–Pack scheme, which resulted in a mesh of six irreducible k points. All calculations were performed with the generalized-gradient approximation (GGA) proposed by Perdew and Wang [16]. As a result, the minimum total energy was calculated to be $E_{\min} = -3.2201$ eV/atom and the corresponding lattice parameters of the hcp phase were $a = 2.84$ Å, $c = 4.66$ Å and the ratio of c/a was approximately to be 1.64, which were also quite close to the experimental results.

In summary, a new metastable Ag₃Ni hcp phase was obtained in the equilibrium immiscible Ag–Ni system by ion irradiation with an important assistant of the excess interfacial free energy stored in the as-deposited Ag–Ni multilayers. Furthermore, an *ab initio* confirmed the existence of the corresponding metastable state in the Ag–Ni system and stability of the Ag₃Ni hcp phase was probably originated from its electronic structure.

Acknowledgments

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