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1993 J. Phys.: Condens. Matter 5 L315

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LETTER TO THE EDITOR

Formation of a metastable cubic phase in an immiscible Fe-Ag system by ion mixing

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Received 4 March 1993, in final form 14 April 1993

Abstract. $\text{Fe}_x\text{Ag}_{1-x}$ ($x = 0.20-0.65$) nano-multilayers were prepared by alternate deposition of pure Fe and Ag metals. The multilayers were then irradiated with 200 keV xenon ions at 77 K. A new metastable crystalline phase with cubic structure was observed in the irradiated samples when the xenon ion dose exceeded $1 \times 10^{16} \text{Xe}^+ \text{cm}^{-2}$ and the fraction of this new phase increased with ion dose.

From the Fe-Ag equilibrium phase diagram, one can observe that Fe and Ag have no solution in liquid and solid states and form no intermetallic compounds either. The Fe-Ag binary system has an accordingly large positive heat of mixing ($+28 \text{kJ mol}^{-1}$) [1]. In recent years, however, it has been reported that metastable phases could be formed in some metal binary systems with large positive heats of mixing by ion-beam mixing, a process far from equilibrium [2-6]. For instance, amorphous, quasicrystal and metastable crystalline (MX) phases were formed in the immiscible Fe-Cu system (whose heat of mixing is $+13 \text{kJ mol}^{-1}$) [1, 6-8]. In previous studies, research into the interactions between ion beams and materials in systems with positive heats of mixing has been focused on exploring the possibility of the formation of amorphous alloys. Less attention has been paid to the formation of the MX phase. In this letter, we report the formation of a new MX phase in the immiscible Fe-Ag system by ion irradiation.

The Fe-Ag multilayered samples were prepared by depositing alternately pure iron (99.99%) and silver (99.99%) at rates of $0.1-0.2 \text{nm s}^{-1}$ onto NaCl single-crystal substrates (with freshly cleaved surfaces) in an electron gun evaporation system with a vacuum of 5×10^{-7} Torr. The total thickness of the films was about 40 nm. The films consisted of four layers of iron and five layers of silver. The relative thickness of the constituent metals was adjusted to obtain the designed alloy compositions, i.e. $\text{Fe}_x\text{Ag}_{1-x}$ ($x = 0.20-0.65$). As-deposited films were then irradiated with 200 keV xenon ions at 77 K (cooled by liquid nitrogen). Six irradiation doses were selected for this study and they were 5×10^{14} , 1×10^{15} , 5×10^{15} , 8×10^{15} , 1×10^{16} and $2 \times 10^{16} \text{Xe}^+ \text{cm}^{-2}$, respectively. The ion current density was about $1 \mu\text{A cm}^{-2}$ and the vacuum level during irradiation was better than 5×10^{-6} Torr. After irradiation, self-supporting films were obtained by first dissolving the NaCl substrates in deionized water and collecting the films on Mo grids for examination by transmission electron microscopy (TEM). The structural and morphological changes of the samples were

analysed by selected area electron diffraction (SAD) and bright field examination. X-ray energy dispersive spectroscopy (EDS) in conjunction with TEM was employed to measure and confirm the atomic concentrations of the alloy films.

The average atomic concentrations of all the samples, determined by EDS within an experimental error of 5%, agreed quite well with the designed values. TEM bright field examination and SAD analysis indicated that the as-deposited Fe–Ag films were composed of a mixture of polycrystalline BCC Fe and FCC Ag phases. The grain size was about 5 to 15 nm. The intensity distribution of the diffraction rings was not uniform, indicating that there was some texturing in the films [9].

The samples were then irradiated by 200 keV xenon ions at 77 K. A relatively low-dose irradiation ($5 \times 10^{14} \text{ Xe}^+ \text{ cm}^{-2}$) induced grain growth in the films and enhanced the (001) texture, but no new phase was formed in the films, in accordance with the expectation of the heat of mixing criterion [10]. High-dose mixing, however, smeared out several diffraction rings from pure iron and silver and some new diffraction lines appeared indicating that a new phase was formed. The diffraction lines of the new phase increased their intensities with increasing radiation dose. The critical dose of the new phase formation depended on the chemical composition of the films, i.e. it increased with increasing Ag concentration in the films. The critical dose of the new phase formation was about 1×10^{15} , 5×10^{15} and $8 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$ for $\text{Fe}_{65}\text{Ag}_{35}$, $\text{Fe}_{40}\text{Ag}_{60}$ and $\text{Fe}_{20}\text{Ag}_{80}$ films, respectively. That is to say, a higher Ag concentration requires a higher dose to form the new MX phase. The intensity of the diffraction lines of the new phase also indicates that, though the critical dose for the $\text{Fe}_{40}\text{Ag}_{60}$ films is higher than that for the $\text{Fe}_{65}\text{Ag}_{35}$ films, the portion of the new phase in the former was greater than that of all the other samples, when the irradiation dose was higher than $1 \times 10^{16} \text{ Xe}^+ \text{ cm}^{-2}$. This means that the composition of the MX phase formed was probably close to $\text{Fe}_{40}\text{Ag}_{60}$.

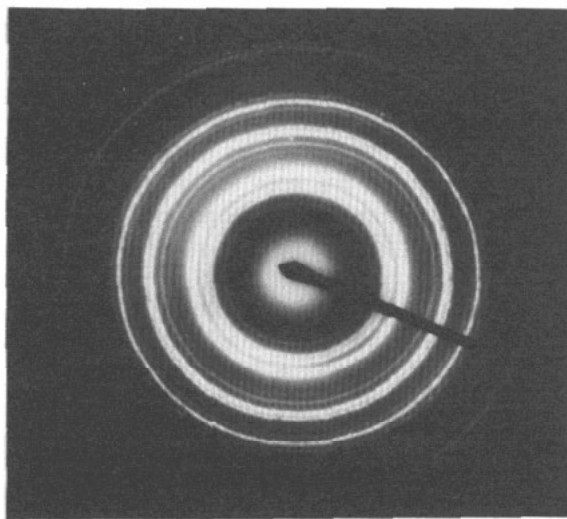


Figure 1. The diffraction patterns of $\text{Fe}_{40}\text{Ag}_{60}$ film irradiated at 77 K to a dose of $2 \times 10^{16} \text{ Xe}^+ \text{ cm}^{-2}$ by 200 keV xenon ions.

Figure 1 shows the diffraction pattern of the $\text{Fe}_{40}\text{Ag}_{60}$ film irradiated at 77 K to a dose of $2 \times 10^{16} \text{ Xe}^+ \text{ cm}^{-2}$. The corresponding crystallographic plane distances shown in figure 1 were measured and are listed in table 1. From these data, the new phase was identified to be of cubic structure with a lattice parameter of $0.844 \pm 0.005 \text{ nm}$. It is worth

mentioning that we have observed a similar cubic MX phase in the immiscible Fe–Cu system by ion mixing and also by solid state interdiffusion [6]. The as-deposited Fe–Ag films were therefore annealed *in situ* in the TEM to make a comparative study between ion mixing and solid state interdiffusion. The experimental results indicated that, except for the grain size increasing with increasing temperature and time, no new phase had been observed in this system by thermal annealing up to a temperature of 900 °C for 0.5 h. The reason the Fe–Ag MX phase cannot be formed by solid state interdiffusion is probably the rather positive heat of mixing, which is not compensated by the contribution of the interfacial free energy in the multilayers. It can also be noted that the texture disappears gradually with increasing radiation dose as the new phase appears.

Table I. Indexing results of the diffraction lines shown in the figure 1.

d_{obs} (Å)	d_{cal} (Å)	Visual intensity	Indices		
			New phase	Fe	Ag
4.86	4.87	vw	111		
2.97	2.98	w	220		
2.55	2.54	M	311		
2.45	2.44	w	222		
2.36	2.36	M			111
2.11	2.11	M	400		
2.04	2.04	w		110	200
1.71	1.72	w	422		
1.62	1.63	w	333, 511		
1.49	1.49	s	440		
1.44	1.43	M	531	200	220
1.32	1.33	w	620		
1.28	1.27	w	533		
1.23	1.22	M	444		
1.18	1.17	w	711, 551, 640	211	222
1.09	1.10	w	553, 731		

s strong, M medium, w weak and vw very weak.

We needed to establish that the new diffraction lines did not arise from another phase formed from any combination of the elements Fe, Ag, Xe, Na, Cl (from NaCl substrates) and O from the vacuum chamber. To this end, we checked all the diffraction lines against available ASTM cards and none of the diffraction lines could be attributed to any known crystalline structure. The EDS analyses also indicated that there was no Na or Cl present and that the concentration of Xe in the films was less than 1%, within the experimental error. It is believed that oxides of Fe and Ag cannot be formed at such low temperature (77 K) and oxygen partial pressure (less than 1×10^{-6} Torr).

In conclusion, a new phase of cubic structure with a large unit cell was formed in the Fe–Ag system by ion irradiation, which demonstrates the feasibility of forming new crystalline phases by ion irradiation in those systems with positive heats of mixing like our Fe–Ag and Fe–Cu [6] systems.

This work is supported in part by the National Natural Science Foundation of China. The authors are grateful to the researchers of the TEM laboratory of Peking University and the Analysis Centre of Tsinghua University for their help.

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