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LETTER TO THE EDITOR

Irradiation-induced metastable phase formation and amorphization in an immiscible Co/Ag multilayer

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Abstract

Co/Ag multilayers were prepared by an alternate deposition of Co and Ag metals using electron beam evaporation. These multilayers were irradiated with 130 keV argon ions at room temperature. Upon irradiation to a fluence of 7×10^{16} ions cm^{-2}, a new metastable phase (DO_{19}) with hcp structure having nanosized grains embedded in a matrix having an amorphous structure was observed.

The Co–Ag equilibrium phase diagram shows that Co and Ag have no solution in liquid and solid states and form no intermetallic compounds. In equilibrium, Co and Ag are immiscible, due to the difference in surface free energy and a large atomic size difference. Apart from that, there is a large lattice mismatch (15%) between Ag and Co. As a result, the heat of mixing is strongly positive ($\Delta H_{mix} = +28$ kJ/mol) with no tendency for phase formation and alloying [1]. In recent years, it has been noticed that nanostructures of Co and Ag have gained in importance as a system with giant magnetoresistance (GMR) and a consequent potential for technical applications. These materials exhibit a maximum GMR for mixtures around 30 at.% Co [2].

Ion beam mixing is a processing tool to synthesize metastable phases such as solid solutions from immiscible elements. Since the 1980s, ion beam mixing of multiple metal layers has produced a large number of metastable alloys with either an amorphous or a crystalline phase in many binary metallic systems. Ion beam mixing of mutilayers composed of immiscible elements leads to an atomic intermixing of the different layers leading to the formation of non-equilibrium alloys with optimum grain size distribution. Depending on the type of ion, flux and its energy, ion bombardment can promote local atomic rearrangement and can modify the microstructure of alloys. These modifications are strongly dependent on the details of the chemical interaction between the constituents, their miscibility and heats of mixing [3, 4]. The

formation of metastable phases in the 200 keV Xe^+ ion-irradiated Co/Ag multilayer is reported by Li *et al* [5]. These authors have reported that the metastable phase formation depends on the interfacial free energy, which enhances the capability of alloying. The same authors have reported a new dodecagonal phase formation in $Co_{50}Ag_{50}$ mutilayers upon 200 keV Xe^+ ion irradiation at room temperature up to a fluence of 5×10^{14} ions cm^{-2} [6]. They have reported that the formation of quasicrystalline phase is due to the interfacial free energy, stresses caused by lattice mismatch and the radiation-enhanced diffusion. A recent TEM study on the 200 keV Xe ion-irradiated Co–Cu ($H_{mix} = 26$ kJ/mol) mutilayers shows the formation of dodecagonal phase and amorphization [7]. These authors have proposed a mechanism for the above structural evolution based on the similarity in the atomic configuration between the quasicrystal and amorphous short-range orders as well as the effect of interfacial free energy stored in the Co–Cu mutilayers. In a similar fashion, there is a report on ion irradiation on an Fe–Cu system, which is characterized by a large positive heat of mixing of +19 kJ/mol [8]. These authors have reported irradiation-induced metastable phases and amorphization in the Fe–Cu system. In this letter we report the ion-induced phase formation and amorphization in immiscible Co/Ag multilayers with the composition of $Co_{25}Ag_{75}$ and also discuss the mechanism involved in the process. To the best of our knowledge, this is the first report on irradiation-induced phase transformation in Co/Ag multilayers with a composition of $Co_{30}Ag_{70}$, which shows the maximum GMR [2].

The Ag(20 nm)/[Co(5 nm)/Ag(20 nm)]$_4$ multilayer films were deposited on NaCl substrates in a UHV chamber at a base pressure of 8×10^{-10} mbar by using electron beam evaporation at a thickness rate of 0.01 nm s^{-1}. Individual layer thickness of the elements has been calculated for an overall composition of 30% Co and 70% Ag, considering the density and volume of the individual layers. The Co/Ag samples were irradiated with 130 keV Ar^+ ions with a fluence of 7×10^{16} ions cm^{-2} at room temperature using a 150 kV ion accelerator. In order to avoid beam heating, the beam current was limited to less than 0.5 μA cm^{-2}. The range of penetration of Ar^+ ions in the multilayered sample was found to be 58 nm with a straggling of 28 nm using Monte Carlo simulation [9] SRIM 2000. All irradiated films were removed from the NaCl substrates by deionized water and put on Cu grids and then analysed by transmission electron microscopy (TEM) and also by selected area electron diffraction (SAED) techniques. The base pressure of the TEM was of the order of 10^{-7} Torr. The chemical composition was examined using a Philips CM200 model TEM equipped with EDAX facility.

Figures 1(a) and (b) show the typical microstructure and the corresponding electron diffraction pattern from the as-prepared Co/Ag multilayer. The EDAX mapping of the as-prepared sample at low magnification ($\sim\mu$m scale) showed that the sample has a homogeneous microstructure. However, at higher magnification ($\sim$nm scale) lateral inhomogeneity is seen as shown in figure 1(a), where the white regions correspond to more Co($Co_{90}Ag_{10}$) and the black regions contain more Ag($Co_{10}Ag_{90}$). It can be seen that the d values corresponding to the diffraction pattern of figure 1(b) is indexed and given in table 1. The electron diffraction pattern shows the sharp diffraction lines from the fcc phase of Ag and Co. In addition to these lines, one can also observe lines corresponding to the hcp phase of Ag which has been reported recently in Ag particles having sizes less than 30 nm [10]. Irradiation of the sample up to a fluence of 5×10^{16} ions cm^{-2} showed that no significant structural change emerged, i.e. the SAED pattern revealed only polycrystalline Co and Ag phases of the as-prepared sample. When the fluence was increased up to 7×10^{16} ions cm^{-2}, interesting structural evolution took place in the multilayered film. Figure 2(a) is a bright field image of the irradiated sample showing some nanosized grains (dark particles) embedded in a grey matrix. Figure 2(b) shows the corresponding electron diffraction pattern of figure 2(a). The formation of a new metastable phase is clearly seen by comparing the electron diffraction patterns of figures 1(b) and 2(b)

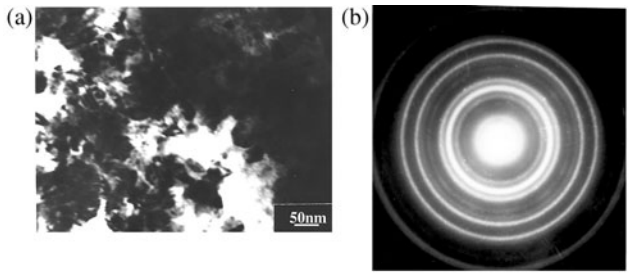

Figure 1. (a) TEM image showing the morphology of the as-prepared Co/Ag multilayer and (b) the corresponding SAD pattern.

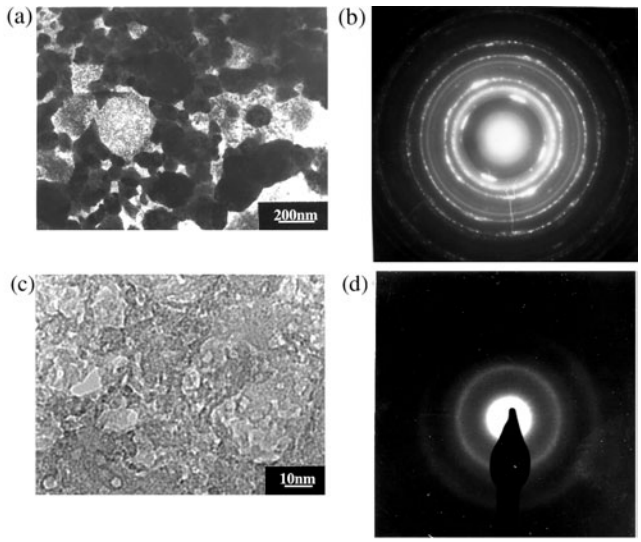

Figure 2. (a) TEM image showing the morphology of the Co/Ag multilayer irradiated with 130 keV Ar^+ ions with a fluence of 7×10^{16} ions cm^{-2} and (b) the corresponding SAD pattern. (c) shows the morphology of the matrix (grey region of figures 2(a)) and (d) shows the corresponding SAD pattern.

given in table 1. The d values of the unknown phase could only be indexed to a hcp phase with an a value of 2.84 Å and the c/a ratio is approximately 1.65. The EDAX analysis gives the composition of the irradiated sample to be $Ag_{76}Co_{24}$, hence the composition of the hcp metastable phase is close to the A_3B type. In the irradiated sample (refer to figure 2(a)), the black particles contain more Ag and the grey region contains more Co. Figures 2(c) and (d) show the microstructure and the SAED pattern taken for the grey region in figure 2(a). The SAD pattern shows hollow rings indicating the amorphous nature of the matrix.

Before discussing the experimental results, we describe briefly the experimental conditions of the present work. In these experiments, the energy of irradiation is chosen such that the thickness of the film is approximately equal to the mean damage depth and mean ion range, thereby maximizing the atomic mixing at the interface regions. For the fluences used (maximum 7×10^{16} ions cm^{-2}) for ion irradiation, the implanted Ar^+ ions are immobile and it results in an Ar concentration of at most 8 at.% at the mean range. However, noble gases

Table 1. Indexing results of the diffraction lines shown in figures 1(b) and 2(b).

d values (Å)			Indices ($h\,k\,l$)			
			New phase (hcp)	Ag hcp		
		New phase	$a = 2.84$ Å	$a = 2.886$ Å	Ag fcc	Co fcc
As-prep.	Irradiated	(DO_{19} phase)	$c/a = 1.65$	$c/a = 3.489$	$a = 4.086$ Å	$a = 3.544$ Å
	2.8585	2.859	4 1 2			
	2.4847	2.485	1 0 0			
2.341					1 1 1	
	2.393	2.393	2 0 4			
2.071	2.071					1 1 1
	1.737	1.7366	2 2 4			
1.775						2 0 0
	1.615			0 0 6		
1.583				1 0 5		
1.468	1.468			1 1 0		
	1.417	1.4167	1 1 0			
1.262						2 2 0
	1.252	1.2519	2 0 0			
1.056						3 1 1
	1.009			0 0 10		
0.961					3 3 1	
	0.9296	0.9229	2 1 0			

diffuse in Ag by a vacancy mechanism [11] and single vacancies and divacancies become mobile at 240 K in Ag [12]. Hence, at the irradiation temperature, i.e. 300 K, there will be a considerable reduction in Ar concentration due to the gas release effect. Trapping of gas atoms by bombardment-induced vacancies will result in very small bubbles, which are practically unresolvable [13]. In fact, we have not observed any gas bubbles during TEM examination of all the samples. However, the volume fraction of these very small bubbles is expected to be less than 2 vol% [12, 13].

In summary, the structural change upon irradiation of a Co/Ag multilayer sample can be expressed as

$$\text{Crystalline(Ag + Co)} \xrightarrow{7\times10^{16}\,\text{Ar}^{+}\text{cm}^{-2}\,130\ \text{keV}} \text{hcp metastable phase(Ag}_3\text{Co)} + \text{crystalline(Ag + Co) + amorphous matrix.}$$

We now discuss the mechanism behind the structural evolution observed in a Co/Ag multilayer upon 130 keV Ar^+ ion irradiation. In the ion beam mixing process, there are two consecutive steps, namely atomic collision and relaxation period. During the first step, the irradiating energetic ion induces a series of atomic collisions, namely an atomic collision cascade, which induces atomic mixing between the Ag and Co layers and drives the resultant atomic mixture to a highly energetic state, which is far from equilibrium. According to atomic collision theory, this highly energetic state relaxes towards equilibrium during the extremely short relaxation period, lasting only for 10^{-10}–10^{-9} s [14]. Consequently the disordered mixture cannot go directly to an equilibrium state in most cases; instead it frequently resides in the possible intermediate energetic states, which correspond to metastable, crystalline, amorphous and some other alloy phases.

Liu *et al* [15] have investigated irradiation and interface-induced formation of a non-equilibrium A_3B type phase in the Ag–Co system. Out of the many possible A_3B type phases, they have calculated the total energy (by the first principle method) for six simple structures,

based on the fact that the non-equilibrium crystalline phases experimentally observed by ion beam mixing are usually of simple structures such as hcp and fcc, due to the restricted kinetic conditions involved in the process. Among these, DO_{19} and $L1_2$ phases have the lowest minimum total energy. Further, the total energy difference between the DO_{19} phase and the $L1_2$ phase is about 0.002 eV/atom, i.e. 0.06%. The difference in atomic volume between the DO_{19} and $L1_2$ structures is less than 0.01%, reflecting the well-known fact that the fcc and hcp structures have similar atomic configurations. Further, these authors observed a metastable fcc ($L1_2$) Ag_3Co phase in the Ag–Co multilayers upon ion irradiation at 77 K. However, our result shows the formation of a hcp metastable Ag_3Co phase upon ion irradiation at room temperature. The a and c/a values found from our experiment match closely the theoretical values obtained by Liu *et al*. Since the total energy of the fcc ($L1_2$) and hcp (DO_{19}) phases of Ag_3Co are too close, the observation of a fcc ($L1_2$) phase at 77 K and a hcp (DO_{19}) phase at 300 K irradiation can be possibly explained from kinetic considerations [15]. The unit cell of the DO_{19} structure contains more atoms per unit cell than the $L1_2$ structure and has a larger unit cell. Therefore, it probably requires a larger critical radius for nucleation and growth. Hence the DO_{19} phase requires a relatively high temperature to enhance the atomic mobility and a longer time to enable the atoms to organize themselves into an ordered configuration.

The above discussion is based on total energy calculation and kinetic considerations. However, the formation energy of these alloy phases is higher [15] than that of the reference state (a mechanical mixture of pure Ag and pure Co with a chemical stoichiometry of 3:1). Hence these phases could be obtained by the non-equilibrium method such as the present one, i.e. ion beam mixing of multilayers, in which the interfacial free energy of the multilayered films is of help in reducing the energy gap between its energetic and reference states. From the calculated free energy diagram of the Ag–Co system [15], the free energy difference between the metastable Ag_3Co phase system and the interfacial energy of multilayers is 0.07 eV/atom. This small energy difference can possibly be overcome by irradiation energy and the interfacial energy of the bubble microstructure produced during Ar^+ ion irradiation, which was discussed earlier.

In conclusion, the formation of a new hcp metastable (DO_{19}) phase has been observed in the immiscible Co/Ag multilayer by ion beam mixing with the matrix being amorphized.

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