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LETTER TO THE EDITOR

The effect of thickness on amorphization behaviour in Fe–Mo multilayered films induced by ion mixing

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Abstract. In Fe–Mo multilayered films, when the number of metal layers is kept constant, the amorphization behaviour relates closely to the thickness of the films upon energetic xenon ion mixing. In 60 nm thick films, amorphization was achieved in a narrow range around the equiatomic stoichiometry, i.e. 40–60 at.% Fe, while in 40 nm thick films it could be reached within a broad range of 23–77 at.% Fe. The grain boundary energy involved in Fe–Mo multilayered films was estimated by a simple model, and is believed to be a major thermodynamic driving force for amorphization.

Amorphous alloys are expected to have many novel properties and have attracted much research endeavour since the first synthesis in the early 1960s [1]. From then on, many techniques, e.g., liquid melt quenching [1], solid state reaction [2], mechanical alloying [3] and ion beam mixing [4], have been developed to produce amorphous materials and to study the amorphization mechanism. The common knowledge to date is that a large negative heat of formation and a large atomic size mismatch favour amorphization in a system [2]. As a step forward, Alonso and co-workers [5] proposed a semi-quantitative approach, which allows the free energy of various phases, e.g. terminal solid solutions, intermetallic compounds and amorphous alloys, to be calculated and compared. From this treatment, it has been made clear that a large negative heat of formation makes amorphous alloys have energies lower than that of the reference state, i.e. mixtures of pure crystalline components in bulk states, and serves as a thermodynamic driving force. In systems with a small negative heat of formation, e.g. -3 kJ mol^{-1} for the Fe–Mo system, however, no thermodynamic driving force is available for amorphization, indicating phase separation. Although amorphization in these systems is predicted to be thermodynamically unstable in the bulk state, it is possible in multilayered films [6]. However, the alloying behaviour and amorphization mechanism in these systems are still open questions. The Fe–Mo system with a small negative heat of formation (-3 kJ mol^{-1}) and a mismatch of 27% in atomic size was therefore selected for this study.

In this letter, we report a thickness-dependent amorphization behaviour in Fe–Mo multilayered films, and a possible thermodynamic interpretation based on a simple model. The influence of the small negative heat of formation on amorphization behaviour was also discussed.

40 and 60 nm thick Fe–Mo multilayered films, with various compositions and consisting of six metal layers, were prepared in an e-gun deposition system with a vacuum level of the order of 10^{-7} Torr by depositing alternately pure Fe (99.99 at.%) and Mo (99.9 at.%) onto newly cleaved NaCl single crystals as substrates cooled by running water. The total

thickness of these multilayered films was designed to match the projected range plus the projected range straggling of the energetic ions, i.e. 40 and 60 nm for 200 and 300 keV xenon ions, respectively. The composition of the films was controlled by adjusting the thickness of each metal layer and was confirmed later by energy dispersive spectrum (EDS) analysis with an error less than 5%. The multilayered films were then mixed by xenon ions at room temperature in an implanter with a vacuum level better than 5×10^{-6} Torr. During irradiation, the beam current density was controlled to be less than $1 \mu\text{A cm}^{-2}$ to minimize the beam heating effect. Transmission electron microscopy (TEM) and selected area diffraction (SAD) were employed to identify the structure of the mixed films and EDS analysis was used to determine the composition of the resultant phases.

We first check the 40 nm thick multilayered films. Table 1 lists the structural changes under energetic xenon ion mixing in 40 nm thick Fe–Mo multilayered films. It is seen that amorphization was achieved in all samples studied, i.e. $\text{Fe}_{23}\text{Mo}_{77}$, $\text{Fe}_{27}\text{Mo}_{73}$, $\text{Fe}_{33}\text{Mo}_{67}$, $\text{Fe}_{44}\text{Mo}_{56}$, $\text{Fe}_{72}\text{Mo}_{28}$, $\text{Fe}_{72}\text{Mo}_{28}$ and $\text{Fe}_{77}\text{Mo}_{23}$, at different irradiation doses. Figure 1 demonstrates corresponding SAD patterns of the $\text{Fe}_{44}\text{Mo}_{56}$ multilayered film before irradiation and amorphized at a dose of $3 \times 10^{15} \text{Xe}^+ \text{cm}^{-2}$. The experimentally determined composition range favouring amorphization in Fe–Mo multilayered films by this study is then 23–77 at.% Fe. It seems that, despite lacking a thermodynamic driving force in the bulk state, amorphization can be easily reached in Fe–Mo multilayered films. In 60 nm thick Fe–Mo multilayered films mixed by 300 keV xenon ions, however, amorphization was only observed around the equiatomic stoichiometry, i.e. 40–60 at.% Fe. This is much narrower than the range in 40 nm thick films of 23–77 at.% Fe. Regardless of the probably negligible effect of ion energy on amorphization, it is the difference in thickness, i.e. 40 and 60 nm, that resulted in the sharp difference in amorphization range in two films.

Table 1. Formation of amorphous alloys in 40 nm thick Fe–Mo multilayered films induced by room-temperature 200 keV xenon ion mixing. ('A' stands for amorphous alloys; 'bcc' stands for solid solution.)

Dosage ($\times 10^{14}$)	$\text{Fe}_{23}\text{Mo}_{77}$	$\text{Fe}_{27}\text{Mo}_{73}$	$\text{Fe}_{33}\text{Mo}_{67}$	$\text{Fe}_{44}\text{Mo}_{56}$	$\text{Fe}_{72}\text{Mo}_{28}$	$\text{Fe}_{77}\text{Mo}_{23}$
3	Fe+Mo	Fe+Mo	Fe+Mo	Fe+Mo	Fe+Mo	Fe+Mo
7	Fe+Mo	bcc	bcc	Fe+Mo	bcc	bcc
9	A			Fe+Mo+A	bcc+A	bcc
30	A+bcc		A	A	A	A
50	bcc		A	A	A	A
70	bcc	A	A	A	A	A

The question that should be first answered is why amorphization could be achieved in Fe–Mo multilayered films. In other words, what is the thermodynamic driving force? Figure 2 shows a free energy diagram calculated according to Alonso's method. Like most systems having a small negative heat of formation, Fe–Mo amorphous alloys are thermodynamically unstable in the bulk form as they have higher free energies than that of the commonly used reference state. It is well known that multilayered films with each layer being several to several ten nanometres thick differ in energy from the bulk state [2]. Among the extra energies possibly involved, e.g. strain energy, surface and interface energy and grain boundary energy, the grain boundary energy, when the thickness of each metal layer decreases to a few nanometres, becomes a major contribution. This term can be calculated by $\Delta E = f(s)\sigma_g V_m/d$, where σ_g is the large-angle grain boundary energy, d is the grain size, V_m is the molar volume and $f(s)$ is a factor determined by the shape of

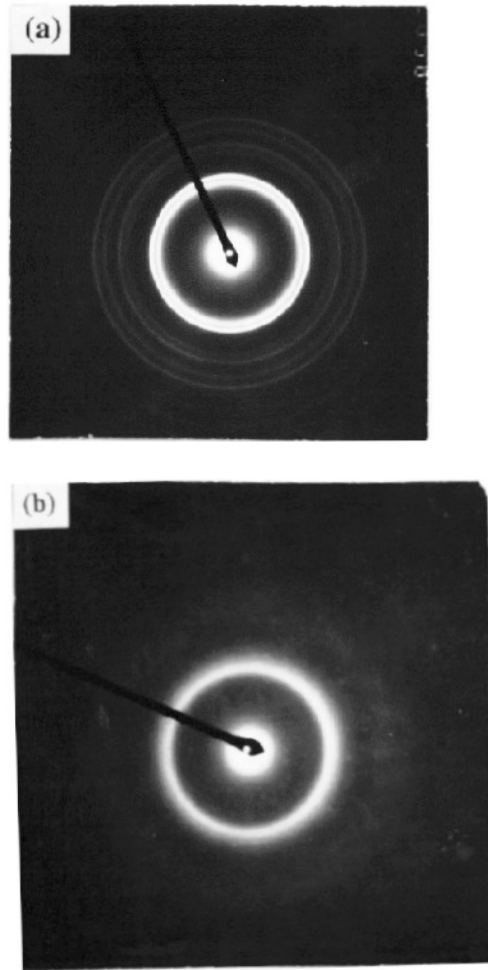


Figure 1. Typical SAD patterns of $\text{Fe}_{44}\text{Mo}_{56}$ multilayered films: (a) as deposited; (b) amorphized at a dose of $3 \times 10^{15} \text{Xe}^+ \text{cm}^{-2}$.

the grains located in the range $2 \leq f(s) \leq 6$. Generally, we can use three perpendicular parameters, i.e. a and b as two in-plane parameters and c as the out-plane parameter, to describe a three-dimensional grain. As a reasonable assumption c can be approximated by the thickness of metal layers, i.e. 10 and 6.7 nm for 60 and 40 nm thick films, respectively. Replacing grain size d with c , $f(s)$ becomes a function of a/c and b/c , which can be estimated experimentally. Figure 3 is a typical bright-field image of a 40 nm thick $\text{Fe}_{44}\text{Mo}_{56}$ multilayered film before irradiation showing the morphology of various grains. One sees that for the majority of grains at least one of the in-plane parameters, i.e. a or b , is close to the value of c . This limits the value of $f(s)$ to be within $4 < f(s) \leq 6$. Accordingly, by using the σ_g data for Mo and Fe [7], the grain boundary energies involved in 40 and 60 nm thick multilayered films were calculated and added to figure 2 as solid lines for $f(s) = 6$ and dashed lines for $f(s) = 4$. These solid and dashed lines form two bands, which give the upper and lower limits of grain boundary energy. It is a good approximation to use the grain boundary energy to present the initial energetic state of the Fe–Mo multilayered

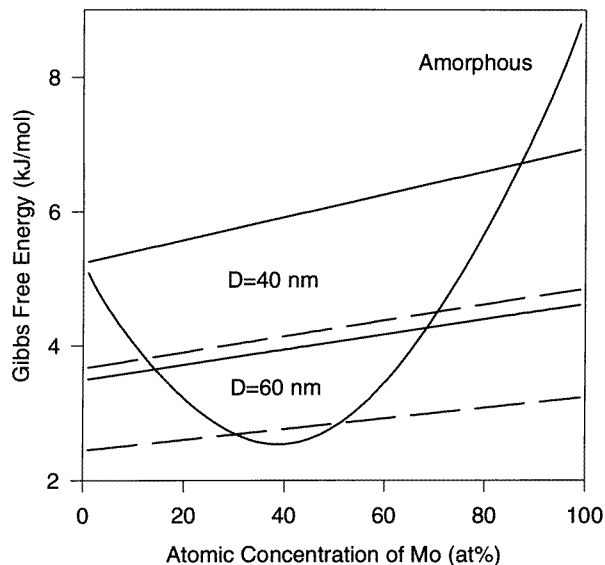


Figure 2. The free energy of the Fe–Mo system based on Alonso’s approach. The two energy bands formed by solid and dashed lines represent the energy levels of 40 and 60 nm thick Fe–Mo multilayered films, and are labelled with $D = 40$ nm and $D = 60$ nm, respectively.

films as other possibly involved extra energies may shift it upwards a little without adding much error. The initial energetic state of Fe–Mo multilayered films is therefore located in the corresponding energy band, and should be used as a reference state since the above amorphization phenomenon occurs in multilayered films. It follows that amorphization is thermodynamically favoured in both 40 and 60 nm thick multilayered films. That is to say, the grain boundary energy could serve as a major thermodynamic driving force.

We now discuss qualitatively the effect of thickness on amorphization behaviour in Fe–Mo multilayered films. The composition range favouring amorphization, if the thermodynamic driving force were the grain boundary energy, would depend on the initial energetic levels of Fe–Mo multilayered films. As the number of metal layers is fixed at six in the present study, the value of c has a positively linear relationship with the thickness. Consequently, the initial energetic level of Fe–Mo multilayered films decreases in a hyperbolic manner when increasing the thickness. Figure 4 illustrates this relationship. The amorphization range in Fe–Mo multilayered films also decreases with increasing thickness, which is what we observed.

A point worth mentioning is that, although amorphization could be achieved in multilayered films of systems with either a small negative heat of formation or a positive heat of formation [8], the alloying behaviour is quite different. In systems such as Fe–Mo, amorphization was relatively easy to achieve around equiatomic stoichiometry, i.e. 40–60 at.% Fe, while in systems of a positive heat of formation it is very hard to reach amorphization in the middle-composition range [8]. This difference was believed to result from the sign of the heat of formation. In the Fe–Mo system, although the small value of the heat of formation cannot serve as the thermodynamic driving force, the negative sign makes amorphous alloys have a concave shape in the energy curve and have the largest driving force around equiatomic stoichiometry. In systems with a positive heat of formation

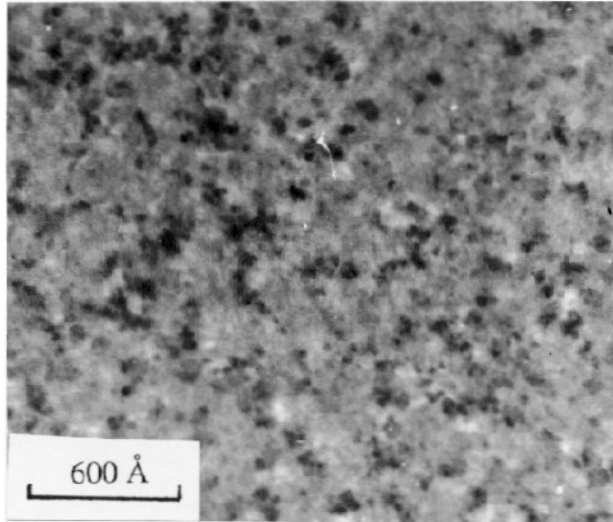


Figure 3. A typical bright image of an Fe₄₄Mo₅₆ multilayered film, showing the morphology of the grains.

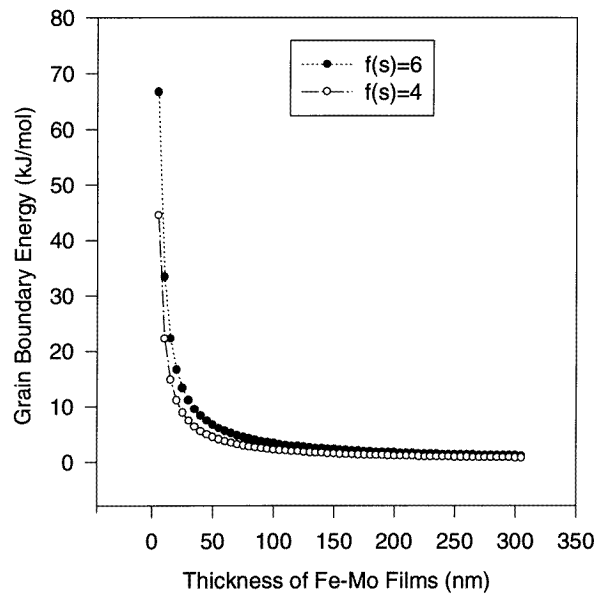


Figure 4. The relationship between the grain boundary energy and the thickness of an Fe₄₄Mo₅₆ multilayered film.

such as Ag–Mo, however, the free energy curve is convex in shape, resulting in the smallest driving force in the middle-composition range for amorphization.

In conclusion, amorphization was achieved by room-temperature energetic xenon ion mixing of Fe–Mo multilayered films. The thermodynamic driving force was the grain boundary energy stored in the multilayered films.

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