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Ion-induced grain growth in multilayer and coevaporated metal alloy thin films

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Irradiation experiments were conducted on multilayer (ML) and coevaporated (CO) thin films in order to examine the role that the heat-of-mixing (ΔH_{mix}) has in ion-induced grain growth. Room-temperature irradiations using 1.7 MeV Xe were performed in the High Voltage Electron Microscope at Argonne National Laboratory. The alloys studied (Pt–Ti, Pt–V, Pt–Ni, Au–Co and Ni–Al) spanned a large range of ΔH_{mix} values. Comparison of grain growth rates between ML and CO films of a given alloy confirmed a heat of mixing effect. Differences in grain growth rates between ML and CO films scaled according to the sign and magnitude of ΔH_{mix} of the system (with the exception of the Pt–V system). Substantial variations in growth rates among CO alloy films experiencing similar irradiation damage demonstrated that a purely collisional approach is inadequate for describing ion-induced grain growth and consideration must also be given to material-specific properties. Results from CO alloy films were consistent with a thermal spike model of ion-induced grain growth. The grain boundary mobility was observed to be proportional to the thermal spike-related parameter, $F_D^2/\Delta H_{coh}^3$, where F_D is the energy deposited in nuclear interactions and ΔH_{coh} is the cohesive energy.

1. Introduction

A number of studies have examined the effect of irradiation on grain growth in elemental [1–4] and coevaporated metal alloy [5] thin films. Grain growth has also been reported in ion beam mixing experiments in a number of different alloy systems [6–8]. However, unlike elemental and coevaporated alloy films, other systematic studies of ion beam mixing-induced grain growth are absent. Previous work [8] examining the effects of ion beam mixing in the Ni–Al system suggested that the heat-of-mixing, ΔH_{mix}, affected ion-induced grain growth. Multilayer Ni–Al films underwent greater grain growth than coevaporated films of the same composition [8]. Because of the multilayer structure, an ion mixing-induced ΔH_{mix} release, could have enhanced the kinetics of grain growth in these films.

The present study systematically examined the impact of ΔH_{mix} on ion-induced grain growth by studying a variety of multilayer alloys with varying heats-of-mixing. The results indicated that a purely collisional approach was inadequate for describing observed grain growth. Furthermore, a trend was present in which, within a given alloy, differences in grain growth rates between multilayered and coevaporated films scaled according to the sign and magnitude of ΔH_{mix} of the system. Additionally, results from coevaporated alloy films were consistent with a thermal spike model of ion-induced grain growth. Here we briefly summarize results the details of which will be published elsewhere [9].

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2. Experimental

Thin (~ 400 Å) films of coevaporated and multilayer alloys of similar composition were prepared by e-beam evaporation in a vacuum system with a base pressure at 2×10^{-7} Torr or less. Since the heat-of-mixing was suspected to influence ion-induced grain growth, the alloys chosen for study spanned a large range of ΔH_{mix} values. Table 1 summarizes the material and irradiation parameters of the alloys used. With the exception of Ni–Al, all the alloys possessed similar mass ratios and therefore had similar nuclear deposition energies as determined from TRIM-90 calculations [13]. As indicated in table 1, films of A-rich A–B alloys were made with A = Ni, Pt or Au and B = Al, Ti, V, Ni and Co. In multilayers, the A layers (A = Ni, Pt or Au) were typically of the order of 50–60 Å thickness and the B layers (B = Al, Ti, V, Ni or Co) were typically 10–20 Å thick.

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Table 1
Summary of material and irradiation parameters used in 1.7 MeV Xe ion-induced grain growth studies

A–B alloy [at.%]	Film type [a]	$\Delta H_{coh(AB)}$ [b] [eV]	ΔH_{mix} [c] [eV]	F_D [d] [eV/Å]
Pt–15Ti	ML	−6.21	−0.52	360
Pt–15Ti	CO	−6.21	none	360
Pt–18V	ML	−6.03	−0.28	360
Pt–15V	CO	−6.04	none	360
Ni–21Al	ML	−4.45	−0.23	225
Ni–23Al	CO	−4.43	none	225
Pt–21Ni	ML	−5.58	−0.03	380
Pt–17Ni	CO	−5.63	none	380
Au–20Co	ML	−3.89	+0.04	340
Au–10Co	CO	−3.83	none	335

[a] Film type: ML = multilayers; CO = coevaporated.
[b] Average alloy cohesive energies determined from elemental values according to $\Delta H_{coh(AB)} = f_A\, \Delta H_{coh(A)} + f_B\, \Delta H_{coh(B)} + \Delta H_{mix}$, where f_A and f_B are the atom fractions of the A and B alloy elements, respectively.
[c] Heat-of-mixing values approximated by values of formation enthalpies for stoichiometric A_5B alloys [10–12].
[d] Energy deposited in nuclear interactions calculated using TRIM-90 Monte Carlo simulation [13]. Values for F_D were determined for each depth bin from TRIM-90 calculated energy deposition parameters according to F_D = (Energy absorbed by recoils) − (Ionization by recoils) + (Phonons by ions). The F_D value quoted in the table is the average of these bin values determined over the 400 Å of the film thickness.

Room temperature irradiations were conducted in the High Voltage Electron Microscope (HVEM) in the Materials Science Division at Argonne National Laboratory. The HVEM was interfaced with a beamline from a tandem accelerator and in situ irradiations were performed using 1.7 MeV Xe ions. Dose rates used were chosen to avoid beam-induced heating and varied in the range of $(0.17–1.7) \times 10^{12}$ cm^{-2} s^{-1}.

Grain size measurements were obtained from dark-field transmission electron microscope images of as-evaporated and irradiated films after increments of ion dose. Sizes were determined from the largest lateral dimension of highlighted grains in the dark-field imaged prints. At least 200 grains were measured per sample.

3. Results

Normal grain growth was observed to proceed according to a power law dependence with ion dose as shown in fig. 1 for Pt–Ti and Ni–Al films. The solid lines in fig. 1 are least-squared-error fits determined according to the expression,

$$L^n - L_0^n = K\Phi, \qquad (1)$$

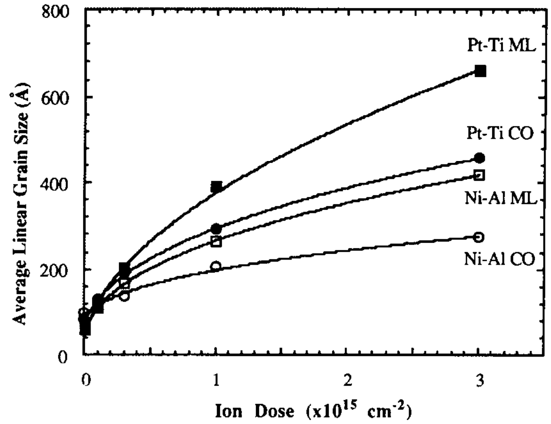

Fig. 1. The effect of ion dose on grain size in Pt–Ti and Au–Co multilayer (ML) and coevaporated (CO) alloy films. Irradiations performed with 1.7 MeV Xe at room temperature. Solid lines are best fit curves to the measured data according to eq. (1).

where L is the average linear grain size, Φ is the ion dose, L_0 is the best fit initial grain size, n is the best fit growth exponent and K is a best fit constant.

Variations in grain growth rates were observed between alloys, and between coevaporated and multilayer films of a given alloy. In order to quantify these differences, ion-induced grain growth rates, dL/dt, were evaluated. Rates for all the alloys and film types were determined according to $dL/dt = \dot{\Phi} dL/d\Phi$ where $\dot{\Phi}$ was the ion dose rate and $dL/d\Phi$ was obtained from the slopes of the fitted grain growth versus ion dose curves evaluated at a dose of $\Phi = 10^{14}$ cm^{-2} (see table 2).

4. Discussion

The differences in growth rates found among the collisionally similar coevaporated films used in this study demonstrated that a purely collisional approach was inadequate for describing ion-induced grain growth.

Table 2
1.7 MeV Xe ion-induced grain growth rates for multilayer (ML) and coevaporated (CO) alloy films at a dose of $\Phi = 10^{14}$ cm^{-2}

Alloy	ΔH_{mix} [eV]	$\left.\frac{dL}{dt}\right\|_{ML}$ [Å/s]	$\left.\frac{dL}{dt}\right\|_{CO}$ [Å/s]	$\frac{(dL/dt)_{ML}}{(dL/dt)_{CO}}$
Pt–Ti	−0.52	0.95	0.70	1.36
Pt–V	−0.28	0.80	0.82	0.97
Ni–Al	−0.23	0.61	0.32	1.89
Pt–Ni	−0.03	0.91	0.89	1.02
Au–Co	0.04	0.86	1.40	0.61

As indicated in table 1, all the alloys used in the irradiations, except Ni–Al, experienced nearly the same energy deposited in nuclear interactions, F_D. However, considerable differences were observed in ion-induced grain growth rates. From table 2 Au–Co coevaporated films were observed to have a factor of two greater grain growth rate than Pt–Ti coevaporated films. According to table 1, both of these alloys have nearly identical F_D values so that both are expected to undergo essentially identical displacement damage.

The conclusion that collisional displacements alone are inadequate for describing ion-induced grain growth is consistent with previous work. Irradiation studies by Liu [5] showed that Ni–Co and Ni–Cu coevaporated films, with similar F_D, underwent substantially different ion-induced grain growth. Li et al. [3] observed considerable deviations in grain growth induced in Au and Pt films, which are similar in mass. Both of these results and those of the present study demonstrate that an understanding of the ion-induced grain growth process also requires consideration of material-specific properties. In the coevaporated films, additions of the alloying element could have substantially modified the activation energy for grain growth, and in turn, enhanced or inhibited growth.

An effect of heat-of-mixing was observed between ion-induced grain growth results in multilayer and coevaporated films of the same average composition. Differences in the ratios of grain growth rates between the two film types were observed to correlate in each alloy (with the exception of Pt–V) with the sign of ΔH_{mix} (see table 2). Negative heat-of-mixing ($\Delta H_{mix} < 0$) values exhibited an enhancement in grain growth rates while the opposite was observed for positive heat-of-mixing ($\Delta H_{mix} > 0$) values when growth rates in multilayers were compared with growth rates in corresponding coevaporated films. In the Pt–Ti and Ni–Al systems, with their large negative ΔH_{mix} (see table 1), the multilayers experienced faster grain growth than their coevaporated counterparts. In the Pt–Ni system, with a small negative ΔH_{mix}, virtually no difference was observed between multilayers and coevaporated films. The Au–Co system with a positive ΔH_{mix}, showed results opposite those observed for the large negative ΔH_{mix} systems. The coevaporated alloy film experienced faster grain growth than the multilayers of similar composition. The magnitude of this difference, however, may have been affected by the fact that a substantial difference (10 at.%) in Co concentration existed between the coevaporated and multilayer alloy films.

The exception to the above trends was the Pt–V alloy system in which both multilayers and coevaporated films experienced nearly identical ion-induced grain growth rates. This occurred despite the fact that the estimated ΔH_{mix} for this system is negative and of the same magnitude as that of Ni–Al (see table 1). However, it is noted that the quoted values in table 1 are based on model calculations [12], and the absolute error associated with the values could be quite large.

The heat-of-mixing might affect the kinetic mechanisms of ion-induced grain growth via a Darken effect in which atomic mobility is either enhanced or inhibited according to the sign of the heat-of-mixing. The magnitude of ΔH_{mix} in many of the alloys, as shown in table 1, is quite substantial in comparison with activation energies for thermally induced grain growth in thin films which are typically on the order of 1 eV. As a result, it appears likely that ΔH_{mix} significantly impacts the grain growth kinetics.

5. Thermal spike model of ion-induced grain growth

The observations associated with ion-induced grain growth described above were in many ways analogous to those associated with ion beam mixing. Systematic studies [14] examining bilayer intermixing under heavy ion irradiation showed that the intermixing rate varied considerably among alloys with similar F_D. Also ΔH_{mix} was observed to affect the intermixing rate, with large negative ΔH_{mix} promoting faster intermixing. The magnitudes of intermixing rates were considerably greater than what was predicted from purely collisional irradiation considerations. Johnson et al. [14] developed a phenomenological model using the concept of thermal spikes to describe ion beam mixing rates across a wide range of alloys.

The analogy between results of ion beam mixing and ion-induced grain growth experiments suggested that a thermal spike model might also be useful in describing ion-induced grain growth. This idea was originally proposed by Liu et al. [2]. Recently, two of us [15] developed a thermal spike model of ion-induced grain growth. The main results of our model can be used to interpret the coevaporated film data presented here.

In the model, spikes occurring on or near grain boundaries thermally activate atoms to jump across the boundary. Within a thermal spike, if a net number of atom jumps occurs in one direction across the boundary (due to some biased driving force), boundary migration occurs in the opposite direction. The grain boundary migration rate may be described by

$$\frac{dL}{dt} = -M_{ion}\frac{\partial\mu}{\partial x}, \quad (2)$$

where M_{ion} is the ion-induced grain boundary mobility and $\partial\mu/\partial x$ is the driving force. For normal grain growth, the driving force is taken to be the grain boundary curvature which is expressed as $\partial\mu/\partial x = 4\gamma\Omega/L\delta$ with γ the surface tension, Ω the atomic volume and δ the grain boundary width. Assuming cylindrical thermal spikes [16] and thermally activated atom jumps driven

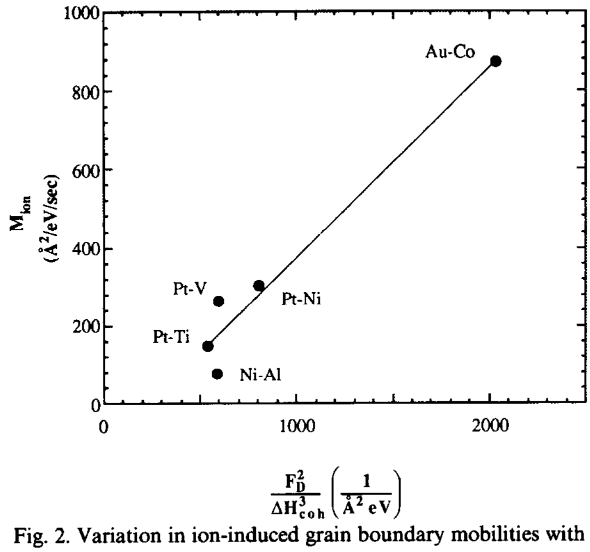

Fig. 2. Variation in ion-induced grain boundary mobilities with the thermal spike-related parameter determined for a grain boundary curvature driving force. Data are for coevaporated films irradiated with 1.7 MeV Xe. Solid line is a linear least-squared-error fit to the data.

by grain boundary curvature, it can be shown [15] that a proportionality exists between the ion-induced mobility and the energy deposited in nuclear interactions, F_D, and the cohesive energy of the alloy, ΔH_{coh},

$$M_{ion} \propto \frac{F_D^2}{\Delta H_{coh}^3}. \quad (3)$$

Experimental values of M_{ion} were determined using eq. (2) for the experimental coevaporated data of the present study. Assuming only a boundary curvature driving force, M_{ion} is determined from the slope of grain growth rate versus this driving force. In fig. 2 these experimentally derived values of M_{ion} are plotted against the corresponding values of the thermal spike-related parameter $F_D^2/\Delta H_{coh}^3$. A trend is clearly present in which larger values of $F_D^2/\Delta H_{coh}^3$ correspond to larger ion-induced grain boundary mobilities. A similar dependence of grain growth rate on F_D was found by Liu [5] in irradiated elemental and coevaporated films.

A similar attempt to describe ion-induced grain growth in multilayers was not successful [15]. In addition to grain boundary curvature, the effect of the driving force due to concentration gradients present in the multilayers was used to model atom migration within thermal spikes. In this manner it was possible to incorporate a ΔH_{mix} effect. The failure to describe the observed data suggested that the physical phenomena modeled, concentration gradients and the heat-of-mixing, were not the prevailing factors affecting ion-induced grain growth in multilayers films.

It is feasible that other driving forces may have been operative in the multilayers that were absent in the coevaporated films. Another possible factor affecting grain growth in multilayers is diffusion-induced grain boundary migration (DIGM) [17]. This phenomenon has often been observed in thin film bilayer couples annealed at relatively low temperatures where volume diffusion is expected to be negligible. It is conceivable that an irradiation DIGM phenomenon may be operative in the ion beam mixed multilayers, promoting grain growth rates that vary compared with those observed in the coevaporated alloy films. This idea was briefly considered by Prasad et al. [7] in a short report examining grain growth in ion mixed Fe–Al bilayers. A systematic study is presently under way to investigate the potential consequences of DIGM in irradiated bilayers.

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