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Temperature-Dependent Ion Beam Mixing*

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Temperature-Dependent Ion Beam Mixing

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Recent work addressing the enhanced interdiffusion rates typically observed during ion-beam mixing at elevated temperatures is reviewed. As discussed previously, the expected increase in ion-beam mixing rates due to "radiation-enhanced diffusion" (RED), i.e. the free migration of isolated vacancy and interstitial defects, is well documented in single-crystal specimens in the range of 0.4 to 0.6 of the absolute melting temperature. In contrast, the increase often observed at somewhat lower temperatures during ion-beam mixing of polycrystalline specimens is not well understood. However, sufficient evidence is available to show that this increase reflects intracascade enhancement of a thermally-activated process that also occurs in the absence of irradiation. Recent evidence is presented which suggests that this process is Diffusion-Induced Grain-Boundary Migration (DIGM). An important complementary conclusion is that because ion-beam mixing in single-crystal specimens exhibits no significant temperature dependence below that of RED, models that invoke only irradiation-specific phenomena, e.g., cascade-overlap, thermal-spikes, or liquid-diffusion, and hence which predict no difference in mixing behavior between single- or poly-crystalline specimens, cannot account for the existing results.

1. INTRODUCTION

Ion-beam mixing, which utilizes the kinetic energy of ion-beams to intermix pre-deposited surface layers with substrate materials, has greatly expanded the potential uses of ion-beams to modify materials properties. No other process appears to be as efficient as ion-beam mixing for introducing large, nonequilibrium concentrations of alloying elements into a wide variety of materials under carefully controlled conditions. The list of potential applications for ion-beam mixing has expanded further with the development of ion-assisted deposition. By combining ion-beam mixing with simultaneous deposition, ion-assisted deposition techniques remove the restriction on altered layer thickness imposed by finite ion ranges. This innovation has spurred renewed interest in understanding fundamental aspects of the ion-mixing process.

Thermally-activated processes provide additional mechanisms for producing ion-bombarded microstructures with novel or improved properties. Hence considerable interest exists in understanding the tempera-

**Although many papers quote "no temperature dependence" in this regime, the vast majority of experimental results display a statistically significant, usually positive increase in mixing rates with increasing temperature in the low-temperature regime.*

ture dependence of ion-beam mixing, and in particular, in determining the temperature range where freely-migrating defects can significantly enhance both the depth and magnitude of the intermixing.

The conclusions reached in an earlier review [1] regarding the temperature dependence of ion-beam mixing remain valid. However, new evidence has appeared which provides additional insight. Here, we provide an overview of the experimental and theoretical work which has appeared since the previous review, and summarize the current state of knowledge.

2. EXPERIMENTAL AND THEORETICAL STUDIES

Experimentally, three temperature regimes [1] of ion-beam mixing have been clearly identified: (1) low temperatures, where only a weak dependence of mixing rates on irradiation temperature is found; (2) intermediate temperatures, typically beginning near or slightly

above room temperature, where mixing rates become more strongly dependent on temperature; and (3) high-temperatures, typically above about 0.6 of the absolute melting temperature, where the additional mass transport induced by irradiation is negligible compared to that of thermally-activated interdiffusion, and therefore where ion-beam mixing becomes insignificant relative to thermal processes.

While the explanation [2] for efficient mixing at low temperatures in terms of enhanced mass transport during the "cooling phase" of energetic displacement cascades has become well established, and the logical basis underlying the high-temperature regime is widely accepted, the atomistic processes responsible for the intermediate temperature regime have remained controversial. This intermediate regime, first reported by Matteson et al. [3] in 1979, was initially attributed to the *thermally-activated, long-range migration of vacancy and interstitial defects generated during ion bombardment, i. e., radiation-enhanced diffusion (RED)*. However, as argued in a previous review, much of the available data on ion-beam mixing at intermediate temperatures differ substantially from measurements of known radiation-enhanced diffusion effects [4] in large-grain and single crystal specimens. In particular, the onset temperature is usually much too low, the measured activation enthalpies are frequently not of the expected magnitude and often display different magnitudes for different ions, and the existence of a well understood dose-rate dependence remains uncertain. Hence, although a region of "radiation-enhanced" ion-beam mixing is to be expected for all materials combinations, there is clearly one or more additional mechanisms which are responsible for the experimentally observed temperature dependence of ion-beam mixing in fine-grained specimens. Based upon the then recent work of Ding et al. [5], which showed a similar change in the temperature dependence of interdiffusion both with and without irradiation, we suggested that the observed increase in ion-beam mixing efficiency in polycrystals was due to an intracascade enhancement of an existing thermal process.

The Ding et al. results [5] for the measured temperature dependence of mixing in Au/Zr and Ni/Zr bilayers are shown in Fig. 1. As is typical for such studies [6], a weak temperature dependence is observed below a critical temperature (T_c), here $\sim 450\text{K}$, and an apparently thermally activated regime, with a much stronger temperature dependence, is found at higher temperatures. Most importantly, however, these results revealed that thermal annealing in the absence of irradiation generated the same Arrhenius region with essentially the identical transition temperature. Although ion irradiation increased the magnitude of interdiffusion, it was clearly not responsible for the existence of the two temperature regimes.

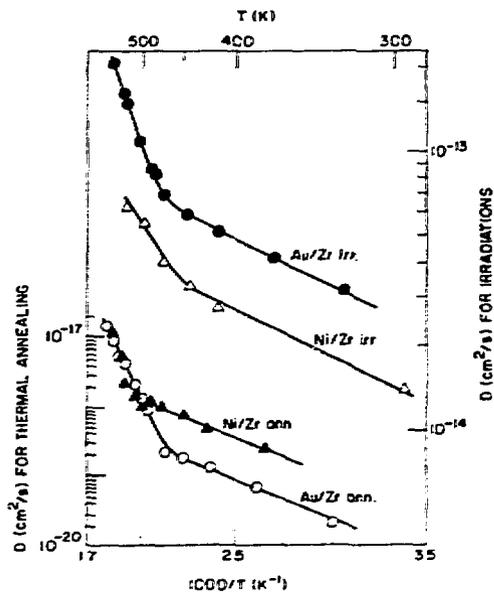


Fig. 1. Diffusion coefficients measured during ion-beam mixing (upper curves) and thermal interdiffusion (lower curves) of Au/Zr and Ni/Zr bilayers. Note that although irradiation clearly enhances the diffusion coefficients, the break in the temperature dependence occurs at essentially the same temperature both with and without irradiation.

Interdiffusion in the systems represented in Fig. 1 produce an amorphous product phase. In order to address the origin of the low onset temperature observed in many ion mixing experiments in amorphous alloys, de Reus et al. [7] suggest a specialized case of RED occurs for binary alloys in which the vacancy (hole) formation enthalpies of the constituents are significantly different. Two critical temperatures are predicted for mixing related to the hole formation enthalpies of the constituent atoms, which in turn are correlated with atomic sizes. At the lower critical temperature (identified as the T_c observed in most experiments) the atoms associated with the smaller constituent become mobile leading to an enhancement of diffusion. The "partial" RED that occurs may not necessarily promote equilibrium conditions and is therefore consistent with observations of metastable phase formation in this temperature regime. At a higher critical temperature, T_{eq} , the larger constituent becomes mobile and "conventional" RED results, i.e. the system tends toward equilibrium. Recent experimental results obtained by Desimoni et al. [8] in Pd/Si showed a T_{eq} substantially different from that predicted on the basis of this model. The situation in amorphous systems is complicated by the difficulty in defining "point defects" in aperiodic structures, and we will therefore restrict the remaining discussion to crystalline materials.

The temperature dependence of ion-beam mixing in self-ion irradiated, single-crystal specimens has been studied in detail by the Berlin group. A range of materials were studied, including Ni [9], Cu [10] and Fe-Cr-Ni alloys [11]. Recently, studies were also performed examining mixing of polycrystalline Pd on single-crystal Cu [12]. As explained previously, the results of these single-crystal experiments can be readily accounted for within the framework of RED.

In contrast to the single-crystal work, a number of ion-beam mixing studies [6]) have been performed on polycrystalline films. Although phenomenological correlations of T_c have been demonstrated with material properties such as cohesive energy [13, 14] and Debye temperature [15], these observations are not consistent with RED being the

mechanism responsible for the enhancement in mixing in the thermally activated regime. For example, Nastasi and Mayer [16] point out that the activation energies predicted by the Cheng et al. correlation are too large for RED.

In response to the growing recognition that RED cannot explain the vast majority of ion-beam mixing results in polycrystalline specimens, recent work has addressed the effect of temperature on cascade processes during ion mixing. Rossi and Nastasi [17] have examined the role of cascade structure. They used a Monte Carlo model to demonstrate that overlapping thermal spikes from displacement cascades can enhance mixing. Following molecular dynamics studies [18], the thermal-spike volume was assumed to increase with sample temperature. As the spike volume increased above a critical size, overlap occurred, increasing the mixing efficiency. In their model, the critical cascade size was determined by ballistic characteristics of the ion/target combination. Activation enthalpies in the range of 0.2-0.8 eV and onset temperatures in the range of $0.2-0.35T_m$ are predicted by the model, assuming parameters characteristic of Cu. The activation energy and onset temperature vary with collisional parameters, consistent with previous experimental observations of Shreter et al. [19] and Rossi and Nastasi [17].

Again following the ideas of cascade-induced melting generated by MD simulations, Alluralde et al. [20] have evaluated the role of temperature on diffusion within a small liquid volume. They used a binary collision code to determine the energy density deposited in the target. The resulting energetic recoils produce liquid droplets (spikes), the temporal and spatial evolution of which are determined by solving the heat conduction equation. Mixing is evaluated by integrating an Arrhenius diffusion function over the volume and lifetime of the spike. Sample temperature is incorporated into the process in two ways. First, in the binary collision calculations, higher temperatures decrease the lengths of replacement-collision-sequences, thus increasing the thermal-spike energy-density. Second, target temperature presumably figures in the boundary conditions for heat conduction. Increasing temperature results in longer-lasting, larger spikes and,

therefore, increased mixing. The onset temperatures for Cu and Ag were found to be in the vicinity of room temperature; activation energies were not determined.

In a similar fashion, Nastasi and Mayer calculated atomic transport within thermal spikes assuming a liquid diffusion process [16]. Diffusion was modeled using a hard sphere fluid and the kinetic gas theory of Enskog. Liquid diffusion data was fit to experimentally determined ion-beam mixing activation energies to obtain the temperature rise induced in a spike for particular materials. This temperature rise was then used with the melting temperature to define the lifetime of a thermal spike, which was determined from an analytic solution to the heat conduction equation. Finally, the mixing rate was evaluated by integrating the liquid diffusivity over the spike lifetime. The results of this approach reproduce the low onset temperature observed in experiments with, for example, Ni/Si. The activation energies are of course reproduced due to the fitting procedure. The model predicts a variation in activation energy with temperature rise induced in a spike. This temperature rise can be altered through variations in damage energy and thus experiments examining changes in activation energy with ion species should be able to test the model's validity.

A major flaw in these theoretical approaches is readily apparent. The single-crystal experiments, as mentioned above, show no enhanced temperature dependence from either cascade overlap or liquid diffusion. Because ion-beam mixing in single-crystal specimens exhibits no significant temperature dependence below that of RED, models that invoke only irradiation-specific phenomena, e.g., cascade-overlap or liquid-diffusion, and hence which predict no difference in mixing behavior between single- or poly-crystalline specimens, cannot account for the existing experimental results.

3. EFFECTS OF MICROSTRUCTURE

As pointed out in the earlier review, the temperature dependence of ion-beam mixing in polycrystalline films appears to be influenced by microstructural aspects, in particular the grain-

size. As an additional example, we take the temperature dependence of mass transport during ion irradiation in Ni. Akano et al. [21] studied mixing of Pd into fine-grained (~10 nm diameter) Ni during 120-keV Ar-irradiation; Muller et al. [9] examined the broadening of an isotopic marker in single-crystal nickel during 300-keV Ni-irradiation. The temperature dependence of the effective diffusion coefficients obtained from these experiments is shown in Fig. 2. Both sets of data exhibit two temperature regimes of mixing with, as expected, each having about the same magnitude of mixing in the temperature-independent regime. However, in the fine-grained films, the enhancement in diffusivity occurs at a noticeably lower temperature than in the single-crystal. Substantial grain growth was also observed by Akano et al., who attributed the simultaneous enhancement in diffusivity to grain boundary diffusion. In the single-crystal Ni experiments, the enhancement of diffusion at higher temperatures is clearly due to RED.

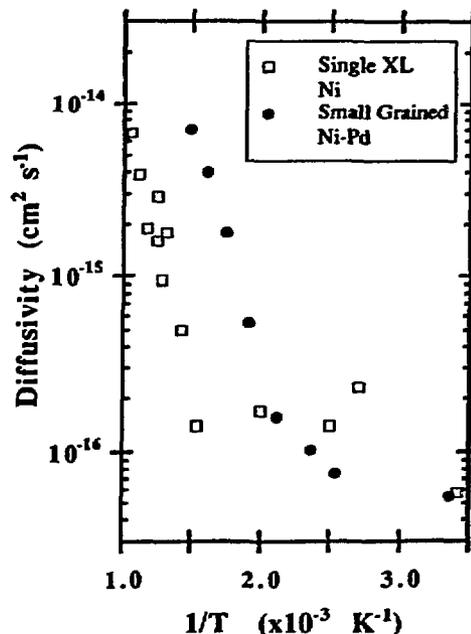


Fig. 2. Comparison of measured diffusion coefficients resulting from ion mixing in single-crystal Ni [9] and fine-grained Ni-Pd [21].

One possible explanation [22] which links microstructural features with enhanced mixing rates is diffusion-induced grain boundary migration (DIGM). DIGM is a highly efficient mode of interdiffusion commonly observed during thermal annealing of metallic films at relatively low temperatures. Systematic investigations of DIGM during ion beam mixing of Au/Cu bilayers were recently completed in our laboratory. A variety of polycrystalline and single-crystal samples were examined. RBS and cross-sectional TEM confirmed the occurrence of DIGM in specially prepared polycrystalline samples irradiated and/or annealed at temperatures near 500 K. Figure 3 shows a TEM view of a cross-section sample that was irradiated to 10^{15} 1.5 MeV-Kr ions cm^{-2} at a temperature of 500K. A distinct Cu-alloyed zone (hatched region in Fig. 3b) was observed by X-ray dispersive energy analysis. The Cu concentrations in this zone were ≥ 20 at. %, compared to the adjacent regions of the Au film which contained ≤ 4 at. % Cu. Convergent-beam analysis from this Cu-alloyed

zone showed it to have the same crystallographic orientation (I) as the adjoining low-Cu region to the right in the micrograph. The alloyed zone is bounded on the left by low-Cu content grains with distinctly different crystallographic orientations (II and III) as determined using convergent-beam analysis. This pattern is consistent with DIGM having occurred, driving the boundary from right to left.

A simple mechanistic model was developed which relates the magnitude of the observed interdiffusion with film thickness, grain-size and irradiation time. If we define the film-averaged Cu composition extracted from the RBS spectra as \bar{C} , the film thickness, l , the treatment (irradiation or annealing) time, t , the average grain-diameter, L , the average alloyed zone composition, C' , and the average grain-boundary diffusivity, D_{DIGM} , then as shown in [22],

$$\bar{C} = 2C' D_{\text{DIGM}} t / lL.$$



Fig. 3. (top) Cross-sectional TEM view of the Au portion of an ion-beam mixed Au/Cu bilayer containing a DIGM alloyed zone. (bottom) Schematic of above micrograph with hatched region delineating the DIGM alloyed (≥ 20 at. % Cu) zone. Different Au grain orientations indicated by I, II, and III.

The result of applying this model to the experimental RBS results obtained at 500K is shown in Fig. 4. The two data sets, annealed and irradiated, fall nicely on two straight lines, as the simple model predicts. Clearly, irradiation enhances DIGM, as demonstrated by the more than factor of two increase in slope for the irradiated specimens. From the above equation, this enhancement may arise either through an increase in the Cu concentration in the alloyed zone, and/or an increase in the grain-boundary diffusivity. Since the average alloyed zone concentration determined from cross-sectional TEM samples was found to be the same for the irradiated and the annealed specimens, the effect of irradiation is to enhance the grain-boundary velocity.

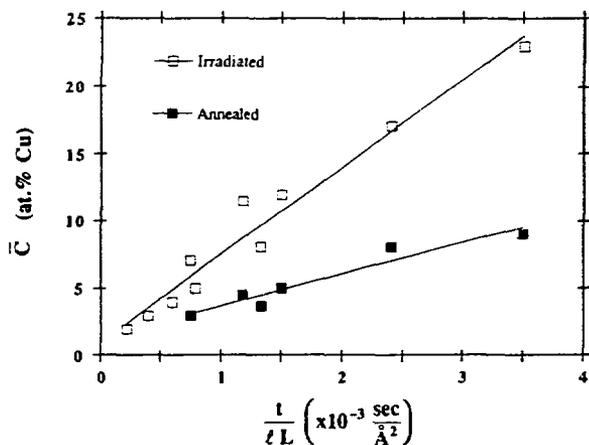


Fig. 4. Average Cu composition of Au layer determined by RBS after annealing (solid squares) or irradiation (open squares) at 500K.

4. SUMMARY

The expected increase in ion-beam mixing rates due to "radiation-enhanced diffusion" (RED), i.e. the free migration of isolated vacancy and interstitial defects, is well documented in single-crystal specimens in the range of 0.4 to 0.6 of the absolute melting temperature. In contrast, the increase often observed at somewhat lower temperatures during ion-beam

mixing of polycrystalline specimens is not as well understood. Because ion-beam mixing in single-crystal specimens exhibits no significant temperature dependence below that of RED, theoretical models that invoke only irradiation-specific phenomena, e.g., cascade-overlap or liquid-diffusion, and hence which predict no difference in mixing behavior between single- or poly-crystalline specimens, cannot account for the existing experimental results. Sufficient evidence is available to show that the increase observed in polycrystalline specimens reflects intracascade enhancement of a thermally-activated process that also occurs in the absence of irradiation. Recent evidence suggests that this process is DIGM.

5. ACKNOWLEDGMENTS

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