

Ion-Bombardment-induced Subsurface Composition Modifications
in Alloys at Elevated Temperatures*

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Ion Bombardment-induced Subsurface Composition Modifications in Alloys at Elevated Temperatures*

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Modifications of subsurface alloy composition during high-temperature sputtering were studied using a comprehensive kinetic model that includes Gibbsian adsorption, preferential sputtering, displacement mixing, radiation-enhanced diffusion, and radiation-induced segregation. Numerical solutions were obtained for a Cu-40 at.% Ni alloy under 5-keV Ar⁺ ion bombardment as functions of time and temperature. The model predictions are in good qualitative agreement with recent experimental measurements.

I. INTRODUCTION

The effects of ion bombardment on the near-surface composition of alloys have been the subject of recent detailed investigations because of the (i) concern about plasma contamination in fusion reactors by sputtered particles from walls and limiters, (ii) increasing use of ion implantation to tailor new materials, and (iii) routine application of ion sputtering in conjunction with various analytical techniques to depth-profile the composition of multicomponent materials. Surface compositional changes due to preferential sputtering have been observed in many alloy systems near room temperature. However, only very limited information is available on sputter-induced composition modifications at elevated temperatures where additional mechanisms should be important [1-8].

To elucidate the essential physics of ion bombardment-induced compositional changes, we have developed a comprehensive kinetic model, which includes the effects of Gibbsian adsorption, preferential sputtering, displacement mixing, radiation-enhanced diffusion, and radiation-induced segregation on the evolution of the near-surface composition of alloys. Information about the dependence of the compositional redistribution on sputtering time and temperature can be obtained using a suitable numerical technique.

II. THE BASIC PROCESSES

A detailed description of the five basic processes mentioned above has been given elsewhere [8]. For the sake of clarity, they are briefly described here.

Gibbsian adsorption is a segregation of alloying elements to surfaces or interfaces that reduces the free energy; it occurs thermally and affects the alloy composition at equilibrium only in one or two atomic layers near the surface.

Preferential sputtering occurs in alloys because of differences in surface binding energies and in energy transfer to component atoms by energetic-ion impact.

Displacement mixing of alloying elements is induced by displacements of atoms in the alloy generated by the bombarding ions. The displacement-induced inter-diffusion coefficient is assumed to be temperature independent.

Radiation-enhanced diffusion is caused by the thermal motion of point defects produced by the bombarding particles within the solid. Below $\sim 0.6 T_m$ (T_m is the absolute melting temperature), the concentrations of radiation-induced vacancies and interstitials can exceed their thermodynamic equilibrium values by several orders of magnitude. Since the average diffusion coefficients of atoms in the alloy are proportional to the concentrations of point defects, diffusion of the alloying elements is strongly enhanced by irradiation at temperatures where point defects are mobile.

Radiation-induced segregation is a result of point-defect fluxes. At sufficiently high temperatures, mobile point defects escape mutual recombination and anneal out by diffusion to sinks. Any preferential association of defects with a particular alloying element and/or preferential participation of a component in defect diffusion will couple a net flux of the alloying element to the defect fluxes. This coupling leads to a compositional redistribution in irradiated alloys.

Calculations were performed for concentrated Cu-40 at.% Ni alloys, for which reliable experimental measurements have been reported [2,3]. Copper atoms were assumed to migrate by preferential exchange with vacancies. The energies of vacancy migration via Cu- and Ni-atoms were taken to be 0.77 eV [9] and 0.82 eV, respectively. The former value is the vacancy migration energy for pure Cu, and the latter is assumed to be appropriate for vacancy motion via Ni-atoms in Cu-Ni alloys. The interstitialcy migration energy was taken to be 0.12 eV [10] via either alloying elements. A heat of adsorption of -0.25 eV [11] was used for Gibbsian adsorption of Cu-atoms onto the surface. Sputtering and damage production parameters used in the calculations correspond to those of 5-keV Ar⁺ ions. The sputtering coefficients for Cu and Ni were taken as 5.5 [12] and 2.8 atoms/ion, respectively; the latter value was obtained using the experimentally-determined ratio $S_{Cu}/S_{Ni} \approx 2$ [3]. An ion flux of 2.5×10^{14} ions/cm²s was used, yielding a peak damage rate of 1 dpa/s. It was assumed that 30 atoms changed sites per dpa.

III. RESULTS AND DISCUSSION

Spatial redistribution of Cu-atoms during sputtering at 400°C is shown in Fig. 1 as a function of time. The spatially-dependent damage rate K_0 used in the calculations is shown by the dashed curve in the top illustration ($t = 0$). A logarithmic scale has been used for the distance from the sputtered surface to efficiently show rapid compositional variations near the surface and moderate ones at greater depth. The compositions of the first two atomic layers, each 0.206 nm thick, are shown in steplike fashion. The thickness of the surface layer removed by sputtering, the rate of which is time-dependent because of the changing surface composition, is also indicated for various times. The Cu concentration at the surface, C_{Cu}^s , increases at short sputtering times owing to dominant radiation-enhanced Gibbsian adsorption, and then decreases towards the steady-state value given by $(C_{Cu}^s/C_{Ni}^s)_{s.s} = (S_{Ni}/S_{Cu})(C_{Cu}^b/C_{Ni}^b)$. At steady state, the surface alloy composition is determined by the sputtering coefficients of the alloy components, S_{Cu} and S_{Ni} , and the bulk composition, C_{Cu}^b and C_{Ni}^b , in such a way that the composition of the sputtered flux equals that of the bulk alloy.

The time evolution of C_{Cu}^s is plotted in Fig. 2 for various temperatures. Near room temperature, Gibbsian adsorption is negligible and C_{Cu}^s changes monotonically to the steady-state value. With increasing temperatures, the effect of radiation-enhanced Gibbsian adsorption becomes stronger; C_{Cu}^s increases more rapidly at short sputtering times, and takes longer to decay to the steady-state value. The time

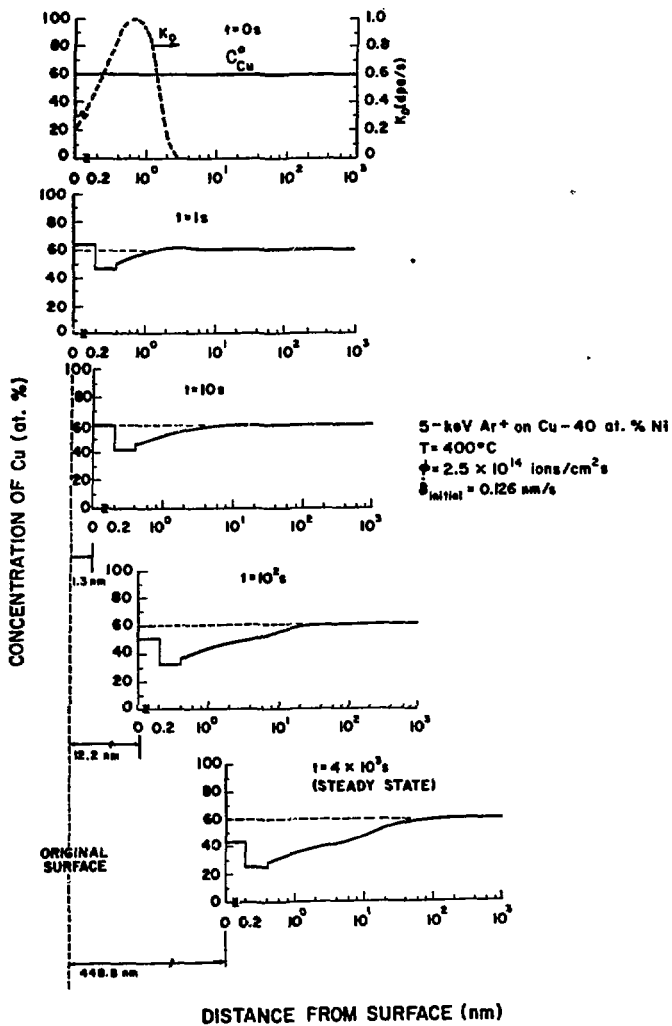


Fig. 1. Time evolution of Cu concentration profiles in a Cu-40 at.% Ni alloy sputtered at 400°C with 5-keV Ar⁺ ions. The sputtering rate for the bulk composition is 0.126 nm/s. The profile of the damage rate, K_D , and the thickness of the surface layer sputtered off are indicated.

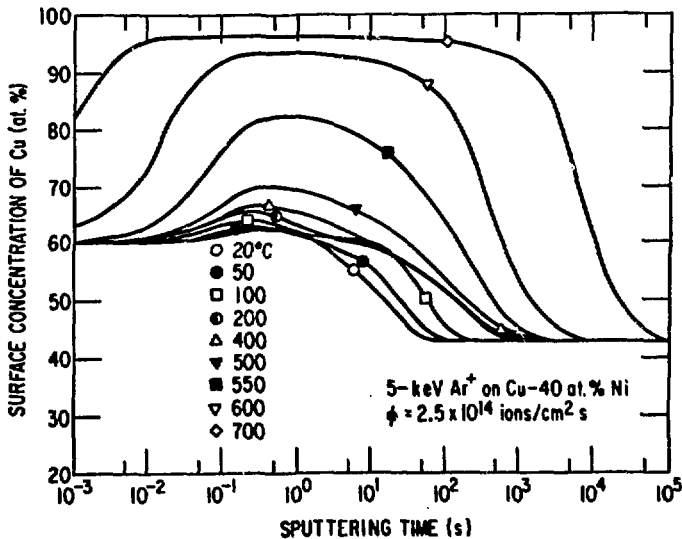


Fig. 2. Time dependence of Cu concentration at the alloy surface during sputtering at various temperatures.

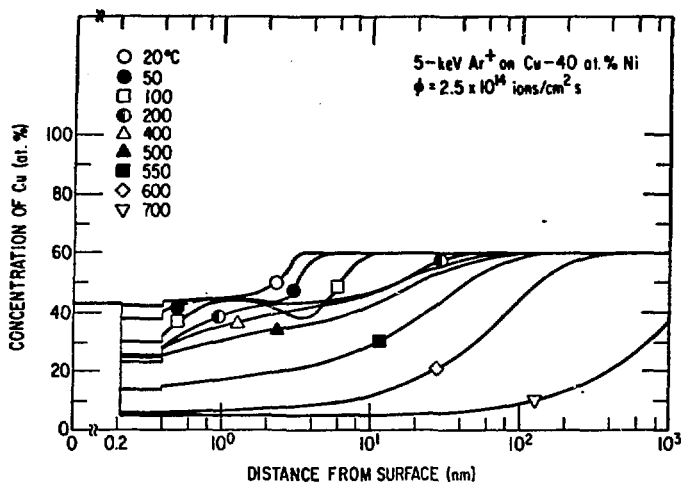


Fig. 3. Steady-state Cu concentration profiles in a Cu-40 at.% Ni alloy sputtered at various temperatures.

required to attain steady-state increases from 80 to 10^5 s as the temperature increases from 20 to 700°C. This is in good qualitative agreement with recent experimental measurements [2].

Figure 3 shows the steady-state concentration profiles in the near-surface region calculated for various temperatures. Below $\sim 100^\circ\text{C}$, point-defect mobility is limited, and the athermal processes (i.e., preferential sputtering and displacement mixing) govern the development of the alloy composition in the altered layer, which extends to a depth approximately equal to that of the damage range; within this altered layer, the alloy composition is nearly uniform. Above 100°C , Gibbsian adsorption, radiation-enhanced diffusion, and radiation-induced segregation become significant, and effectively determine the extent and composition of the altered layer; the higher the temperature, the thicker the altered layer. At 700°C , for example, the thickness of this layer is $\sim 3 \mu\text{m}$, which is ~ 1000 times larger than the damage range. This is consistent with the experimental observations [2,3].

The model developed should find useful applications in the areas of plasma contamination of fusion reactors, sputter depth-profiling, and high-temperature ion implantation.

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