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STUDY OF ION BOMBARDMENT-INDUCED SUBSURFACE COMPOSITIONAL MODIFICATIONS IN Ni-Cu ALLOYS AT ELEVATED TEMPERATURES BY ION SCATTERING SPECTROSCOPY*

N. Q. Lam, H. A. Hoff, H. Wiedersich and L. E. Rehn
Materials Science and Technology Division
Argonne National Laboratory
Argonne, IL 60439

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STUDY OF ION BOMBARDMENT-INDUCED SUBSURFACE COMPOSITIONAL MODIFICATIONS IN Ni-Cu ALLOYS AT ELEVATED TEMPERATURES BY ION SCATTERING SPECTROSCOPY

N. Q. LAM, H. A. HOFF, H. WIEDERSICH and L. E. REHN
Materials Science and Technology Division, Argonne National Laboratory,
Argonne, IL 60439

ABSTRACT

Changes in the subsurface composition of Ni-40 at.% Cu alloys during 3-keV Ne^+ bombardment at temperatures between 25 and 700°C were studied by means of ion scattering spectroscopy. Both the time evolution of the composition in the surface atom layer during ion bombardment and subsurface concentration profiles after rapid specimen cooling to room temperature were measured as a function of temperature. Radiation-enhanced diffusion coefficients were derived from the effective altered-layer thicknesses obtained. A comparison of the experimental measurements with theoretical calculations based on a phenomenological model enabled the identification of processes and kinetics responsible for subsurface compositional modifications.

INTRODUCTION

Subsurface compositional modification of alloys during elevated-temperature ion sputtering has been a subject of detailed investigations over the past few years. The interest in this phenomenon was motivated by recent concern about plasma contamination by sputtered particles in magnetic fusion devices and wide application of ion-beam processing in many areas of materials science.

Changes in the near-surface composition due to preferential sputtering near room temperature have been observed in many alloy systems (extensive reviews have been given recently by Betz [1], Kelly [2], and Andersen [3]). At high temperatures where additional thermally-activated processes are expected, this phenomenon is more complex. In fact, it is now established that at least five distinct processes, including preferential sputtering (PS), displacement mixing (DM), Gibbsian adsorption (GA), radiation-induced segregation (RIS) and radiation-enhanced diffusion (RED), can contribute to subsurface compositional alterations of alloys during elevated-temperature ion sputtering. Recent model calculations of Lam and Wiedersich [4-6] have provided new insights into the simultaneous effects of these processes and helped understand a number of experimental observations.

Most of the measurements of ion bombardment-induced alloy composition changes at high temperatures were made by means of Auger electron spectroscopy (AES) [7-12]. Unfortunately, owing to the finite escape depth of the Auger electrons, the AES technique cannot yield definitive information about the composition in the outermost atom layer, where the effects of PS and GA are known to be significant. In a recent work, Swartzfager et al. [13] employed the ion-scattering-spectroscopy (ISS) technique, which is extremely sensitive to the first surface atom layer. However, the time

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evolution of the alloy composition in the first atomic layer during ion bombardment was not reported. Most recently, Andersen et al. [14] used a new technique, in which the angular distribution of the sputtered-flux composition was measured, to obtain qualitative information on near-surface compositional gradients.

In the present study, both the evolution of the surface alloy composition during sputtering and subsurface concentration profiles after rapid specimen cooling to room temperature were measured as a function of temperature using ISS. Information regarding the enhancement of diffusion by irradiation was obtained from the measurements of the effective altered-layer thicknesses. The experimental observations are compared with the results of model calculations in order to identify the mechanisms and kinetics responsible for ion bombardment-induced modifications of alloy composition.

EXPERIMENTAL

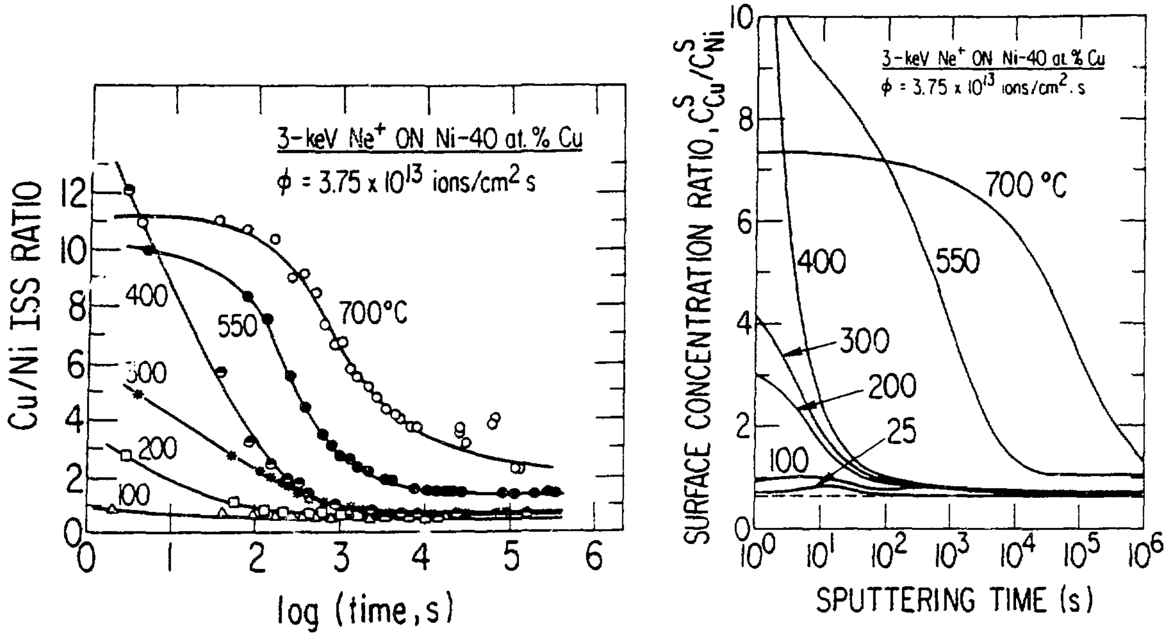
The Ni-40 at.% Cu alloy was prepared by arc melting and subsequent levitation melting in an induction furnace. Rectangular specimens (~0.5 x 1.5 x 0.05 cm^3) cut from rolled material were metallographically polished to obtain an optically flat surface, and then solution annealed in a vacuum of <10^{-6} Pa at 800°C for 5 hours. The average grain size in the specimens was measured to be ~41 μm in diameter. The specimens could be resistance-heated to temperatures up to 1000°C, and rapidly cooled by interrupting the current. The temperature was measured with a chromel-alumel thermocouple spot-welded to the back side of the specimen. Before each at-temperature sputtering experiment, the specimen surface was sputter-cleaned at room temperature until a steady-state alloy surface composition was attained. The sample was then heated and maintained at temperature for ~20 min before the start of sputtering.

The ion scattering spectrometer used is a 3M (now Kratos) model 535. All experiments were performed with a normally incident beam of 3-keV Ne$^+$ ions (the static beam diameter was 125 μm). During sputtering, the ion beam was rastered over an area of 1 mm^2, and the scattered ion signal was electronially gated (to ~60%), so that only the central portion of the rastered area was probed. The ion flux was measured to be 3.75 x 10^{13} ions/cm^2.s (i.e. ~6 μA/cm^2). Taking 2.5 and 2.0 atoms/ion to be the sputtering coefficients for Cu and Ni, respectively [15], we estimated a sputtering rate $\dot{x} \approx 9 \times 10^{-3}$ nm/s. The damage distribution for 3-keV Ne$^+$ on Ni was calculated using the TRIM code [16]. The peak damage occurs at ~1 nm and the total range is ~7 nm. With the above-mentioned ion flux, the peak-damage rate is ~3.5 x 10^{-2} dpa/s.

RESULTS AND DISCUSSION

Effect of temperature on surface and subsurface compositional modification

Figure 1a shows the ratios of Cu to Ni ISS intensities measured during ion bombardment at various temperatures. Changes of these ratios in time reflect the temporal evolution of the alloy composition in the first surface atom layer. Since the specimen was held at temperature for ~20 min before the start of sputtering, the Cu concentration at the surface, C^s_{Cu}, was very high at short sputtering times because of Gibbsian adsorption [17]. With increasing time, C^s_{Cu} decreased, owing to the dominant effects of RIS and PS, to a steady-state value. Below ~100°C, steady state was attained quickly, within ~1 min of sputtering. At higher temperatures, increasingly longer times were required to achieve steady state. In contrast to previous theoretical predictions, which were based on the

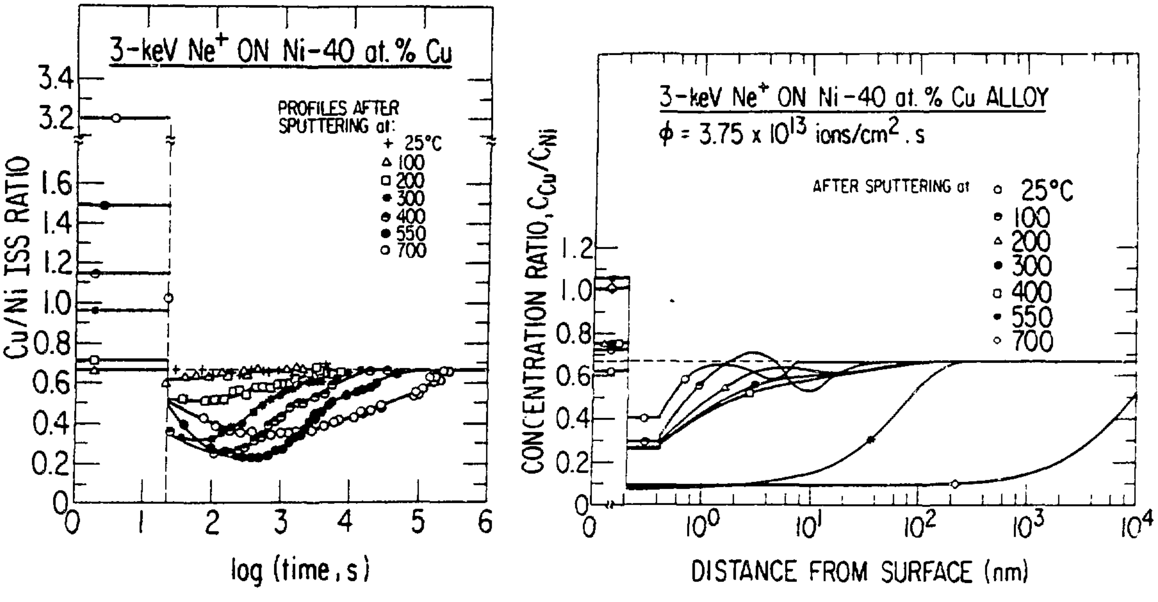


(a) (b)

Fig. 1. Time evolution of the composition in the outermost atom layer of a Ni-40 at.% Cu alloy during sputtering at various temperatures: (a) measured by ISS; (b) calculated using the Lam-Wiedersich model, with 37% contribution of the second layer to the sputtered-atom flux.

assumption that sputtered atoms originated entirely from the first atomic layer [4-6], the steady-state C^s_{Cu} was found to be temperature dependent. This dependence can be interpreted in terms of significant contributions to the sputtered-atom flux from deeper layers. Gibbsian adsorption tends to increase the Cu concentration in the first atomic layer relative to that in the subsurface layers, as the rate of atom exchange between these layers increases with increasing temperature. The steady-state condition, i.e. the composition of the sputtered-atom flux must equal the alloy composition in the bulk, can be met with an increased C^s_{Cu} if this increase is balanced by a corresponding decrease in the deeper layers. That is, a sufficient fraction of the sputtered-atom flux must originate from the deeper layers. Previous model calculations [4-6] and experimental results [8,9] have shown a substantial Cu depletion of subsurface layers, relative to the top layer, during sputtering at high temperatures. This is confirmed by the present measurements (see Fig. 2a).

New model calculations were performed to lend support to this interpretation. Our recently-developed kinetic model, which takes into account the interplay of the five basic processes mentioned above [4-6], was slightly modified by including significant contributions of the second atom layer to the sputtered-atom flux. Details of the theoretical treatment will be given in a separate publication [17]. Some theoretical results are illustrated in Fig. 1b. The experimentally-observed temperature dependence is indeed reproduced by model calculations. However, good qualitative agreement between experiment and theoretical predictions can only be obtained, if one assumes that at least 37% of the sputtered Cu flux comes from the second atom layer [17]. This contribution seems to be somewhat



(a) (b)

Fig. 2. Steady-state concentration profiles of the altered layers in a Ni-40 at.% Cu alloy after sputtering at various temperatures: (a) measured by ISS after rapid cooling to room temperature, $\dot{x} = 9 \times 10^{-3}$ nm/s; (b) theoretically calculated. The vertical lines indicate the boundary between the first and second atomic layers.

high, though not unreasonable, in light of the results of molecular-dynamics calculations by Harrison et al. [18].

In order to obtain information on the extent of alloy compositional alterations in the subsurface region, the ion beam and heating current were turned off simultaneously after steady-state surface composition had been achieved, and the Cu/Ni ISS intensity ratios were subsequently measured as a function of sputtering time at room temperature. The resulting Cu concentration profiles obtained are shown in Fig. 2a. Near room temperature, no subsurface compositional changes could be detected by the ISS. At 100°C, minor compositional alterations were revealed; the thickness of the region in which the alloy composition was modified was approximately equal to the damage depth. At higher temperatures, as the thermal processes (GA, RIS and RED) became more effective in modifying the alloy composition, the Cu depletion in the subsurface region was more severe and extended to much larger depths. For example, at 700°C, the modified layer was more than two orders of magnitude larger than the total damage range. The calculated Cu concentration profiles are displayed in Fig. 2b for comparison with experiment. Except for the fine structures in profiles calculated for sputtering temperatures below ~200°C, which result from the significant effect of RIS [19], the theoretical profiles are generally in good qualitative agreement with experimental measurements.

Radiation-enhanced diffusion in the altered layer

The subsurface Cu concentration profiles shown in Fig. 2a can be further analyzed in order to extract information regarding RED of Cu in the alloy. Based on the steady-state equation formulated by Ho [20] for the

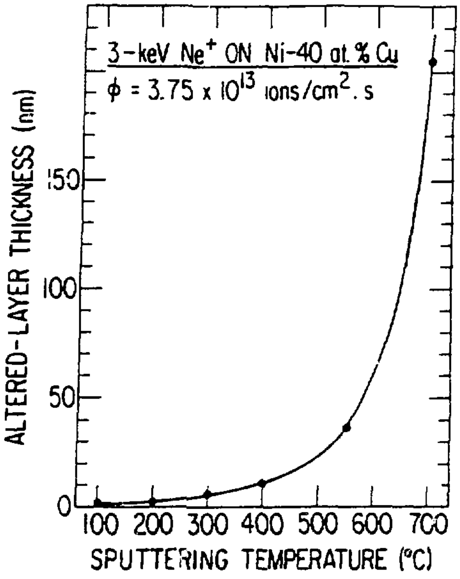


Fig. 3

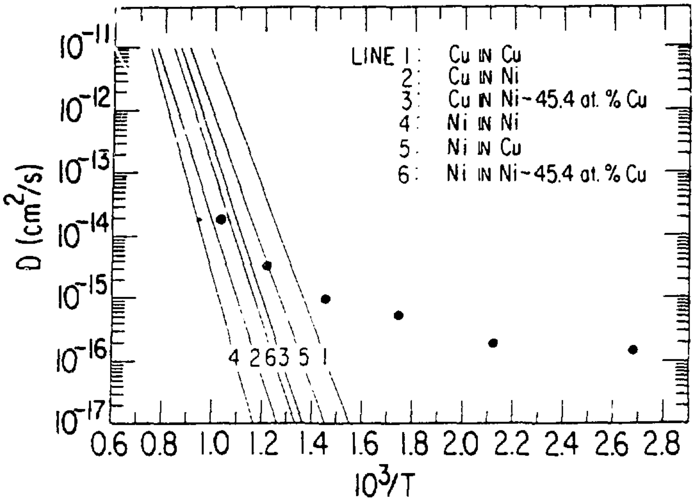


Fig. 4

Fig. 3. Temperature dependence of the effective altered-layer thickness.

Fig. 4. Arrhenius plot of the radiation-enhanced diffusion coefficients. The numbered lines correspond to various data for thermal diffusion (lines 2, 3, and 6 were obtained by extrapolation of high-temperature data given in refs. 25 and 26).

alloy composition in the altered layer, we plot the natural log of the difference between the bulk concentration and the concentration in the altered layer versus the distance from the surface. The plot consists of two straight portions of different slopes: the first portion contains information about RED, and the second one reflects the effects of RIS. The RIS effects are discussed in more detail in ref. [21]. The first portion can be used to deduce the effective altered-layer thickness, δ, which is strongly temperature-dependent above ~400 °C, as illustrated in Fig. 3. Then, using the relationship $\delta = D/\dot{x}$ [20], we calculate the RED coefficients, D. The Arrhenius plot of the results is shown in Fig. 4. Compared with various data for thermal diffusion [22-26], the results show that diffusion in the altered region is significantly enhanced by ion bombardment-induced point defects below ~550°C. Even though defects are produced only in a 7 nm thick zone, a large number of them survive annihilation and move deeper into the region beyond the ion range, promoting diffusion. In addition, below ~400°C, RED is virtually temperature-independent, indicating that, in this temperature regime, nonequilibrium point defects annihilate mainly by diffusion to sinks. The present results are in good agreement with previous ISS measurements by Swartzfager et al. [13], and consistent with AES data of Rehn et al. [21].

CONCLUSION

1. Using ISS, we found that, during high-temperature sputtering, the steady-state surface concentration of Cu was temperature dependent, which could be explained in terms of significant contributions of the second atomic layer to the sputtered-atom flux. Results of our recent model calculations support this interpretation.

2. The coefficients for radiation-enhanced diffusion of Cu in the bombarded alloy were deduced from steady-state concentration profiles of the compositionally-altered layers whose thicknesses were strongly temperature-dependent. The results are in good agreement with previous ISS and AES measurements.

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