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*This work was supported by the U.S. Department of Energy.
†Visiting scientist from Centre d'Etudes Nucléaires de Saclay, Gif-sur-Yvette, FRANCE.

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ABSTRACT

Surface and subsurface compositional changes induced by heating and by ion sputtering of a Ni-6 at.% Au alloy at temperatures between 25 and 600°C were measured in situ, using the ion-scattering-spectroscopy technique. Upon heating, Au atoms segregated to the alloy surface; the enthalpy and entropy of Gibbsian adsorption were found to be -0.45 eV and -1.09k. During sputtering, the steady-state surface composition was noticeably temperature-dependent above ~400°C, which could be interpreted in terms of significant contributions of the second atom layer to the sputtered-atom flux. Steady-state concentration profiles measured after rapid cooling of the target to room temperature were analyzed to gain information about the temperature dependence of the effective altered-layer thickness, from which the radiation-enhanced diffusion coefficients in the bombarded alloy were determined.

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1. Introduction

Ion bombardment-induced modification of surface and subsurface composition in alloys at elevated temperatures has recently become a research subject of considerable interest. This field of study has been motivated by serious concern about plasma contamination by sputtered particles in fusion reactors and by potential applications of high-temperature ion implantation to design new materials with a specific surface property.

Recent studies have shown that elevated-temperature ion sputtering can drastically modify the surface composition in a number of alloys: Ni-Cu [1-9], Ni-Si [10], Cu-Li [11], Au-Pd [5] and Au-Ag [5]. With the aid of good insights provided by theoretical modeling [12-14], it is now believed that the large compositional changes observed result from the synergistic effects of several processes, including preferential sputtering, ballistic mixing, Gibbsian adsorption, radiation-enhanced diffusion and radiation-induced segregation. The relative importance of each process depends principally on the alloy system, the species, energy and flux of the bombarding ions, and the target temperature. In a previous work [7,9], we used the ion-scattering-spectroscopy (ISS) technique to investigate this surface-modification phenomenon on the Ni-Cu system, in which the alloying elements practically have the same mass, Gibbsian adsorption is strong, and Cu atoms are known to segregate away from defect sinks during irradiation [15]. Sputtering of Ni-Cu alloys by 3-keV Ne^+ ions was also found to be nonpreferential [9]. The present paper reports the results of our recent study on Ni-Au alloys. In this system, the alloy constituents are quite different in mass; however, the radiation-induced segregation behavior of Au solutes is similar to that of Cu in Ni-Cu alloys [15]. The equilibrium surface composition during heating, the time evolution of the composition in the surface atom layer during sputtering, and subsurface concentration profiles after rapid specimen cooling to room temperature were measured as a function of temperature.

2. Experimental procedure

The Ni-6 at.% Au 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 and then solution annealed in a vacuum better than 10^{-6} Pa at 800°C for 5 hours. The average grain size in the specimens was measured to be 38 μm in diameter.

The sample heating, sputtering and data collection procedures were the same as in our previous experiment on Ni-Cu alloys [7,9]. A typical ISS spectrum of a sputter-cleaned Ni-6 at.% Au alloy surface at room temperature is shown in Fig. 1, where the major scattering peaks of Ni and Au are indicated. Taking 2 atoms/ion as the sputtering coefficient for 3-keV Ne^+ on both Ni and Au [16], the sputtering rate was calculated to be $\dot{x} = 8.5 \times 10^{-3}$ nm/s for an ion flux of 3.75×10^{13} ions/cm^2.s used in the present study. With this flux, the peak-damage rate was $\sim 3.5 \times 10^{-2}$ dpa/s.

3. Results and discussion

3.1 Gibbsian adsorption during heating prior to sputtering

When the sample is heated to a high temperature, Gibbsian adsorption of Au atoms occurs at the alloy surface. This surface segregation reaches thermal equilibrium after a certain time. The higher the temperature, the shorter this time is. At equilibrium, the atom fractions of Au and Ni in the surface atom layer, C^s_{Au} and C^s_{Ni}, are related to the respective atom fractions in the bulk, C^b_{Au} and C^b_{Ni}, by the equation [17]

$$C^s_{Au}/C^s_{Ni} = (C^b_{Au}/C^b_{Ni})\exp(\Delta S_a/k)\exp(-\Delta H_a/kT) \tag{1}$$

where ΔS_a and ΔH_a are the entropy and enthalpy of Au adsorption, respectively, k is the Boltzmann constant, and T is the absolute temperature.

In the present study, the ratios of Au to Ni ISS intensities (I_{Au}/I_{Ni}) were measured as a function of temperature (from 500 to 975°C). The data points were found to lie on a straight Arrhenius plot. In addition, in a calibration experiment, in which the ratios I_{Au}/I_{Ni} were measured on alloys of known compositions (C^b_{Au}/C^b_{Ni}) after sputter cleaning at room temperature, we obtained $I_{Au}/I_{Ni} = 20.38$ (C^b_{Au}/C^b_{Ni}). Thus, assuming that Ne^+ sputtering of Ni-Au alloys is nonpreferential (based on the similarity between the elemental sputtering coefficients [16]), we can use the slope and the intercept of the above-mentioned Arrhenius plot to determine ΔH_a and ΔS_a for Au, according to eq. (1). It is found that $AH_a = -0.45$ eV and $\Delta S_a = -1.09k$. This value of ΔH_a is in good agreement with the result (-0.52 eV) of Burton et al. using Anger electron spectroscopy [17] and with the recent ISS measurement by Kelley et al. [18].

3.2 Effect of temperature on surface and subsurface compositional modification

The Au/Ni ISS ratios measured during ion bombardment at various temperatures are shown in Fig. 2a. At short irradiation times, C^s_{Au} was very high because of dominant Gibbsian adsorption. With increasing time, C^s_{Au} decreased, owing to the effects of radiation-induced segregation and sputtering, to a steady-state value. The time required to attain steady state increases with temperature. For example, at 100°C, steady state was achieved within ~1 min of sputtering, whereas it took ~2 x 10^5 s to reach this state at 600°C. Similar to the case of Ni-Cu alloys [7,9], the steady-state C^s_{Au} was found to be temperature dependent, which could be interpreted in terms of a significant contribution to the sputtered-atom flux from the second layer. Preliminary theoretical calculations based on the Lam-Wiedersich model [12] have indicated that this contribution could be ~35%.

Figure 2b shows the Au concentration profiles which were measured by sputtering the alloy at room temperature, after rapid specimen cooling at the end of a high-temperature bombardment. At 100°C, minor compositional changes were observed within the damage range. At higher temperatures, however, as the thermal processes (Gibbsian adsorption, radiation-induced segregation and radiation-enhanced diffusion) became more efficient in modifying the alloy composition, the Au depletion in the subsurface region was more severe and extended to much larger depths.

3.3 Radiation-enhanced diffusion in the altered layer

Based on the equation formulated by Ho [19] for the steady-state alloy composition in the altered layer, we could analyze the subsurface Au concentration profiles presented in Fig. 2b to obtain information about radiation-enhanced diffusion of Au in the bombarded alloy. First, we plotted the natural log of the difference between the bulk concentration and the concentration in the altered layer versus the distance from the surface. As in the case of Ni-Cu alloys [9], the resulting plot consisted of two straight portions of different slopes: the first portion controlled mainly by radiation-enhanced diffusion, and the second affected by radiation-induced segregation [8]. The first portion could thus be used to determine the effective altered-layer thickness, δ, which was strongly temperature dependent above ~400°C, as presented in Table 1. Then, using the relationship $\delta = D/\dot{x}$ [19], we estimated the radiation-enhanced diffusion coefficients, D. The results, summarized in Table 1, are plotted and compared with various data for thermal diffusion [20-21] in Fig. 3. Diffusion in the altered region is strongly enhanced by ion bombardment in the temperature range under study. Furthermore, the values of D depend only slightly on temperature below ~400°C, indicating that Au diffusion was mainly promoted by annihilation of radiation-produced point defects at extended sinks at these temperatures. These results are consistent with previous ISS measurements on the Ni-Cu alloy system [5,7,9].

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Figure Captions

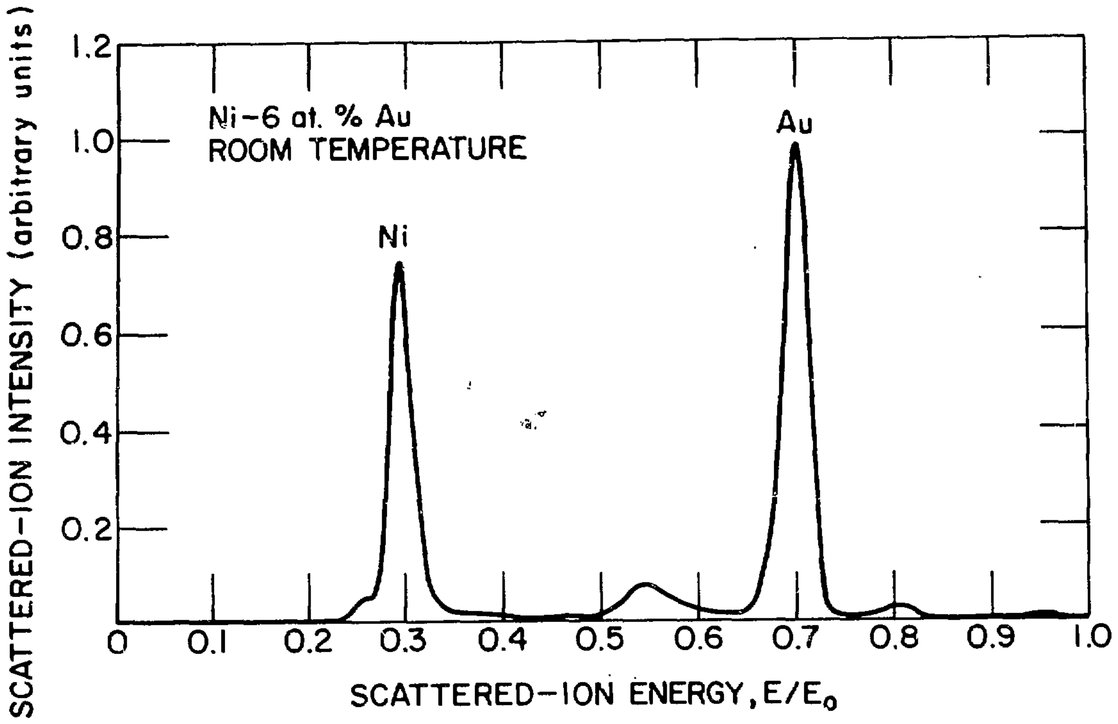
Fig. 1. ISS spectrum of sputter-cleaned surface of a Ni-6 at.% Au alloy. A normally incident beam of 3-keV Ne^+ ions was used. The major peaks of Ni and Au are indicated.

Fig. 2. Time evolution of the compositon in the outermost atom layer of a Ni-6 at.% Au alloy during sputtering at various temperatures (a), and steady-state concentration profiles in the altered layers measured by ISS after rapid cooling to room temperature (b). The vertical dashed line indicates the boundary between the first and second atomic layers.

Fig. 3. Arrhenius plot of the radiation-enhanced diffusion coefficients. The numbered lines correspond to reported data for thermal diffusion (lines 2, 3, and 4 were calculated from high-temperature information given in ref. 21).

Table 1. Values of the altered-layer thickness, δ, and radiation-enhanced diffusion coefficients, D, deduced from steady-state concentration profiles.

Sputtering temperature (°C)	δ (nm)	D (cm^2/s)
100	4.45	3.78×10^{-16}
200	8.40	7.14×10^{-16}
300	11.20	9.52×10^{-16}
400	20.76	1.77×10^{-15}
500	55.52	4.72×10^{-15}
600	127.40	1.08×10^{-14}



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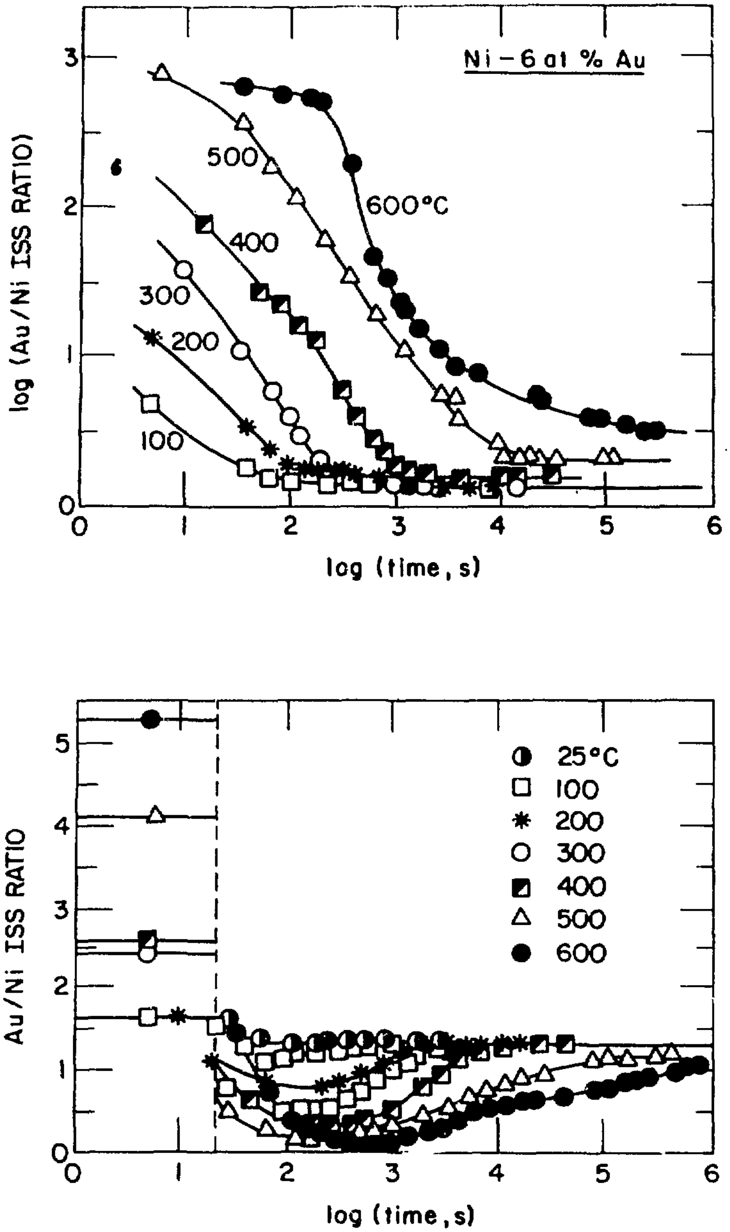

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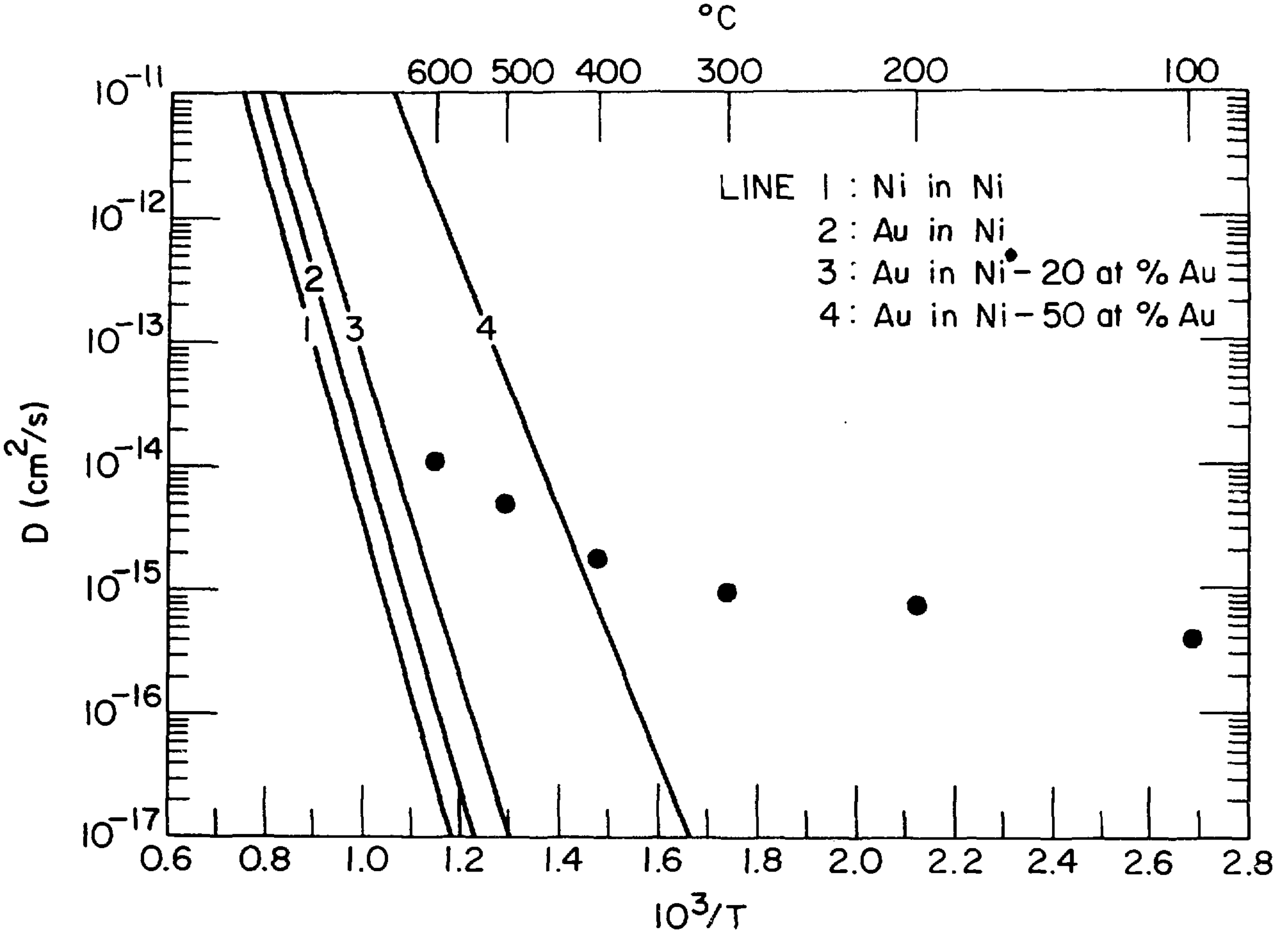

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