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EFFECTS OF RADIATION-INDUCED SEGREGATION AND PREFERENTIAL SPUTTERING ON THE SPUTTERING RATE OF ALLOYS*

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Changes in the surface composition and in the sputtering rate of binary alloys were calculated using a kinetic model that includes the effects of radiation-induced segregation and preferential sputtering. Numerical solutions were obtained for two dilute Ni-based model alloys, Ni-Cu and Ni-Mo, under 5-keV Ar⁺ ion bombardment as functions of sputtering time, temperature, and initial alloy composition. In the temperature range 200 - 850°C, the sputtering rate is initially affected by strong radiation-induced segregation. As the bombardment time increases, preferential sputtering becomes dominant; the surface composition and hence, the sputtering rate, approach the steady-state values determined entirely by the sputtering coefficients of the alloy components. Below 200 and above 850°C, the sputtering rate is controlled by preferential sputtering only because radiation-induced segregation is insignificant in these temperature regimes.

1. INTRODUCTION

During sputtering of alloys, near-surface atoms are dislodged and ejected into the gas phase, leading to an erosion of the alloy surface. Since the sputtering coefficients of the alloying elements are likely to differ from each other, atoms of different elements are sputtered off at different rates, which gives rise to the preferential sputtering phenomenon. In addition, the bombarding particles also produce damage within the solid, creating point defects and displacement cascades in a random fashion. At sufficiently high temperatures, those defects that are mobile and escape recombination tend to anneal out by diffusion to internal sinks such as dislocations and grain boundaries and to external surfaces. Migration of defects involving preferential exchange with a particular alloying element leads to a disproportionate transport of alloy constituents. As a result, significant spatial redistribution of alloying components can be expected. Preferential sputtering and sputter-induced segregation are inter-related: segregation causes a compositional change which, in turn, affects the sputtering rate.

In the present work, the effects of simultaneous radiation-induced segregation and preferential sputtering on surface composition and sputtering rate have been investigated using a kinetic model based on the preferential coupling between the flux of an alloying element and

radiation-induced defect currents to a surface which recedes at time- and composition-dependent sputtering rates. The evolution of alloy composition in time and space as well as the sputtering rate were calculated for various temperatures, ion fluxes and alloy systems. The results may enhance our understanding of high-temperature sputtering of fusion-reactor first-wall materials.

2. BASIC KINETICS

We consider a binary alloy A-B bombarded with an ion flux ϕ (ions/cm²s). The atom fractions of the two alloy components are C_A and C_B . To avoid excessively high concentrations at the surface which would induce precipitation, we assume the alloy is dilute with A being solute in B. As a consequence of energetic irradiation, the local total concentrations of interstitials C_I^t , vacancies C_V^t , and A-atoms C_A^t change with time according to the system of equations

$$\frac{\partial C_I^t}{\partial t} = -\nabla J_I^t + K_0 - R$$

$$\frac{\partial C_V^t}{\partial t} = -\nabla J_V^t + K_0 - R \quad (1)$$

$$\frac{\partial C_A^t}{\partial t} = -\nabla J_A^t$$

where the first terms on the right-hand side of the equations are the divergences of the total fluxes J^t of interstitials, vacancies and A-atoms, respectively; K_0 is the defect-production

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rate; and R is the total rate of mutual recombination of vacancies and interstitials. In any local region that does not contain a defect sink, the rates K_0 and R for vacancies are, by necessity, equal to those for interstitials. Defect clusters produced in cascades are assumed to decompose thermally, and the resultant point defects are included in K_0 and R . Interstitials and/or vacancies can combine with A-atoms to form mobile complexes with binding energies H_{iA}^b and H_{vA}^b , and migration energies H_{iA}^m and H_{vA}^m . These defect-solute complexes can diffuse to sinks and/or dissociate thermally to maintain their local thermodynamic equilibrium with an energy of dissociation that is set equal to the sum of the binding energy of the complex and the migration energy of the free defect $H_{(i,v)A}^0 + H_{(i,v)}^m$. The total currents of interstitials, vacancies, and A-atoms are set equal to the sum of the contributory currents of individual mobile species

$$J_i^t = - (1 + \sigma_i C_A) D_i \nabla C_i - D_{iA} \nabla C_{iA} \quad (2)$$

$$J_v^t = - (1 + \sigma_v C_A) D_v \nabla C_v - D_{vA} \nabla C_{vA} \quad (3)$$

and

$$J_A^t = - D_{iA} \nabla C_{iA} - D_{vA} \nabla C_{vA} - \sigma_i C_A D_i \nabla C_i + \sigma_v C_A D_v \nabla C_v \quad (4)$$

The total fluxes of interstitials and vacancies consist of two contributions each, i.e., those of the free defect fluxes and those of the complex fluxes. The total solute flux is the sum of the fluxes of complexes and of free A-atoms driven to defect sinks by coupling with the free interstitial and vacancy fluxes. The currents of mobile species are proportional to their concentration gradients, the proportionality constants being the diffusion coefficients D_i , D_v , D_{iA} , and D_{vA} of the free point defects and defect-solute complexes that are present at concentrations C_i , C_v , C_{iA} , and C_{vA} . The concentration of free A-atoms is C_A , and the constants σ_i and σ_v are the capture factors for interstitial- and vacancy-A atom encounters [1]. Note that the vacancy flux-induced solute current, which is the last term of eq. (4), has the opposite sign of the other terms because atom transport occurs in the direction opposite to that of the vacancy flux.

Concurrently with radiation-induced compositional changes in the damaged matrix, surface atoms of the two components are sputtered off at rates per unit area

$$\frac{dN_A}{dt} = \phi S_A C_A^s \quad (5)$$

and

$$\frac{dN_B}{dt} = \phi S_B C_B^s = \phi S_B (1 - C_A^s) \quad (6)$$

Here C_A^s and $C_B^s = 1 - C_A^s$, and S_A and S_B are the surface concentrations and the sputtering coefficients of A- and B-components, respectively. The concentration C_A^s is determined from the solution of eqs. (1). The coefficients S_A and S_B are the numbers of target atoms sputtered per incident ion and per unit concentration and may depend on the alloy composition. However, in the present calculations S_A and S_B were assumed to be equal to the coefficients of pure A and B metals, respectively. At high temperatures, $T > 0.7 T_m$ (T_m is the absolute melting temperature), S_A and S_B may become temperature dependent [2], but such a temperature dependence was neglected here. Also, effects of thermal or Gibbsian adsorption on surface composition has been ignored.

Thus, the sputtered surface recedes at a velocity or sputtering rate

$$\dot{\delta} = \frac{d\delta}{dt} = \phi \bar{\Omega} [S_A C_A^s + S_B (1 - C_A^s)], \quad (7)$$

where δ is the thickness of the surface layer removed by sputtering and $\bar{\Omega}$ is the average atomic volume.

Equations (1) and (7) were solved numerically for a semi-infinite medium by means of the GEAR package of subroutines [3], starting from the thermodynamic equilibrium conditions. A moving boundary, which represents the receding surface, was accommodated by a transformation of the physical space x to a reduced space Z : [4]

$$Z = 1 - \exp[-\beta(x - \delta)], \quad (8)$$

where β is a scale factor. With this transformation the region $\delta \leq x < \infty$ is mapped into the fixed region $0 \leq Z < 1$.

The calculations were performed for two dilute model alloys intended to be representative of the Ni-base alloys, Ni-Cu and Ni-Mo. We used the same physical parameters as tabulated in several previous papers [5-7]. Since both Cu and Mo are oversized solutes in Ni, the interstitial- and vacancy-solute binding energies were chosen to be 0 and 0.05 eV, respectively. Sputtering and damage production by 5-keV Ar^+ ions were assumed. The sputtering coefficients for Ni, Mo, and Cu are 3.6, 1.5, and 5.5 atoms/ion, respectively [8]. The damage distribution for 5-keV Ar^+ ions in Ni was estimated using the Edgeworth expansion [9]. The peak damage occurs at 7 Å and the total range is ~30 Å. An ion flux of 2.5×10^{14} ions/cm²s (i.e., 40 $\mu\text{A}/\text{cm}^2$) corresponds to a peak-damage rate of 1 dpa/s (displacement per atom per second).

3. RESULTS AND DISCUSSION

To understand the time evolution of the sputtering rate $\dot{s}$, eq. (7), we first discuss the time dependence of the compositional change at the alloy surface. This time dependence is shown in figs. 1 and 2, in which the surface concentrations of Cu and Mo in Ni-1 at.% Cu and

Fig. 1. Time dependence of Cu concentration at the surface of a Ni-1 at.% Cu alloy sputtered with 5-keV Ar^+ ions for several temperatures as indicated.

Fig. 2. Time dependence of Mo concentration at the surface of a Ni-1 at.% Mo alloy sputtered with 5-keV Ar^+ ions for various temperatures as indicated.

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Ni-1 at.% Mo alloys, respectively, are plotted for various temperatures. During sputtering at elevated temperatures, the surface composition of the alloy is altered by two distinct processes: radiation-induced segregation and preferential sputtering. Segregation is negligible at low temperatures, below $\sim 200^\circ\text{C}$, because the mutual recombination of point defects is dominant due to the high concentration of practically immobile vacancies, thus reducing defect fluxes to sinks. The alloy composition at the surface is primarily affected by preferential sputtering. The surface solute concentration changes monotonically to the steady-state value defined by [10]

$$\left(\frac{C_A^s}{C_A^0}\right)_{s.s.} = S_B / [S_A - C_A^0(S_A - S_B)]. \quad (9)$$

In the temperature range from 200 to 850°C , segregation dominates the change in the surface composition at short sputtering times; the sink surface is depleted of the oversized solutes Cu and Mo. Segregation is maximum around 600°C . As the bombardment time increases, segregation rapidly achieves a quasi-steady state. However, since solute and solvent atoms are sputtered off at different rates, the quasi-steady-state surface concentration set up by segregation is gradually altered by preferential sputtering. A true steady state is attained only when the rate of loss of solute and solvent atoms from the altered layer at the surface is balanced by a corresponding gain from the bulk as the altered layer recedes into the alloy. Equation (9) expresses this balance. At temperatures above $\sim 850^\circ\text{C}$, the equilibrium vacancy concentration and the solute diffusivity are high, defect recombination and back diffusion are large, and segregation becomes unimportant. The surface concentration of A-atoms changes monotonically from its initial value to the steady-state value as defined by eq. (9). The steady-state value in any of the temperature regimes discussed is independent of segregation and is controlled by preferential sputtering.

Fig. 3. Steady-state solute concentration profiles in a Ni-1 at.% Mo alloy sputtered at different temperatures.

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The time required to achieve steady state increases with increasing temperature because the thickness of the altered layer is larger at higher temperature, as shown in fig. 3 in which steady-state Mo concentration profile in the Ni-Mo alloy are plotted. For example, the buildup times to steady-state are $\sim 10^4$ s and $\sim 10^6$ s at 400 and 1000°C, respectively. During these times, a layer several times the thickness of the altered layer is sputtered off.

The effects of both radiation-induced segregation and preferential sputtering on the sputtering rate of the two alloys are shown in figs. 4 and 5. For the Ni-Cu alloy, the time and

Fig. 4. Time dependence of sputtering rate of a Ni-1 at.% Cu alloy calculated for various temperatures.

temperature dependence of the sputtering rate is similar to that of the surface solute concentration. The reason for this is clear. The sputtering coefficient for 5-keV Ar⁺ ions on Cu is larger than that for Ni. As Cu atoms segregate away from the surface, the sputtering rate is expected to decrease. At steady state, the surface concentration of Cu is lower than its initial value as indicated by eq. (9), the sputtering rate is smaller than the rate prior to the occurrence of segregation and preferential sputtering. In the case of the Ni-Mo alloy the time dependence of the sputtering rate is reversed from that of the Mo concentration at the alloy surface. This is also expected because the sputtering coefficient of Mo is much smaller than that of Ni. When the alloy

surface is enriched with Ni during the segregation stage, the sputtering rate of the alloy increases above the initial value. However, when preferential sputtering over-balances the effect of radiation-induced segregation, the

Fig. 5. Time dependence of sputtering rate of a Ni-1 at.% Mo alloy calculated for various temperatures.

alloy surface becomes enriched with Mo. Consequently, at longer times, the sputtering rate decreases below the initial value to the steady-state value as shown in fig. 5.

Fig. 6. Dependence of sputtering rate on initial Mo concentration in Ni-Mo alloys sputtered at 400°C.

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The time dependence of the sputtering rate was also calculated for various initial alloy compositions, as shown in fig. 6 for Ni-Mo bombarded with 2.5×10^{14} ions/cm²s at 400°C. The effects of sputter-induced segregation and preferential sputtering on the sputtering rate are more pronounced in more concentrated alloys since the contribution of the first term on the far right-hand side of eq. (7) to the sputtering rate δ becomes more significant. However, the buildup time to steady state depends only slightly on the initial alloy composition.

4. SUMMARY AND CONCLUSION

1) The time evolution of the surface composition and of the sputtering rate of alloys during sputtering was calculated using a kinetic model that includes the effects of radiation-induced segregation and preferential sputtering. The moving boundary, i.e., the surface which recedes at the sputtering rate, was taken into account in the mathematical formalism by a transformation of the physical space.

2) Numerical solutions were obtained for two dilute alloy systems Ni-Cu and Ni-Mo under 5-keV Ar⁺ ion bombardment as functions of time, temperature, and initial alloy composition. Below 200 and above 850°C, radiation-induced segregation is negligible; the alloy surface and, hence, the sputtering rate, are primarily affected by preferential sputtering. In the temperature range 200 - 850°C, radiation-induced segregation is dominant initially and the surface is depleted of the oversized solutes Cu and Mo. As the sputtering time increases, the effect of preferential sputtering becomes dominant, and the sputtering rate approaches a steady-state value. The buildup time to steady state increases with increasing temperature.

3) Although Cu and Mo show the same segregation patterns in Ni-Cu and Ni-Mo alloys, the time dependence of the sputtering rate of these alloys is not the same because of the difference in magnitudes of the sputtering coefficients of Cu and Mo relative to that of Ni.

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4) The numerical calculations have been performed for sputter-etching conditions, i.e., a high flux of 5-keV Ar⁺ ions, because experimental data for the sputtering coefficients are available. However, the present model can be applied to any low-energy ion bombardment situation, e.g., sputtering with D⁺, T⁺, and He⁺⁺ ions in fusion reactors, provided that the damage distribution and partial sputtering coefficients are known. The general trends in the surface-composition changes reported here will remain the same; the magnitudes will, of course, be different owing to different dose rates and sputtering coefficients. The buildup time to steady state increases with decreasing ion flux [4]. However, the total amount of material removed before steady state is reached is approximately flux independent.

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