SEGREGATION PROCESSES IN ALLOYS DURING ION BOMBARDMENT*

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October 1993


To be published in the Meeting Proceedings of the Japan Society for the Promotion of Science - Microbeam Analysis Committee (JSPS - 141).

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ABSTRACT

Both Gibbsian and radiation-induced segregation processes occur in alloys under irradiation. The mechanisms involved and the fundamental differences in their effects on near-surface compositional redistributions are summarized in the present paper. A good grasp of the synergistics of preferential sputtering and these segregation processes is important for the understanding of ion beam-induced surface modifications.

1. INTRODUCTION

Until 1979, surface and subsurface composition changes in ion-bombarded alloys were interpreted in terms of 'true' preferential sputtering (PS) - a primary effect of ion-solid collisions governed by differences in atomic mass and surface binding [1] - and radiation-enhanced diffusion (RED) [2]. Many experimental observations were found to be inconsistent with theoretical predictions. In more recent studies, the important roles of segregation processes - Gibbsian segregation (GS) and radiation-induced segregation (RIS) - in changing the near-surface compositions of alloys during irradiation were recognized [3-15] and, as a result, the cause of the earlier disagreement between theory and experiment became transparent: the segregation effects had been neglected in older theoretical works. Current models of alloy sputtering take into account these processes in addition to many others [16].

The present paper provides a short summary of the basic aspects of GS and RIS. The emphasis is placed on the synergistic effects of these segregation phenomena and PS on compositional changes in the surface layer, hence the sputtered flux, and the subsurface region. It is important to realize a number of fundamental differences between GS and RIS. GS is an equilibrium phenomenon which can be enhanced by irradiation, whereas RIS is a nonequilibrium process driven only by persistent fluxes of radiation-generated defects. GS causes a compositional perturbation only in one or two atom layers at the surface. Once set up by GS, steep compositional gradients in these layers remain stable, even after the interruption of irradiation. On the contrary, RIS can alter the target composition to depths that are substantially greater than the projected ion range. When the irradiation is stopped, the resultant concentration gradients become unstable and tend to decay under thermal conditions.

2. GIBBSIAN SEGREGATION

2.1 Basic Description

When an alloy AB is maintained at a given temperature T, a thermodynamic driving force causes a compositional readjustment in the "surface" phase, confined to the outermost few atomic layers, in order to minimize the surface free energy. This process, called GS, requires atom exchange between the surface (s) and the bulk (b), the rate of which is determined by the atom jump frequencies. To achieve equilibrium, the jump frequencies of, e.g., A-atoms from the bulk into the surface layer and from the surface back into the bulk, \( v_A^{bs} \) and \( v_A^{sb} \), respectively, have to fulfill the following requirement \[9\]

\[
v_A^{sb} = v_A^{bs} \exp \left( \frac{\Delta G_S}{kT} \right).
\]

where \( \Delta G_S \) is the GS free energy. That is, for a surface-segregating element (i.e., \( \Delta G_S < 0 \)), the activation energy for a backward surface-to-bulk jump must be effectively increased by the segregation energy, relative to the migration energy in the bulk (Fig. 1). The difference between the surface and bulk concentrations is then established and maintained by the reduced probability of thermally-activated jumps of A-atoms from the surface into the bulk. In thermodynamic equilibrium, the atom fractions of A and B atoms in the surface layer, \( C_A^s \) and \( C_B^s \), are related to the respective atom fractions in the bulk, \( C_A^b \) and \( C_B^b \), by the well-known relation [17]

\[
\frac{C_A^s}{C_B^s} = \frac{C_A^b}{C_B^b} \exp \left( \frac{-\Delta G_S}{kT} \right).
\]

During ion bombardment, if the sputtering rate is sufficiently slower than the rate of atom exchange between the outermost and underlaying layers, a surface composition spike dictated by eq. (2) will be established. In addition, since the forward atom jump frequency, \( v_A^{bs} \), is proportional to the concentrations and jump frequencies of point defects in the bulk, GS can be strongly enhanced by irradiation at temperatures where thermal vacancies are less abundant than the defects created by irradiation. The enhancement may occur even at very low temperatures, because interstitials or interstitialcies may still be highly mobile in many alloy systems and diffusional lengths of one or two interatomic spacings are required. Mixing-induced motion of atoms within the cascades may also promote GS.

Figure 1: Gibbsian segregation: its energetics and effect on near-surface composition.
2.2 Manifestation during Ion Bombardment

While PS tends to pin the alloy surface composition at a value dictated by the law of mass conservation in steady state, GS tends to readjust the surface composition in order to drive the system toward equilibrium. The thickness of the Gibbsian-segregated layer is comparable with the sputter depth. Moreover, as a rough rule, it is the weakly-bound species that segregates to the surface and that is sputtered preferentially [7,8]. Thus, although GS can be well characterized in equilibrium experiment using techniques which do not involve sputtering, the complex interplay between radiation-enhanced GS and PS during bombardment makes it difficult to derive definitive information about PS.

The synergistic effects of GS and PS on the development of the near-surface concentration profile are schematically illustrated in Fig. 2 for the case where the component sputter yield of A-atoms is larger than that of B-atoms ($y_A > y_B$) and initially $C^s_A > C^b_A$. At short bombardment times, enhanced PS of the A-component leads to a strong A enrichment in the sputtered-atom flux. As the sputtering continues, preferential loss of A-atoms causes a deviation of $C^s_A$ from the equilibrium value, which leads to a decrease in the A concentration in subsurface layers as the alloy system attempts to approach thermodynamic equilibrium [eq. (2)]. Gradually, the composition of the sputtered flux becomes equal to the bulk composition and steady state is attained. At low temperatures, the region of depletion is spread out mainly by collisional mixing; the thickness of the resulting altered layer is commensurate with the projected ion range. However, at elevated temperatures where the vacancy mobility is significant, point defects escape from the damage region, and RED and RIS result in large altered layers that extend far into the target.

![Figure 2: Effects of PS and GS on the evolution of the sputtercd-flux composition and the formation of the subsurface altered layer. The positions of the sputtered surface, $S$'s. at different bombardment times, t's, are indicated.](image)

The effect of irradiation temperature on bombardment-induced surface composition change and the formation of the altered layer in alloys has been theoretically modeled and experimentally investigated by many groups in recent years (see [16] and references therein). Surface compositional spike and concentration gradients that extend to large depths have been observed.
3. RADIATION-INDUCED SEGREGATION

3.1 Basic Description

Nonequilibrium point defects that are responsible for RED can also induce elemental segregation in alloys. In contrast to RED which accelerates the approach to thermodynamic equilibrium, RIS produces steep local concentration gradients, driving the alloy system away from equilibrium.

RIS results from two combined factors: radiation-induced point-defect fluxes that persist in time and preferential coupling of a particular alloy component to these fluxes. During ion bombardment at temperatures where point defects are mobile, there are always persistent defect fluxes which originate from the spatial nonuniformity in defect annihilation and/or defect production. Local elimination of radiation-induced point defects at extended sinks such as grain boundaries and free surfaces is a common cause of defect fluxes. Nonuniform distribution of defect-production rates also gives rise to persistent defect fluxes out of the damage peak into the mid-range and beyond-range regions. Almost always, these fluxes are preferentially coupled to certain solute elements.

The flow of defects involves a corresponding flow of lattice atoms: an interstitial flux is associated with an atom flux of the same magnitude and in the same direction, whereas a vacancy flux induces a flux of atoms equal in magnitude but opposite in direction. The total fluxes of interstitials ($J_i$) and vacancies ($J_v$) can be partitioned into partial defect fluxes occurring via different alloy components or partial atom fluxes occurring via different defects [18]:

$$J_i = J_i^A + J_i^B = J_A^i + J_B^i$$

and

$$J_v = J_v^A + J_v^B = -(J_A^v + J_B^v)$$

If the partitioning of the defect fluxes is exactly in the same proportion as the atomic fractions of the alloy constituents, i.e., $J_i^A / J_i^B = J_v^A / J_v^B = C_A / C_B$, then there is no disproportionate transport of A- or B-atoms into or out of any local regions, and consequently there is no RIS. In general, however, the various alloy components do not participate in the defect flow strictly in proportion to their local concentrations, i.e., $J_i^A / J_i^B \neq C_A / C_B$ and/or $J_v^A / J_v^B \neq C_A / C_B$; for example, interstitials may migrate preferentially via A-atoms, and vacancies may preferentially exchange with B-atoms. Therefore, a preferential coupling between defect and solute fluxes will ensue, and RIS will take place.

Note that RIS only occurs within the temperature range where annihilation of mobile defects by diffusion to extended sinks is important, i.e., between $-0.2$ and $-0.6T_m$. Outside this range, RIS is unimportant because dominant defect recombination reduces long-range migration of defects at lower temperatures, and effective back-diffusion prevents concentration gradients from building up at higher temperatures.

3.2 Manifestation during Ion Bombardment

RIS has been investigated systematically over the past 20 years, often under conditions where sputtering was not an issue, mainly because of its profound effect on the performance of nuclear reactor components. In fact, among the various processes that alter the stability of alloy phases during irradiation, RIS was found to be the most important one [19].

During ion bombardment at elevated temperature, the evolution of the solute concentration profiles can be complex, as schematically shown in Fig. 3, due to additional effects of defect flows from the peak-damage region [20]. If RIS occurs via a vacancy mechanism, solute enrichment in the peak-damage region at the expense of solute depletion on both sides of the peak is observed, in addition to strong solute depletion near the bombarded surface. On the contrary, if segregation takes place via an interstitialcy mechanism, the opposite effect will be measured. Furthermore, if vacancies interact strongly with a particular alloy component, forming tightly-bound but mobile vacancy-solute complexes, the atom and defect fluxes will be in the same direction.
RIS and GS may or may not result in elemental redistributions in the same direction, depending on the alloy system. For example, in Ni-Si alloys, Si enrichment at the surface can result from either GS or RIS, whereas, in Ni-Cu alloys, GS causes Cu enrichment at the surface and RIS gives rise to near-surface Cu depletion (see [16] and references therein). It is pointed out that the thickness of the layer affected by RIS is considerably (maybe orders of magnitude) larger than that of the Gibbsian-segregated layer. Moreover, RIS can be more effective than RED in altering the alloy composition at large depths during sputtering [21].

The interplay of PS and one or both of these segregation processes in changing the surface and subsurface compositions was modeled [6,9,22,23], and considerable insight into their intricate, individual and combined effects has been obtained.

4. CONCLUSION

The effects of segregation processes on near-surface alloy compositions during ion bombardment have been summarized. Gibbsian segregation causes significant compositional change in the first few surface atom layers. Any component which is Gibbsian-segregated to the surface will be preferentially removed by sputtering because more of it is located within the sputter depth. The synergistics of Gibbsian segregation and sputtering during bombardment makes it difficult to identify genuine preferential sputtering. Radiation-induced segregation, on the other hand, is driven by nonequilibrium defect fluxes. It is effective in causing steep compositional gradients in local regions where defect fluxes persist, and thus tends to drive the alloy system away from thermodynamic equilibrium. Depending on the alloy, Gibbsian segregation and radiation-induced segregation do not necessarily occur in the same direction. Therefore, a fundamental understanding of these two processes and a
good grasp of their differences are essential for assessing the development of compositional profiles in the altered layer.

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