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Surface segregation of Ti atoms during NiTi alloy sputtering

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ABSTRACT

The paper addresses NiTi alloy sputtering by 9 keV He and Ar ions and discusses the experiment performed by V.S. Chernysh et al. about 10 years ago. The binary collision simulation has been applied to extract the concentrations of surface Ni and Ti atoms from the experimental data. The results of simulations favor segregation of Ti for both He and Ar ion bombardment. The effect of non-symmetric surface collisions (Ti on Ni and Ni on Ti) was found to be negligible. A pronounced effect of the interatomic (target–target) potential is noted.

1. Introduction

Segregation of alloy atoms to the surface is a mechanism by which the material tries to redistribute atoms near the surface and minimize their overall energy. Segregation is strongly material- and thermo-dependent and affects such important properties of solids as adsorption, corrosion, catalysis, epitaxial growth, surface magnetism and tribology [1,2]. Surface segregation may be initiated or enhanced by ion bombardment. This phenomenon is known to occur in many alloys and compounds. Usually, the weaker-bound species tends to segregate to the surface, but exceptions to this general rule are also possible (e.g. [3–6]).

Segregation has dramatic influence on the angular distribution of sputtered atoms originating mostly from the first (top) monolayer. In this context, one should note recent progress in understanding the nature of the angular distributions of atoms sputtered from Ni_xPd_y [7] and CuPt [8] alloys by Ar ions. The results of measurements were used to extract the concentrations of atoms near the surface. This was done by comparison between experimental and computer simulation data. It was shown that in both cases bombardment-induced segregation plays a significant role in explaining the experimental data. The surface-segregated atoms may focus the underlying atoms to the surface normal in accordance with the gradient model by Sigmund et al. [9]. Therefore, the angular spectra of sputtered atoms are a unique source of information on the segregation phenomenon as such and on the surface morphology.

This paper addresses alloy sputtering and discusses the experiment [10] performed by Chernysh et al. about 10 years ago. The experiment investigated the angular distributions of sputtered atoms for a NiTi alloy (nitinol) bombarded with 9 keV He and Ar ions at high fluences. The distributions were used to obtain the Ni/Ti yield ratio, Y_{Ni}/Y_{Ti}, as a function of the polar ejection angle θ in a wide interval of angles ($\theta = 10–85°$). Fig. 1 presents the results for both He and Ar ion bombardment. It is seen that the dependences are almost linear and that for Ar ions the angular dependence of the Ni/Ti yield ratio is more pronounced. In addition to the angular spectra of sputtered atoms, the depth profile of the Ni/Ti concentration ratio was also measured using Rutherford backscattering spectroscopy (RBS) and Auger electron spectroscopy (AES). It was found that the bombardment of the NiTi alloy by He and Ar ions results in the formation of the altered layer of atoms with a steady-state surface composition about Ni_2Ti. For He ions, the extrapolated value of the surface Ni/Ti composition ratio is equal to 2.5 ± 0.5 (see Fig. 2 in [10]). It was noted [10] that the depth resolution of RBS and AES is insufficient to make final conclusions about the composition of the first two top layers of atoms.

The high values of Y_{Ni}/Y_{Ti} at small ejection angles (Fig. 1) were explained [10] by the difference in scattering of the target atoms

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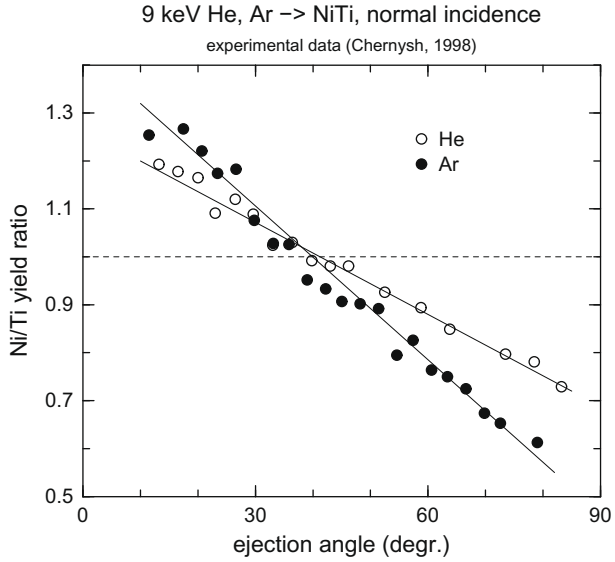

Fig. 1. The angular dependencies of the Ni/Ti yield ratio measured for a NiTi alloy bombarded with 9 keV He and Ar ions at normal incidence [10]. The solid lines are fitted to guide the eye.

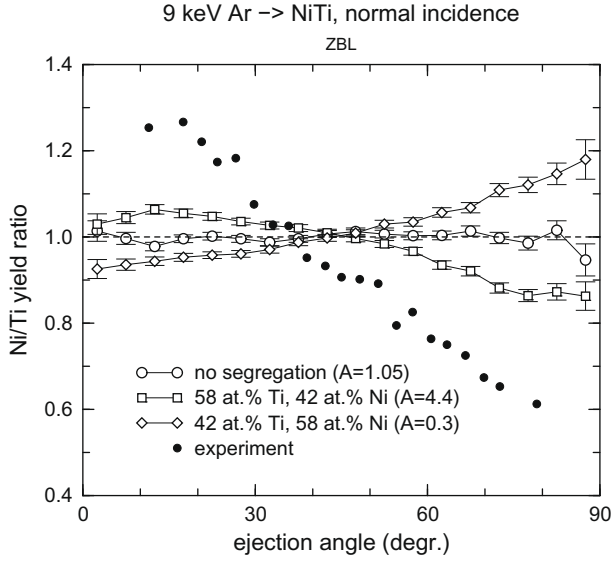

Fig. 2. The angular dependencies of the Ni/Ti yield ratio calculated at various concentrations of the top-layer atoms for a NiTi alloy bombarded with 9 keV Ar ions. Numbers in brackets indicate the corresponding values of A in Eq. (1). Dots are the experimental data [10].

in the non-symmetric collisions (Ti on Ni, Ni on Ti) initiated by backscattered ions. It should be noted, however, that such a difference might be essential only in large-angle scattering events, which are not characteristic of sputtering. For small-angle scattering events, this difference should be much less pronounced because the angle of small-angle scattering is roughly proportional to the product Z_1Z_2, where Z_1 and Z_2 are the atomic numbers of colliding particles.

The aim of the present computer simulation research, which resembles those in [7,8], is the following: to simulate sputtering of a NiTi alloy by 9 keV He and Ar ions and to search for segregation effects, which may be relevant to the behavior of the experimental angular spectra [10].

2. Computer simulation

The physical model and the simulation program used were described in detail in Refs. [7,8]. Briefly, the simulation code is based on the binary collision approximation and takes into account weak simultaneous collisions at large distances. The structure of the target is considered to be random (amorphous), as it is often assumed in calculations of sputtering of polycrystalline materials [11]. The universal (ZBL) potential [12] is applied as the interaction potential for colliding particles, unless otherwise stated. The surface potential barrier simulating the action of the long-range attractive force was planar. The atomic densities of elemental Ni and Ti targets differ by a factor of 1.6 (N = 0.09126 and 0.05682 atoms/Å^3 for Ni and Ti, respectively), thus for a NiTi alloy the density value, which takes into account the actual concentration of Ni and Ti atoms, was used. The effective surface binding energy was calculated in a similar way (model 2 in [13]) by using the heats of sublimation for elemental Ni and Ti targets (U = 4.46 and 4.89 eV, respectively). The bulk binding energy was assumed to be zero. Considering the fact that NiTi alloy after a prolonged irradiation did not reveal any pronounced topographical features [10], the target surface was assumed to be flat. Sputtering occurs atom by atom and is characterized by some equilibrium concentration of surface vacancies (e.g. [14–16]). The model used accounts for this peculiarity of sputtering.

To take into consideration composition changes in the target due to the effect of preferential sputtering [4], the ratio of Ni and Ti concentrations, C_{Ni}/C_{Ti}, as a function of depth z was given by the linear dependence [7]

$$\begin{aligned} C_{Ni}/C_{Ti} &= [A-(A-1)z/B] \qquad 0 \leqslant z \leqslant B \\ C_{Ni}/C_{Ti} &= 1 \qquad z > B \end{aligned} \tag{1}$$

Here, the zero value of z corresponds to the target surface, B is the energy-dependent thickness of the altered layer, $B \approx 2R_p$, where R_p is the average projective range of ions. The fitting parameter A was found in such a way to satisfy the steady-state sputtering condition

$$\hat{Y}_{Ni} = \hat{Y}_{Ti}, \tag{2}$$

where $\hat{Y}_{Ni}$ and $\hat{Y}_{Ti}$ are the total (integrated over θ) sputtering yields.

The above model does not take into account any segregation effects. To do this, the first monolayer of atoms was considered as a layer, which contains some amount of segregated atoms. Their concentrations, S_{Ni} and S_{Ti}, were prescribed ($S_{Ni} + S_{Ti} \leq 100$ at.%) and the ratio of Ni and Ti concentrations in deeper layers was given again by Eq. (1) with a new value of A satisfying Eq. (2) (model 1 in [7]). Eq. (1) describes reasonably well the concentration ratio measured on PtSi targets bombarded with 10–80 keV Ar ions [17]. In the general case, the steady-state concentration ratio may differ from the linear dependence due to interplay between preferential sputtering, surface segregation, recoil implantation and diffusion. For this reason, in [7] several other models of the concentration ratio were also applied (models 2–4). At fixed concentrations of segregated atoms models 1–4 gave almost identical results. (The same was observed in simulations with very different values of B [7].) This is understandable since the angular spectrum of sputtered atoms is governed mainly by the last (near-surface) collisions. In the present work, only model 1 was used.

The calculation procedure was organized as follows. For each selected pair of S_{Ni} and S_{Ti}, the value of A in Eq. (1) was initially found. This A-value was then used to calculate the angular distributions of sputtered Ni and Ti atoms with good statistics and to get the angular dependence of the ratio Y_{Ni}/Y_{Ti}. The latter dependence was compared with the corresponding experimental data (Fig. 1) and the root-mean-square deviation