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Simulation of sputtering of deformed regions in binary alloy crystals

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ABSTRACT

The influence of changes in lattice constant and binding energy of surface atoms of binary alloys on sputtering of deformed areas has been examined by a molecular-dynamic method. As a target we chose materials, which are used for coin manufacturing: tin bronze $Cu_{87}Sn$ and Ni–Fe alloys with different component concentration. Energy and spatial distributions of sputtered atoms before and after deformation are studied for mono- and polycrystals by considering segregation and heating of targets. The results obtained can be used for improving procedures for detecting deformed areas hidden under the surface of different products.

1. Introduction

Sputtering processes are widely used for analyzing a solid's surface, in particular, to clarify the target's grain structure [1–7]. The atoms located on grain boundaries have smaller binding energy than those on the sides of crystallites, and are more easily sputtered. In the case of complex materials it is possible, by means of ion bombardment, to reveal separate phases and areas enriched by certain elements if their sputtering yields are different [7,8].

In Refs. [9–17,58] it is revealed that, by means of ion sputtering, it is possible to visualize areas of deformation on a metal surface; for example erased pictures on coins, worn-off stamps and other products. An example of identification by sputtering of the erased image of a modern coin of 50 kopeks is shown in Fig. 1. The obtained visible contrast of the previously erased image is connected with the increase of sputtering of deformed areas due to reduction in the sizes of grains and a corresponding increase in the number of atoms with low binding energy on their boundaries. Optical contrast of the deleted pattern also appears due to radiation-induced diffusion of defects, admixtures, alloy components and implanted ions leading to mechanical stresses [13,17,58].

In addition, preferential sputtering of deformed areas occurs due to variations of the lattice constant and as a result of the binding energy of surface atoms. A new investigation of this process by molecular-dynamic simulation is described in the present work.

As samples we chose poly- and monocrystals of binary alloys, which are used for coin manufacturing. A typical feature of binary alloys is their essential difference of structure, composition and properties between surface and bulk [18–21], including surface segregation, disordering and reconstruction. For binary alloys it is revealed experimentally and theoretically that the surface of poly- and monocrystals is enriched by the heavy component depending on its content in the bulk [22–31]. This regularity is verified by comparing experimental and numerical results for sputtering and for secondary ion emission [22–28]. For monocrystals a composition oscillation in near surface layers and their reconstruction is observed [32–34]. In Refs. [35,36] the composition variation in the near surface layer is explained by a competition between mechanical stress (which causes heavy component segregation on the surface) and a chemical effect (which causes nearest ordering). In some cases segregation features are considered for binary alloys in the calculations presented.

Sputtering simulation is performed for the case of irradiation of a surface by Ar ions with energy E_0 ranging from 0.1 up to 10 keV under different deforming loads, which are typical for coin stamping, or, for product manufacture by sudden impact. The investigation is carried out mostly under Ar ion incidence normal to a surface ($\alpha = 0°$), and for a temperature of the sputtered alloy of 20 °C (but also for several cases of 300 °C). Sputtering processes for tin bronze $Cu_{87}Sn_{13}$ (for which there are experimental data [17,37–39]) and for $Ni_{97}Fe_3$ and $Fe_{97}Ni$ alloys are calculated in detail.

2. Computer simulation procedure

We used a Molecular-Dynamic (MD) model [7,40–42] with a movable monocrystal block comprising 250 atoms [43–45]. For calculating the polycrystal sputtering yield, the block is turned by

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Fig. 1. (a). Bronze coin of 50 kopeks. (b) The same coin after ion bombardment (Ar^+, $E_0 = 10$ kseV) when the pattern has previously been deleted. The erased picture is visible on the coin surface since deformed areas that appear under mint coins are sputtered preferentially.

arbitrary angles for each incident ion. Equations of motion are integrated according to the Euler modified predictor–corrector scheme, which is stable [41,46,47]. Inelastic losses are calculated using the Firsov formula [48]. Thermal oscillations are accepted as uncorrelated. The interaction potential is as follows: $U(r) = A_{bm}\cdot\exp(-r/a_{bm}) + (A_b/r)\cdot\exp(-2r/a_{bm})$ with constants $A_{bm} = 52(Z_1Z_2)^{3/4}$ [49], $a_{bm} = 0.219$Å, $A_b = (Z_1Z_2\cdot e^2)$, where Z_1 and Z_2 are atomic numbers for the incident ion and for the target atom and r is a radius-vector. During calculation the following parameters are fixed: sputtered atom momentum and coordinates, the length of cascade trajectory that causes sputtering, sputtering time, the number of sputtered atom generation and the depth of sputtering source. We studied the sputtering process both for the undeformed surface of crystal faces for $Cu_{87}Sn_{13}$ (FCC lattice), $Ni_{97}Fe_3$ (FCC lattice) and $Fe_{97}Ni_3$ (BCC lattice) [50] and considered segregation. The binding energy of surface atoms E_b is taken from Refs. [46,51]. For an undeformed surface the values are: 3.49, 4.44, and 4.08 eV for polycrystals of $Cu_{87}Sn_{13}$, $Ni_{97}Fe_3$, and $Fe_{97}Ni_3$ alloys, respectively. For monocrystal faces the binding energy for Cu, Ni, and Fe is taken from Ref. [52].

3. Results and discussion

Under compressive deformation, the lattice period a changes in the deformation direction and normal to it according to the modular ratio between transverse and longitudinal relative deformations, i.e. according to the Poisson coefficient, μ.

It is known that, under pressure, the elementary cell volume V (and lattice constant a) and binding energy of surface atoms change according to the following law: $dE_b = -dpV$, where dE_b is the binding energy variation and dp is the pressure variation. In this case dp is connected with the volume variation dV in the following way: $dp = B\cdot dV/V$, where B is the bulk modulus of elasticity. From here $dE_b = -B\cdot dV$.

For the alloys examined the Poisson ratio is small (for $Cu_{87}Sn_{13}$ $\mu \sim 0.32$, for $Ni_{97}Fe_3 \sim 0.33$, and for $Fe_{97}Ni_3$ $\mu \sim 0.25$) and due to this fact compression in the normal direction is small. The modulus of elasticity B is equal to 105 GPa, 160 GPa, and 210 GPa for $Cu_{87}Sn_{13}$, $Ni_{97}Fe_3$, and $Fe_{97}Ni_3$, respectively. For calculation we use a pressure value of 5 GPa. This pressure value is used in industry for shock stamping products and the binding energy E_b increases by 11%. For the same pressure for $Ni_{97}Fe_3$ value a decreases by 5% and E_b rises by 16%; for $Fe_{97}Ni_3$ value a decreases by 10% and E_b increases by 19%. Only these values of a and E_b are used for calculating the sputtering process during deformation.

It is of interest to study how segregation influences the sputtering process during deformation. For $Ni_{97}Fe_3$ and $Fe_{97}Ni_3$ segregation is insignificant since the component masses are close to each other and, for this reason, we do not study it. As for $Cu_{87}Sn_{13}$, where there is a large difference in component masses, there is no published information on its segregation. Due to this fact we perform

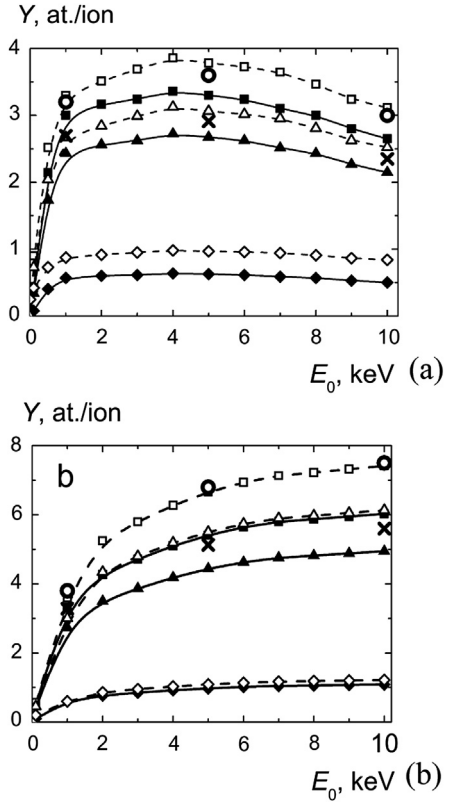

Fig. 2. (a)Energy dependence for the (100) face of tin bronze $Cu_{87}Sn_{13}$ monocrystal and (b) of polycrystal : ■Cu + Sn, ▲Cu, ◆ Sn. Solid lines – without deformation, dashed lines – under compressive deformation: ○, ×–Cu + Sn by considering segregation under deformation and without deformation, respectively.