Cooperative mixing induced surface roughening in bilayer metals: a possible novel surface damage mechanism

P. Süle\textsuperscript{1}, M. Menyhárd\textsuperscript{1}, K. Nordlund\textsuperscript{2}

\textsuperscript{1} Research Institute for Technical Physics and Material Science, Konkoly Thege u. 29-33, Budapest, Hungary, sule@mfa.kfki.hu
\textsuperscript{2} Accelerator Lab., Helsinki, Finland

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Molecular dynamics simulations have been used to study a collective atomic transport phenomenon by repeated Ar\textsuperscript{+} irradiations in the Ti/Pt interfacial system. The ion-induced injection of surface atoms to the bulk, the ejection of bulk atoms to the top layers together with surface erosion is strongly enhanced by interfacial mixing. This process leads to a dense interfacial material, and broadening of the interface region. The process scales with the relative difference of the atomic masses. We find that surface roughening and interfacial mixing is strongly coupled via an enhanced counterflow material transport normal to the surface which might be a novel surface damage mechanism. This cooperative phenomenon is active when the bilayer system is subjected to a high dose ion irradiation (multiple ion irradiations) and leads to surface cavity growth.

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1 keV at grazing angle of incidence (83°). Though the applied conditions can be considered gentle still strong mixing was observed. We will conclude that because of the presence of two unlike atoms enhanced material transport resulting in roughening and mixing occurs. We would like to show that in the case of a sample made of thin layers of different atoms with large difference in the atomic mass, not ion sputtering causes the surface erosion but it is rather induced by interfacial mixing. Moreover the mixing of atoms with different atomic mass and the cavitation at the surface is strongly coupled via the ion induced atomic transport normal to the surface leading to a cooperative phenomenon. This process might be a novel surface damage mechanism never reported before.

We irradiate a Ti/Pt system using several ion impacts consecutively. The reason for choosing such an irradiation mode is evident, since practically in all applications a series of ions hit the surface, even for low ion doses.
[20]. We show through MD simulations of 1 keV Ar ions impacting the Ti surface of the Ti/Pt system that near surface interfacial mixing has a profound effect on the mass transport.

II. SAMPLE PREPARATION AND SIMULATION TECHNIQUE

Classical molecular dynamics simulations (MD) were used to simulate the ion-solid interaction using the PARCAS code developed by Nordlund et al. [17]. Here we only shortly summarize the most important aspects. Its detailed description is given in [17] and details specific to the current system is in a recent communication [15].

The sample consists of 37289 atoms for the interface (IF) system with 4 Ti top layers and a bulk which is Pt. The lattice constants for Pt is $\approx 3.92$ Å and for Ti $a \approx 2.95$ and $c \approx 4.68$ Å. At the interface (111) of the fcc crystal is parallel to (0001) of the hcp crystal and close packed directions are parallel. The interfacial system as a heterophase bicrystal and a composite object of two different crystals with different symmetry are created as follows: the hcp Ti is put by hand on the (111) Pt bulk and various structures are probed and are put together randomly. Finally that one is selected which has the smallest misfit strain prior to the relaxation run. The remaining misfit is properly minimized below $\approx 6\%$ during the relaxation process so that the Ti and Pt layers keep their original crystal structure. The corresponding Ti-Ti and Pt-Pt interatomic distances are 2.89 and 2.73 Å at the interface. The Ti (hcp) and Pt (fcc) layers at the interface initially are separated by 2.8 Å and allowed freely to relax during the simulations. The variation of the equilibrium Ti-Pt distance within a reasonable $2.6 - 3.0$ Å interval in the interatomic potential does not affect the final results significantly. We find the average value of $d \approx 2.65$ Å Ti-Pt distance in the various irradiation steps and also in the nonirradiated system after a careful relaxation process. We believe that the system is properly relaxed and equilibrated before and between the irradiation steps. We found no vacancies at the interface or elsewhere in the system after the relaxation procedure. We visually checked and found no apparent screw dislocations, misorientations or any kind of undesired distortions (in general stress-generator dislocations) at the interface or elsewhere in the system which could result in stressed induced rearrangements in the crystal during the simulations. The temperature scaled softly down towards zero at the outermost three atomic layers during the cascade events [17]. The simulations are repeated in a much larger system consisting of $\approx 72000$ atoms in order to rule out any kind of size effects. The simulation cell is of particular interest because it has been shown [15] that at the applied sputtering conditions (1 keV Ar$^+$ with grazing angle of incidence) the thermal spike is typically formed at the interface and thus the emerging processes can be easily studied.

The initial velocity direction of the impacting atom was 7 degrees with respect to the surface of the crystal. Further details are given in Ref. [15]. A series of up to 10 ion impacts are employed in order to study the effects of multiple ion irradiations, e.g. to simulate high dose effect. Between impacts the simulation time was $\approx 20$ ps. This time was found to be sufficient to reach a relaxed system after each ion impact (e.g. the temperature approaches zero). Thus direct interaction between the cascade processes of various irradiation steps are excluded. It should also be remarked that the damage rate is extremely high due to the high dose effect and therefore some recovery process might occur between the irradiation steps. Although we did not find significant recrystallization effects up to several hundred ps. Thermally activated process might induce, however, further recovery in the system. We have done relaxation simulations on the irradiated sample at 300 K and found no recrystallization of the amorphised top layers in the irradiated zone up to several hundred ps. In any case, we do not think that the alloy phase would phase separate either at room temperature or on a longer time scale. We will demonstrate in the Discussion section that the the alloy phase is energetically competitive with the phase separated system (based on the cohesive energies).

To obtain a representative statistics, the impact position of the incoming ion is varied randomly within a $10 \times 10$ Å$^2$ area. We find considerable variation of mixing as a function of the impact position of the recoil. Using a $20 \times 20$ Å irradiation area (with 80000 atoms or more) we checked that a further increase of the irradiated area does not affect the final results heavily, except that the larger the area, the larger the number of incoming ions needed to get the same extent of interfacial mixing (IFM) and surface roughening. This is because individual ions with impact positions far from each other do not result in the high dose effect ($\approx 10^{15}$ Ar$^+$ ions/cm$^2$) we are interested in in this article. Impact positions with sufficient proximity to each other (that is within the characteristic area $\approx 5 \times 5$ Å$^2$, $\approx 10^{15}$ ion/cm$^2$) lead to the phenomenon called mixing induced enhancement of surface roughening (MIESR). The overlap of these individually eroded surface areas might lead to the macroscopic phenomenon of sputter removal when a sufficiently high dose of ions are bombarded to the surface in that case when sputtering is the only active mechanism for surface damage. However, the final morphology of the sputtered surface might also be affected by MIESR if sufficiently large interfacial mixing occurs close to the free surface.

We saw no further recovery process after 20 ps simulations although we have extended several runs until 500 ps. Thermally activated processes do not also play a significant role up to moderate temperatures (room temperature or so). Also we set the quenching rate to a value (5 K/fs) which seems to be a reasonable choice. Reasonable variation of the quenching rate does not affect the cooling of the system and does not lead to the recovery of the original crystal order in the upper layers.
During the simulations we observe extensive depression of the bombarded surface with respect to the non-sputtered surface. This depression did not result in a flat bottom, rather a rough surface had formed. We estimate the extent of cavitation by counting the number of missing atoms in the cavity using the same procedure introduced for vacancies [15].

Vacancies were recognized in the simulations using a very simple analysis. A lattice site with an empty cell was considered to be a vacancy, where the diameter of the cell sphere is set to $\sim 2\text{Å}$ (the radius of a sphere around the relocated atom around its original position) which is about 60% of the average atomic distance in this system. We find this criterion is suitable for counting the number of vacancies.

We used a many body potential, the type of an embedded-atom-method given by Cleri and Rosato [18], to describe interatomic interactions. This type of a potential gives a very good description of lattice vacancies, including migration properties and a reasonable description of solid surfaces and melting [18]. Since the present work is mostly associated with the elastic properties, melting behaviors, surface, interface and migration energies, we believe the model used should be suitable for this study. The Ti-Pt interatomic potential of the Cleri-Rosato [18] type is fitted to the experimental heat of mixing of the corresponding alloy system. Further details are also given elsewhere [15].

An atom is labeled mixed if it moved beyond the interface by more than $d/2 \approx 1.4\text{Å}$ along the $z$-axis, where $d$ is the interfacial Ti-Pt distance. The broadening at the interface (or interfacial mixing, IFM) is calculated as follows:

$$b = N_{mix}^{-1} \sum_{i=1}^{N_{mix}} \Delta z_i,$$

where $N_{mix}$ is the number of mixed atoms and $\Delta z_i$ is the distance of the mixed atom $i$ from the interface ($z$-axis depth position). $b$ is a useful quantity for comparison with measurements only in that case when $\Delta z_i$ is larger than the interlayer distance. The reason is that the measured broadening is dominated by those intermixed atoms which move beyond the interface by more than the inter-layer distance (2nd layer mixed atoms). Using this condition we get a reasonable agreement with Auger depth profiling [20].

III. RESULTS AND DISCUSSION

The detailed analysis of the mixing process in the Ti/Pt interfacial system after a single ion irradiation process has been given recently [15]. Here we restrict ourselfs to the study of the effect of multiple ion impacts on mixing as well as on surface erosion.
FIG. 3. The Cross-sectional view of pure hcp Ti (upper figure) and fcc Pt (lower) after 5 Ar$^+$ irradiations.

In FIGs (1)- (2) the $xz$ cross-sectional and $xy$ top plots of the Ti/Pt system are shown after the 5th irradiation. It is evident that a considerable amount of material has been removed from the irradiated area. Since the height of the non-irradiated surface did not change apart from some adatoms the material removal produces a feature like a crater. It should be added, however, that the feature formed has a rough surface. The volume of the crater is much larger than which is expected considering only sputtered atoms. The number of sputtered atoms is less by an order of magnitude then the number of intermixed Ti atoms which are pushed into the Pt bulk. These atoms cause the considerable interface broadening visible in FIGs (1) and (4). Indeed, the majority of removed atoms are the intermixed Ti atoms (injected to the bulk). In FIGs (3) we show the corresponding pure components after the 5th bombardment and see no apparent surface morphology development. This also shows that the degree of the material removal by sputtering is much weaker than the amount of the missing atoms in the case of the multilayered material. Since the difference between the pure material and the Ti/Pt system is that in the case of the latter a two component system forms due to ion sputtering, we should conclude that the presence of the second component seriously affects the mass transport and thus most likely leads to morphology development as well. Let us check more closely the correspondence between IFM and mass transport (which is measured by the volume of the apparent crater). Our primary intention is then to point out that the enhancement of surface cavitation in Ti/Pt is due to interfacial mixing. MIERSR is strongly connected to a two-way material transport (with counterflow motion) which might be understood as a radiation-induced flow of Pt atoms to the surface and the injection of Ti to the bulk.

We see the strong enhancement of IFM due to the repeated irradiation of the surface in FIG (4) where the broadening at the IF is plotted against the number of irradiation steps (upper figure). Anomalously large intermixing in metal bilayers have recently been seen as well by Buchanan et al. [21]. Surprisingly, we see the saturation of mixing (broadening) at the 5th step. The magnitude of mixing at saturation shows no dependence on heat of mixing as it was obtained in the first irradiation step [15]. Hence MIESR is not governed by thermal spikes.

In the lower part of FIG (4) the number of "missing" atoms in the top layer (vacancies) is plotted against the number of irradiation steps. The number of missing atoms is proportional roughly to the volume of the surface cavity which are mostly injected to the bulk. Interestingly these features coincide with each other: the number of intermixed Ti atoms (the "missing" atoms) saturates also at the 5th step.

The volume of the cavity rapidly increases in the first three irradiation steps and a crater similar to that of reported in earlier studies by Bringa et al. at higher impact
energies with single ion bombardment, forms [8]. In these cases cratering is attributed to the high deposited energy close to the free surface at certain nonchanneling directions. In our case, however, after repeated irradiation of the surface, there seems to be a strong correlation between interfacial intermixing and material removal from the surface (material injection to the bulk). Pt atoms intermixed to the top layers, however, do not occupy the empty sites in the cavity. Rather they form a dense phase at the surface of the cavity. The concentration of atoms in the irradiated region (10 × 10 × 10 Å³) increases from the initial 6.1 × 10²² atom/cm³ to 6.8 × 10²² atom/cm³ in the 5th irradiation step. The atomic concentration n in TiPt alloy is ∼ 7.2 × 10²² atom/cm³, therefore the increase of n in the irradiated region indicates the formation of a broad alloy phase at the interface. However, the saturation of the curves in FIGs (4) indicates that the simultaneous process of intermixing and surface cavitation is limited. A possible control factor can be the increase in the number of the undercoordinated surface atoms which is always unfavored. Another factor could be the saturation of the broadened interface. No more intermixing of Ti atoms is observed possibly due to the denseness of the alloy phase formed in the original Pt bulk which does not permit the further transport of Ti atoms to the Pt bulk. Anyhow the maximal broadening of the IF seems to be limited to b ≈ 10Å. This restriction on broadening seems not to be affected by chemical forces since it was found that the heat of mixing did not affect the IFM [15].

In order to understand more fundamentally the mechanism of MIESR we vary the atomic mass of the top layer constituent (m_{top}), keeping the same potential which can be done easily in MD simulations [17]. According to our expectations we find the suppression of IFM and surface cavitation when m_{top}/m_{Pt} → 1.

We plot in FIG (5) the number of Ti atoms which was removed from the top layers by MIESR (cavitation) as a function of the atomic mass ratio obtained from simulations in the third irradiation step. In this step we obtained extensive mass transport especially for lighter atoms (m_{top} ≈ 2 – 11 g/mol, δ ≈ 0.01 – 0.05, see also FIG (1)). Notable feature is in lower FIG (1) the enhanced cavitation with small mass ratio in the third irradiation step.

It can obviously be seen that the lighter the atoms of the top layers, the larger the extent of the mass transport. At the same time we see no obvious effect of heat of mixing on IFM [15]. It is therefore quite probable that IFM and surface roughening is governed primarily by the atomic mass difference between the constituent atoms of various layers. Mass transport from the surface layer is strongly enhanced for multilayers with light atoms in the thin top layer. This finding supports our previous conclusion [15] that the ballistic mechanism governs the IFM.

This is interesting because we are not aware of similar results where the mass transport is strongly coupled to interfacial mixing. Moreover the bulk process (mixing) and surface roughening are coupled via the enhanced material transport normal to the surface leading to a cooperative phenomenon. The importance of this finding is to point out that the surface of materials which include more components close to the surface might behave in a different way than the pure components. The surface erosion is governed not primarily by sputtering but rather by mixing. A specific feature of this system is that we found no effect of chemical forces (heat of mixing) on IFM [15]. The process is governed by the large difference of atomic mass between Ti and Pt.

In order to understand the energy saldo of mixing we plot in FIG (6) the cohesive energy (binding energy) of various atoms as a function of their depth position. The data points are collected from the 10th irradiation...
step. The atomic cohesive energy $E_{coh}$ is averaged with that of every atom’s nearest neighbors to reduce the atom-level scatter in the values. It can obviously be seen that the cohesive energy of Pt atoms decreases when the atoms move towards the surface while Ti atoms gain energy when mixed to the Pt bulk. The energy gain per Ti atom is $\sim 1$ eV on average while approximately the same energy loss occurs for the intermixed Pt atoms. Above the depth position of $\sim -30$ Å the widening of the cohesive energy “window” can also be seen for Pt. This is due to the formation of an alloy phase at the broadened interface. Close to the free surface no features of alloy phase formation can be seen, e.g. the $E_{coh}$ values are rather close to the atomic value of pure Ti. Also the $E_{coh}$ of the intermixed Pt atoms decreases at the surface which is due to their decreased coordination number ($<12$) with respect to the bulk value of 12.

Finally it should also be mentioned that the ion-induced surface cavity growth might have many common features with the growth of cavities found on boundaries in stressed polycrystals or with cracking and in general with various fracture processes at heterophase interfaces [16]. This is because we do not rule out the possibility of a cavity growth mechanism induced by a stress field generated by the thermal spike. This is, however, beyond the scope of the present article and needs further studies.

IV. CONCLUSIONS

We have shown that the mass transport for the studied double layer system is different from that of the corresponding pure elements. We have also shown that the observed apparent cavitation is in correlation with the interfacial mixing and it increases with increasing mass difference of the constituents. The most important consequence of this finding is that a reliable theory describing the surface morphology development of a system containing two components should also account for the mixing near the surface. Presently available theories are missing this point. This novel surface damage mechanism might be applicable for those multicomponent systems (e.g. thin films) where the material is subjected to low energy ion-irradiation and the interface is close to the free surface. The mechanism is regressively reliable for systems with mass ratio approaching 1.

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