

COLLISIONAL ASPECTS OF PREFERENTIAL SPUTTERING USING THE MONTE CARLO METHOD

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In fusion reactors, surface coatings such as TiC and TiB₂ are susceptible to the influence of preferential sputtering caused by plasma ion bombardment. The preferential sputtering is the result of chemical, diffusional, and kinetic processes. The kinetic processes are dominant at low energy and moderate ion flux.

A Monte Carlo code, TRIPOS, is developed for analysis of the preferential sputtering phenomenon. Argon, helium, deuterium, and tritium ion bombardment of LuFe, CuAu, TiC, and laminated AuPt alloys are simulated. The results from TRIPOS are compared with the results from other theoretical and experimental works. For helium incident on CuAu, TRIPOS gives good agreement with experiment. While TRIPOS shows general agreement with the corresponding program TRIDYN, results for argon on laminated AuPt are not in agreement with EVOLVE. Finally the case of TiC is investigated, where preferential sputtering of carbon atoms under fusion ion bombardment is observed.

1. Introduction

Because of the high heat flux on the limiter and the first wall of a fusion reactor, high-Z materials are used for their good thermal conductivities. However, the sputtering erosion of high-Z materials can jeopardize the fusion power balance by inducing excessive radiative energy losses through the introduction of impurities into the plasma. Application of surface coatings such as TiC and TiB₂ to surface components is proposed to mitigate these potential hazards.

In multicomponent materials, it has been observed that surface ion bombardment leads to preferential erosion of one of the constituents. The preferential sputtering phenomenon is not unique to nuclear fusion reactors, but is commonly observed in ion bombardment of alloy surfaces. Earlier investigations on semiconductor materials [1] also indicated this behavior. Recently, this phenomenon has been extensively investigated in experiment and theory. A complete review of experimental work in preferential sputtering is given by Betz and Wehner [2]. However, theoretical progress in this area is hampered by the complexity of the mechanisms controlling preferential sputtering.

The mechanisms for preferential sputtering involve synergistic dynamic, diffusional, and microchemical processes. Dynamic processes arise from differences in recoil energy partitioning, implantation, and range for different types of bulk atoms in an alloy. Diffusional processes are mainly caused by differences in recoil diffusion, segregation, radiation enhanced diffusion, and radiation enhanced segregation for bulk atoms of different types. Microchemical processes originate from local chemical property changes caused by stoichiometric changes such as the changes in surface binding energy, the formation of new phases, and the implantation of incident ions. The interplay of these three processes obviously complicates the theoretical analysis of preferential sputtering.

It is necessary to isolate each individual mechanism so that a better understanding of this phenomenon can be achieved. This view is reflected in earlier studies such as EVOLVE [3] and TRIDYN [4] which explored the kinetic aspect of preferential sputtering. Such analysis is generally justified under the situation when the energy of the incident ion is low and the ion flux is moderate. The requirement for a moderate ion flux is due to the fact that the ion flux needs to be high enough so as to avoid the domination of the chemical and thermodynamical processes at low flux levels.

The energy partitioning in the kinetic process favors matrix atoms with masses close to those of incident ions. This can be readily seen in the kinetic energy transfer factor, \mathcal{A} , defined as follows:

$$\mathcal{A} = 4M_1M_2/(M_1 + M_2)^2, \quad (1)$$

where M_1 and M_2 are the masses for incident and recoil atoms, respectively. For identical masses, \mathcal{A} is 1 and perfect energy coupling is achieved. On the other hand, for larger mass differences, \mathcal{A} can be close to 0 leading to poor energy transfer. In a fusion reactor, the plasma is mostly composed of deuterium and tritium ions. It is therefore anticipated that light atomic constituents in the first wall and limiters can gain higher recoil energy than the heavier constituents. Furthermore, the interaction cross section for lighter ions is small compared to that of heavier ions. Therefore, lighter recoils can be transported deeper into the surface because of their higher energy and lower interaction cross section. This fact can lead to the depletion of lighter atoms in the surface regions bombarded by fusion ions.

Because of the implantation of incident ions, sputtering of surface atoms and the recoil mixing effect, the surface composition of an alloy is a function of both ion flux and irradiation time. This renders the analysis for preferential sputtering both time and fluence dependent. The study of the kinetic aspect of preferential sputtering is based on the Monte Carlo code, TRIPOS,

developed and used in an earlier paper [5]. A time dependent option is introduced into the original TRIPOS code. Because of the disagreement in the results from TRIDYN and EVOLVE [4], we investigate the cases of 2 keV Ar on laminated AuPt as in ref. [3] and 5 keV Ar on LuFe as in refs. [4] and [6]. We also compare our theoretical work to the experimental results of Nelson and Bastasz [7] for the case of 150 eV ^3He on CuAu. Finally, the preferential sputtering effect in TiC coatings caused by fusion ions is investigated.

2. Application of TRIPOS to surface modification problems

The energy losses for ion transport in a solid are caused by nuclear collisions and interaction with the electron system (electronic stopping). TRIPOS uses continuous power law cross sections to treat the nuclear energy loss and the Biersack–Hagmark electronic stopping [7] to treat the electronic energy loss. It is worth mentioning here that the codes TRIM [7] and MARLOWE [8] use an empirical fitting function to estimate the numerical solution for the time integral for nuclear energy losses. Similar to the code HERAD [9], TRIPOS uses a continuous form of the power law cross section which is derived using the power law approximation to the Thomas–Fermi potential [10,11]. At low energies, the cross section derived from the Born–Mayer potential is used [11]. The power law cross section is used to estimate the free path between two large-angle collisions, while on the other hand, for the small angle nuclear collisions, the nuclear stopping cross section is used. This scheme allows the free path to be of the order of several lattice constants. Therefore, TRIPOS bypasses the limitation that the free path be on the order of a lattice constant even though the nuclear energy loss can be negligible.

Because the statistical error associated with analog Monte Carlo decreases with the inverse of particle histories, particle splitting and Russian roulette techniques are used in TRIPOS. The importance zone is taken to be the first few atomic layers where most of the sputtered particles originate. The analog Monte Carlo code TRIPOS is a factor of 3–10 faster than the TRIM code. A 4 to 1 kill outside the importance zone can effectively reduce the computation time by an extra factor of 3. Detailed studies of the relative speed between TRIM and TRIPOS are given in ref. [12].

The preferential sputtering of an alloy is both time and flux dependent because of the evolution in surface compositions. Therefore, the original TRIPOS code has been modified to have time-dependent and composition modification capabilities. There are also other phenomena in preferential sputtering processes requiring further modifications of the TRIPOS code. For example, the recoil implantation and mixing can cause the formation of local super-dense material which leads

to local relaxation and expansion. This process is related to the phenomenon of recoil mixing. The super-dense solid is modeled to expand homogeneously until the theoretical density is reached. Because light ions are implanted deeper, such a process can lead to the de-enrichment of heavier atoms in the bulk in a fusion environment. For more detailed description of the dynamic TRIPOS code, please refer to Ch. 7 of Chou's dissertation [12].

3. Results of preferential sputtering calculations

The results from TRIPOS simulations of four different cases of preferential sputtering arising from ion bombardment are presented below:

3.1. Ar on AuPt

In the work by Roush et al. [3], a surface composed of alternating pure gold and platinum layers with a thickness of 40 Å each was studied. The front surface is gold. The argon ion beam impinges on the surface at an angle of 70° with an energy of 2 keV. The surface binding energies are 3.8 eV and 5.9 eV for gold and platinum atoms, respectively. Their results predict a zone of atomic mixing with a depth of about 40 Å. However, our calculations using TRIM and the static version of TRIPOS indicate that the projected range for those argon ions is between 14 and 16 Å. Also results from dynamic TRIPOS show a 15 Å thickness of the mixing zone. This result is not in agreement with the results of EVOLVE. However, it is consistent with the projected range for the incident argon ions. Fig. 1 shows plots for relative concentrations (represented by pseudo particles) of gold and platinum as functions of pseudo particle histories.

The disagreement between EVOLVE and TRIPOS can be explained by the following argument. Because gold and platinum recoils have very short projected ranges, it is unlikely for argon ions to generate significant recoil implantation-mixing effect at the end of their ranges. The EVOLVE analysis apparently over-estimates the projected range of ions. The sputtering yield from the EVOLVE calculation is larger by a factor of 30% compared to that from TRIPOS. This explains the differences in the rates of surface recession due to sputtering erosion.

3.2. Ar on LuFe

In the investigations conducted by Roush et al. and Moller et al. [4,6], a surface made of 50% iron and 50% lutetium alloy is bombarded with 5 keV argon ions at a normal angle of incidence. The surface binding energy is 4.7 eV for both iron and lutetium atoms. The composition profiles from TRIDYN and EVOLVE also show some discrepancies. TRIDYN predicts a de-

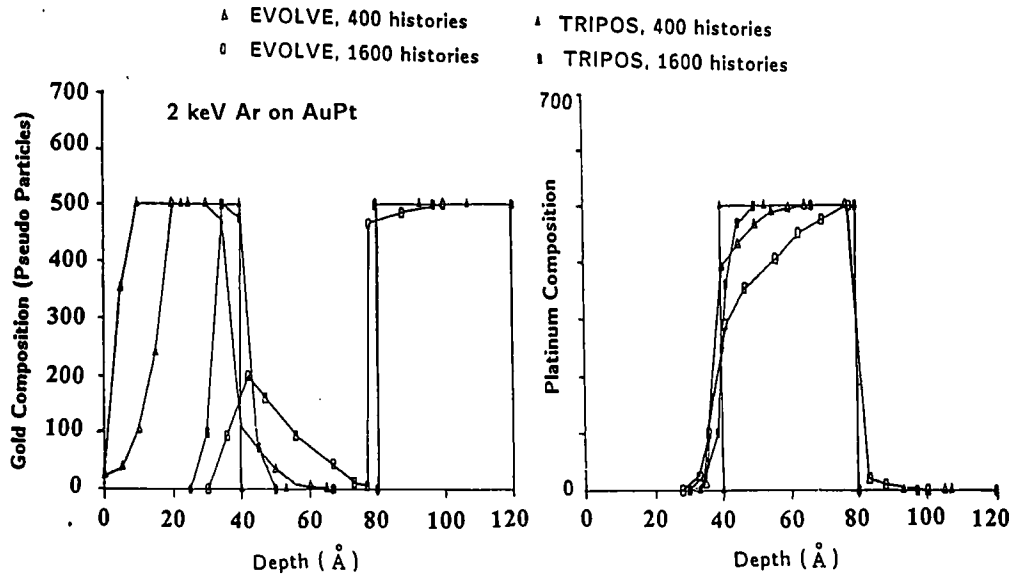


Fig. 1. Composition of gold and platinum as a function of depth predicted from EVOLVE and TRIPOS for 400 and 1600 pseudo particle histories of 2 keV argon ions on laminated AuPt. A pseudo particle history represents a fluence of 5.9×10^{12} ions/cm².

pletion of iron atoms below the surface; this depletion zone corresponds to the projected range of the argon ion which is 65 Å [4]. For the region beyond the projected range, depletion of lutetium atoms is observed because of iron recoil implantation. For the surface layer, EVOLVE predicts an enrichment of iron ions at low fluences and a depletion of iron ions at high fluences. For regions beyond the projected range, an enrichment of lutetium atoms is predicted by EVOLVE for all fluences.

TRIPOS simulation yields results similar to those from TRIDYN as shown in fig. 2. The enrichment of lutetium atoms is below the surface and enrichment of iron atoms around the projected range. Also given in fig. 2 are the results from EVOLVE simulations. Only the enrichment of lutetium is observed over the whole zone. The results from both TRIPOS and TRIDYN strengthen the argument we presented for the previous case of Ar on AuPt. Recoil implantation and mixing of very heavy atoms at the end of range for light incident ions are unlikely to occur, which can be a source of error.

3.3. ³He on CuAu

In the experimental work of Nelson and Bastasz [13], a surface composed of Cu–Au 3% is irradiated with 150 eV ³He ions at a normal angle of incidence. The surface binding energies for copper and gold atoms are 3.5 eV and 3.8 eV, respectively. Their results show that the enrichment of gold in the surface increases linearly with the ion fluence with 5% Au at a fluence of 6×10^{17} cm⁻². Based upon a simplified analytical

theory, they concluded that the altered layer, which is the recoil mixing zone, has a thickness equal to the projected range of the incident ion. The projected range of 150 eV ³He ions is about 16 Å.

TRIPOS simulation shows an enrichment of gold atoms within a few atomic layers (5–7 Å) from the surface. Beyond this region, there is an enrichment of copper atoms from light recoil implantation and mixing up to the end of the projected range. Fig. 3 shows that the average enrichment for gold over the projected range agrees well with the experimental results by Nelson and Bastasz [13] for ion fluences up to 4×10^{17} cm⁻². For

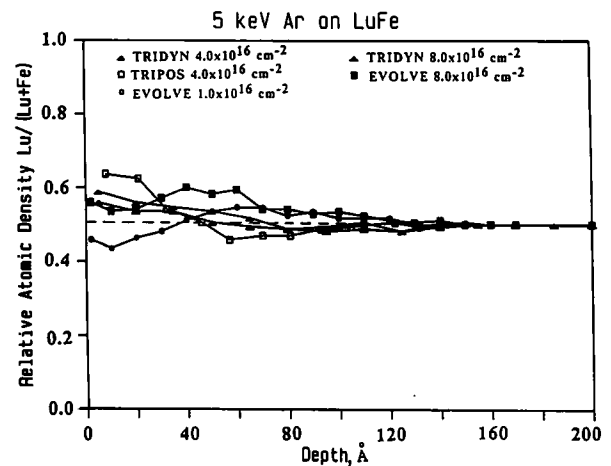


Fig. 2. Relative atomic density of lutetium as a function of depth predicted from EVOLVE, TRIDYN and TRIPOS for 5 keV argon bombardment of LuFe at different fluences.

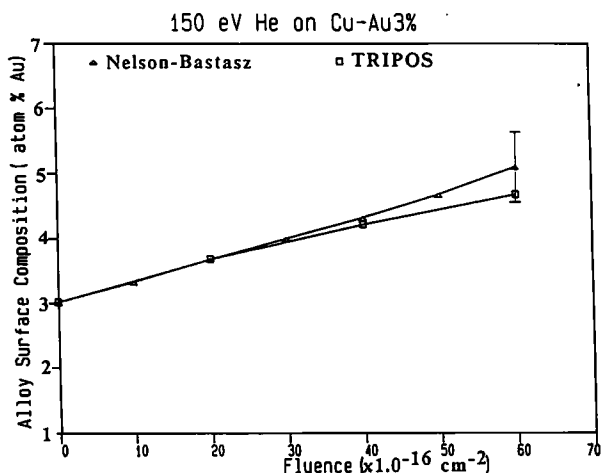


Fig. 3. Gold surface composition in atomic percent as a function of fluence. Experimental work is by Nelson and Bastasz and theoretical calculations are from TRIPOS for 150 eV ^3He on Cu-Au 3%.

higher fluences, there is about an 8% difference which is within the experimental error. A possible cause for this difference can be the formation of a monolayer of gold on the surface which in turn reduces the sputtering of copper atoms. Our observation of gold atom enrichment in the first 5–7 Å below the surface seems to support this argument.

3.4. Fusion ions on TiC

The ion considered for this analysis consists of average fusion plasma ions. Because of the presence of the Debye layer in which ions are accelerated to several times their original energy along the surface normal, the angle of incidence is assumed to be perpendicular to the surface and ion energy is taken to be a factor of 3 to 5 higher than the average edge plasma temperature. Varga and Taglauer [14] analyzed TiC surfaces bombarded with hydrogen ions with energies in the range of 300 eV and 4 keV. Their observation shows that carbon atoms are enriched on the surface [20]. Such behavior, i.e., the enrichment of light atom, is also observed for other alloys such as carbon enrichment on the surface of NbC, MoC and NiC [15,16] as well as lithium monolayer formation on CuLi [17]. The mechanisms behind this behavior are attributed to the diffusional processes where radiation-enhanced diffusion and segregation occur. Franconi et al. [18,19] and Oishi et al. [20], however, have experimentally and qualitatively observed that carbon atoms are preferentially sputtered and consequently titanium atoms are enriched in the surface regions:

The TRIPOS simulations were performed with the surface binding energies of 4.89 eV and 7.47 eV for titanium and carbon atoms, respectively. The energy of incident ions is assumed to be 300 eV. TRIPOS re-

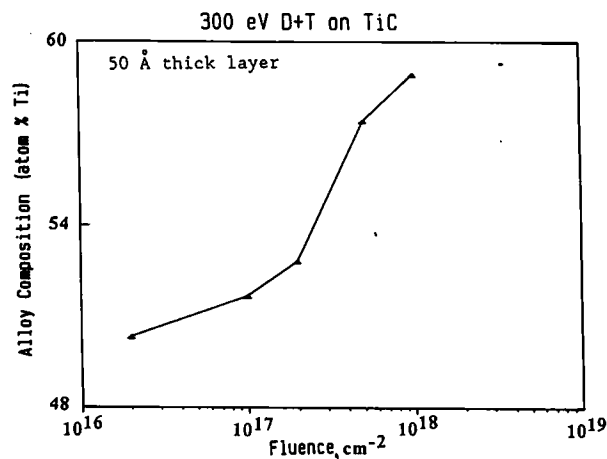


Fig. 4. Titanium surface composition in atomic percent as a function of fluence calculated by TRIPOS for 300 eV fusion ions on a TiC coating.

sults show that the sputtering rate for carbon atoms is about twice that for titanium. The projected range is about 80 Å. A hundred thousand pseudo particles were used with each representing a fluence of $1 \times 10^{13} \text{ cm}^{-2}$. For fluences up to $1 \times 10^{18} \text{ cm}^{-2}$, a 50-Å-thick layer below the surface is enriched with titanium atoms as shown in fig. 4.

This result seems not to agree with the experimental observations by Varga and Taglauer [14]. The discrepancy may probably be attributed to the strong influence of microchemical and non-equilibrium thermodynamic processes unique to their experiment. Nevertheless, this result agrees qualitatively with the observations by Franconi et al. [18,19] and Oishi et al. [20].

4. Conclusions and future directions

The phenomenon of preferential sputtering is an important physical process for fusion reactor and other technological applications. This phenomenon is dominated by the kinetic process at low energy and moderate ion fluence.

A Monte Carlo ion transport code, TRIPOS, is developed for study of the collisional effect on preferential sputtering and surface evolution. This code can simulate the ion bombardment-induced composition changes as a function of time and ion fluence. A static version of TRIPOS is more efficient than TRIM which is a static version of TRIDYN. TRIPOS is applied to the preferential sputtering of several alloys under different ion bombardment conditions. While the results of TRIPOS on LuFe and CuAu agree with those of TRIDYN as well as with experimental work, our calculations on laminated AuPt show some disagreements with EVOLVE.

Because of the complex nature of preferential sput-

tering, theoretical methods seem to fall short of predictions for one of the TiC cases. Neglecting other preferential sputtering mechanisms besides collisional processes seems to result in disagreement between theoretical and experimental results. For other TiC cases, however, theoretical prediction confirms the experimental observation. A more comprehensive treatment of preferential sputtering including accurate surface modeling is required to resolve these discrepancies.

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