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**PLASTIC FLOW IN FCC METALS INDUCED
BY SINGLE-ION IMPACTS***

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Abstract

Irradiation of Au and Pb foils with Xe ions at temperatures between 30 and 450 K has been monitored using in-situ transmission electron microscopy. Single ion impacts give rise to surface craters on the irradiated surface with sizes as large as 12 nm. Approximately 2 – 5 % of impinging ions produce craters on Au while only about 0.6% produce craters on Pb. Larger craters on Au frequently have expelled material associated with them.

Temporal details of crater formation and annihilation has been recorded on video with a time-resolution of 33 milliseconds. Craters annihilate in discrete steps due to subsequent ion impacts or anneal in a continuous manner due to surface diffusion. Craters production (those persisting for one or more video-frames) as a function of temperature indicates that the surface diffusion process responsible for thermal annealing of craters has an activation energy of 0.76 eV in Au.

Crater creation results from plastic flow associated with near surface cascades. Crater annihilation in discrete steps results from plastic flow induced by subsequent ion impacts, including those that do not themselves produce a crater.

Introduction

Most measurements and observations of ion impacts on surfaces have been of the collective effects of many displacement spikes, the ensuing thermal spikes and both thermal and irradiation-assisted defect annealing that may subsequently take place. In recent work, we have irradiated thin gold specimens in-situ in a transmission electron microscope (TEM) to study the effects of spikes resulting from the impact of individual Xe ions. Single ion impacts on very thin foils (<50 nm) generate holes [1] while ion impacts on thicker films produce craters [2]. We identified pulsed, localized plastic flow associated with heavy ion impact as important to the surface evolution of Au during irradiation [1,2]. These effects are driven by dense displacement cascades located at or near the specimen surface. Surface spikes can, by either melting or ballistic atomic displacements,

transport of tens of thousands of atoms on to the surface. Years of experimental observations have yielded only two other reports of cratering on Au [3] and Mo [4], both of which were post irradiation examinations. In this work we have made in-situ observations of heavy-ion irradiated Au as a function of temperature, and extended the study to include Pb at room temperature.

Experimental

In situ ion irradiations were carried out in a Hitachi A-9000 TEM operating at 300 keV at the IVEM/Accelerator Facility located at Argonne National Laboratory [5]. Two types of specimens were used. Thin Au films were made by thermal evaporation of 99.999 at % pure starting material onto NaCl at a temperature of 350°C. This resulted in a largely monocrystalline film with a $\langle 100 \rangle$ surface normal. Bulk specimens of Au and Pb were produced by electrochemically thinning 3 mm discs were punched from rolled, annealed foils with a 99.999 purity. The ion beam in the IVEM/Accelerator Facility is oriented 30° from the microscope axis. The specimens were tilted 15° towards the ion beam so that both ions and electrons were incident on the specimen at 15° to the foil normal. Specimens were irradiated with Xe⁺ ions at energies in the range 50 to 400 keV at dose rates between 10^{10} and 10^{12} ions/cm²/s. In addition to normal photographic recording, images from a Gatan 622 video camera and image-intensification system were viewed with total magnifications of approximately 2 million, and recorded on video tape with a time resolution of 33 ms (1/30 second—a single video frame).

Results

Room Temperature Irradiation

Figure 1 shows typical craters observed on the surfaces of gold at 50 keV and 400 keV. Note that craters are made visible using phase contrast by defocusing the objective lens, and the images in figure 1 are the result of averaging four video frames. The specific details of cratering in is briefly discussed below. Detailed results for gold have been reported elsewhere [2]. Single Xe ions, with energies between 50 and 400 keV, produce craters that have sizes ranging from 2 to 10 nm. Crater have a size distribution that extends down to our resolution limit, but on average the craters produced by 50 keV ions are smaller than craters produced by 200 or 400 keV ions. When ions can penetrate

the foil, craters are observed on both surfaces. Between 2% and 5% of ion impacts result in craters.

In many cases, videotape recordings of in-situ irradiation experiments reveal that material can be expelled from the crater leading to a volcano-like structure, or a solidified droplet of gold in close proximity to the crater. This is strengthened by a pseudo 3-D image of a volcano-like crater, produced by transforming intensity resulting from TEM defocus contrast into a height variation [6]. Examples of such droplets and lids associated with large craters are shown in figure 1. The lids and droplets first appear on the same video frame as their crater. Lids and droplets were not seen during the 50 keV irradiation or in association with smaller craters during other irradiations. These observations are clear evidence that plastic flow processes are responsible for crater formation. An energetic ion creates a displacement spike leading to the formation of a small zone, ≈ 10 nm in diameter, in which the gold is melted for a brief time. The resultant expansion is sufficient (and the time for which the material is molten is sufficiently long) to expel much of the molten gold on to the surface where it may either diffuse from the impact site or solidify near the crater.

Craters on Au are stable at room temperature when the ion beam is off. Subsequent ion impacts are observed to lead to the annihilation of the crater in one or more discrete steps. In some cases this is seen to occur as a consequence of plastic flow from a neighboring impact site. In other cases, the impact of the ion that causes the full or partial annihilation is not observed. Small craters, less than XX nm in diameter are generally annihilated in a single step. Assuming that all impinging ions may annihilate existing craters, the cross section for crater annihilation on gold is approximately 85 nm^2 .

The life cycle of a crater on Pb is shown in figure 2. In general, it was difficult to discern the precise shape of craters on Pb, likely due to the higher degree of defocus required to image the craters. The necessity for a higher degree of defocus indicates that craters on Pb were shallower than on Au. However, faceting is visible in the craters. Unlike gold, there was little evidence of material ejected from the craters visible as particles on the surface. Approximately 0.3% of ion impacts result in craters. Craters on lead are thermally stable at room temperature when the ion irradiation is halted.

Under conditions of continual irradiation, as previously reported for gold, the craters are annihilated by subsequent ion impacts. Careful inspection of the video recording indicates that the partial annihilation of craters that reduces their

sizes is not a continuous process but takes place in discrete steps. This process is shown in figure 2 where a crater disappears in three discrete steps. The numbers on each segment refer to the number of video frames after the crater was formed (30 frames per second). The crater disappeared at frame 134. The ion flux was 6×10^{10} Xe/cm² sec, and 2.8×10^{11} Xe/cm² impacted the specimen during the crater life. If it is assumed that all impacts are able to cause the partial annihilation of a nearby crater, then the cross section for this process is approximately 120 nm², a circular area approximately the size of the initial crater.

A final important point with regard to Pb is that until the specimen had been bombarded with a dose of approximately 4×10^{14} ions/cm², no cratering was observed. At doses below this value, inspection of the diffraction pattern indicated that an amorphous oxide layer was present on the specimen surfaces. When cratering began to occur, the diffraction pattern revealed that the oxide layer had been removed by sputtering. The clear implication of this observation is that cratering is suppressed if an oxide layer is present on the specimen. This is consistent with the finding by Merkle and Jager [3] that a thin amorphous layer of carbon deposited on gold films reduced the incidence of cratering on the gold surface.

High Temperature Irradiation

Elevated temperature in situ irradiation experiments were performed on Au using a heating stage in the TEM. The crater production efficiency as a function of temperature is shown in figure 2 for 200 keV Xe ions. Craters were not observed (or more accurately crater persistence was less than 33 ms) above some temperature. At elevated temperatures, the observed cratering is a result of competition between the displacement process, the direct ion-induced annihilation process and thermal recovery processes that occur on the time scale of a video frame. The craters observed are those that last at least one video frame or 1/30 sec. As the temperature is increased there is an increasing probability that a newly produced crater will shrink below a detectable size or not survive long enough to be recorded on video.

Crater annealing is a radiation-assisted, thermally activated process with the smallest craters annealing away before the largest craters. The mobile defect responsible for annealing is most likely the surface adatom produced by the irradiation. The self interstitial is able to migrate at temperatures below 5 K in both metals studied here. At the temperatures used in this study interstitial atoms

will quickly reach the surface and migrate as adatoms by surface diffusion. Taking the crater to be a hemisphere of radius r that anneals by the arrival of surface diffusing defects, the number of missing atoms in a crater, n , is described by

$$dn/dt = -P_n P_i D_0 e^{Q/KT} \quad 1$$

where the number of lattice sites around the rim of the crater is given by $P_n = 2\pi r/a = (12\pi^2)^{1/3} n^{1/3}$ where a^3 is atomic volume and recovery by surface diffusion is described by a radiation-induced surface adatom concentration P_i that is proportional to the ion flux, a diffusion rate D_0 and an activation energy Q . The solution to equation to 1 is

$$n^{2/3} - n_0^{2/3} = -\{2/3 (12\pi^2)^{1/3} P_i D_0 e^{Q/KT}\} t \quad 2$$

The lifetime of a crater of initial size r_0 is given by the time interval between creation and the moment when n goes to zero:

$$t = 1/2 (r_0/a)^2 e^{-Q/KT} / P_i D_0. \quad 3$$

Crater lifetime depends on the initial crater size, irradiation flux and the temperature.

During observation of crater production, all cratering events were counted regardless of their duration providing that they survived long enough to be recorded on a single video frame, $t > 1/30$ sec. Only craters with sizes larger than a minimum size, given by the relationship in equation 3, have the required lifetime. Given the minimum size required for survival at a given temperature, the total number of craters that will be recorded can be calculated from the size distributions at a temperature where they are thermally stable. This approach was used to determine the activation energy Q , by fitting the measurements in figure 2, and the results are shown as the solid lines in the figure. The activation energy determined from this fit is 0.76 eV for Au. A value of 0.9 eV has been measured for thermal annealing of surface roughness on Au [7]. The difference may be associated with defect formation.

Discussion

The energy deposited in damage by Xe ions incident on Au can be estimated using the Monte-Carlo program TRIM 96 [8]. A xenon ion incident on Au, with any of the three energies studied, deposits most of its energy in

approximately spherical volumes between 5 and 10 nm in diameter. Although, not every atom in this volume is involved in the ballistic cascade, prompt processes result in the distribution of the energy throughout the cascade volume. Within $\approx 10^{-11}$ sec of ion impact, atoms within the cascade volume will have an average energy, E , of approximately 2 eV. Such an energy would result in melting and a 11% free volume expansion.

The hot zone of a cascade close to a surface creates a pressure spike that is able to expand freely in one direction. A likely consequence of the sudden melting of this volume of material, with its concomitant volume change of 11%, is an explosive funneling of gold atoms to the surface in a manner similar to that observed by in molecular dynamics simulations of gold ions impacting on gold [9,10]. Material expelled from a new crater may flow across the surface and annihilate a nearby pre-existing crater. It is important to note that, on average, insufficient energy per atom is available to overcome the surface binding energy of 3.8 eV and that the majority of gold atoms will therefore remain on the surface.

If the molten core of a spike does not directly erupt through the surface, the high localized pressure may result in the ejection of a plug of solid material that then permits the subsequent explosive flow of molten gold to the surface. In this case, a crater can also form. We believe that this is the origin of the craters with associated lids or mounds. Finally, the appearance of an isolated particle, may result either from the punching out of a number of dislocation loops to the surface by a subsurface pressure spike or the complete ejection of a solid plug that comes to rest at some distance from its crater.

The survival of surface features for sufficiently long to be recorded is dependent on the mobility of surface defects. The crater creation efficiency in Au is a function of temperature as shown in figure 3. Above some temperature, cratering is not observed or recorded. This is due to our using a recording system with a quantized time resolution. For our TV-rate system this is 1/30 of a second. Above the temperature limit, we believe that craters are still being formed in the same manner as at lower temperatures, but the diffusion of surface defects (probably adatoms) is occurring at a sufficient rate so as to rapidly fill-in the craters to the point that they are not recorded. This allow extraction of an activation energy of 0.76 eV for the crater annealing process on Au.

Even during low temperature irradiations, crater lifetime is relatively short under conditions of continued irradiation. Craters on the materials studied

were observed to filled in by discrete steps. In some cases, plastic flow is clearly observed to be responsible (i.e., when a neighboring crater is formed) but, in many cases, craters are observed to be annihilated by impacts that do not themselves leave a crater. This may simply be a consequence of defects arriving at the surface from individual ion impacts whose cascade occurs below the surface.

The pressure spike model does not provide an explanation for the efficient annihilation of craters by subsequent ion impacts. While material ejected from the small percentage of spikes that occur at a surface may result in the direct annihilation of nearby pre-existing craters, this is not the case for the majority of subsurface spikes. We speculate that during the quenching phase of these spikes, irradiation stimulated surface atom mobility of previously ejected material and crater edges combined with defect fluxes to the surface leads to the annihilation of craters and particles. Similarly, the faceting of craters and particles, which may be irregular when created, occurs due to irradiation stimulated surface diffusion processes. These processes go to completion during the time required to record one video frame (1/30s) so that all observed craters are the result of both the creation and subsequent annealing processes taking place during the quenching phase of the spike as well as any diffusion processes that go to completion at room temperature on a time-scale of $\approx 1/30$ s.

Conclusions

Single ion impacts produce dense, near surface, displacement spikes in high density materials. These spikes produce surface cratering. The mechanism is the explosive outflow of material from the hot molten core of the spike. The presence of an oxide film on the surface suppresses this process. Direct crater annihilation occurs as a result of material transport from the sites of subsequent ion impacts. At temperatures where surface defects are rapidly mobile, irradiation enhanced annealing of craters occurs.

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Figures

- Figure 1** Craters on Au produced at room temperature by 50 or 400 keV Xe irradiation.
- Figure 2** Life cycle of a crater on Pb produced at room temperature by 200 keV Xe irradiation. The numbers on each segment refer to the number of video frames after the crater was formed (30 frames per second). The crater disappeared at frame 134. The ion flux was 6×10^{10} Xe/cm² sec.
- Figure 3** Temperature dependence of cratering on Au by 200 keV Xe ions.

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