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Letter to the Editor

Electron radiation damage of α-alumina

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Electron irradiation studies of α-alumina were conducted in both high vacuum and ultra-high vacuum (UHV) environments. In the high vacuum (10^{-5} Pa) of a conventional high resolution electron microscope (C-HREM), the crystal surfaces damaged to form characteristic "dark-line" facets under low-flux (10 A/cm^2) conditions. However, in the UHV (10^{-8} Pa) environment and similar electron flux, the surfaces did not facet and only suffered from oxygen loss. Under continued irradiation crystallites of aluminum formed on the surfaces. The damage process was accelerated at 100 keV, a regime where relative rate of ionization is favored and ballistic knock-on processes are minimized. These results signify that the damage process in α-alumina is associated with an ionization mechanism where the reaction products are greatly controlled by the ambient vacuum in the microscope.

1. Introduction

Alumina is a very important material with wide commercial and industrial applications. Alumina is also a candidate material for potential use in outer space as protective coating on dynamic solar power modules. As a forerunner to space applications, materials must be tested to determine their ability to withstand the ionizing environment. The electron microscope serves a useful function to this end; the vacuum in the column is close to that in low earth orbits, and the electron beam provides the ionizing radiation as well as a means to observe the structural changes occurring at the atomic level during the radiation process.

The behavior of alumina under ionizing radiation has been the subject of much interest. Pells and Phillips [1,2] irradiated alumina in a high-voltage microscope (HVEM) to determine the temperature and dose dependence of the damage thresholds. Stathopoulos and Pells [3] extended the study to measure thresholds for ballistic knock-on damage as determined by the formation of dislocation loops. Recently, the formation of "dark-line" faceting in alumina in a medium-voltage EM was reported by Bursill et al. [4]. This faceting phenomenon was attributed by Bursill and Lin [5] to a monolayer of a spinel phase, though detailed image simulation was absent from the report. In addition to facet formation, Bursill et al. [4] reported the formation of a "patchwork quilt" pattern in alumina. Under an intense electron beam, Mochel et al. [6] were able to drill holes in metal β-aluminas. Berger et al. [7] also drilled holes in both β- and amorphous aluminas where metallic aluminum was detected by electron energy loss spectroscopy (EELS). They attributed the damage mechanism to a Knotek–Feibelmann [8,9] process whereby oxygen atoms are desorbed from the surface by a core-level ionization process.

As part of a wider study of the behavior of materials in the space environment, α-alumina was damaged in the electron microscope under various conditions. Consistent with earlier results, facet formation was detected on the crystal surfaces. Facet formation occurred rapidly under electron irradiation and, in most cases, can be considered a feature of the initial surface. Whereas Bursill et al. reported facet formation on the $[11\bar{2}0](0006)$ habits of alumina, we have determined that the facet formation is not limited to this zone and occurred on almost all crystal orien-

tations. In addition, the facet formation appears to be intimately linked with the ambient vacuum at the specimen. While we detected facets in the C-HREM, they did not form when alumina was irradiated under UHV conditions. Instead, small crystallites of aluminum formed on the surface of the irradiated alumina. In this Letter we describe the results of our investigation of the electron radiation damage in α-alumina under both high vacuum and UHV conditions.

2. Experimental method

The specimens were prepared by crushing Aesar corundum (99.99%) in a methanol slurry. The re-

Fig. 1. Irradiation of α-alumina in the C-HREM at 300 keV in a time sequence. The initial surface of the [11$\bar{2}$0] zone (a) has some facets present. The same surface (b) after 30 minutes of low flux irradiation (10 A/cm^2). After 2 hours or irradiation (c) the faceting becomes more extensive and progresses into the bulk. There is evidence, though unclear, of a phase transformation at the surface. Other crystal orientations such as the [2$\bar{2}$01] zone (d) also facet in C-HREM.

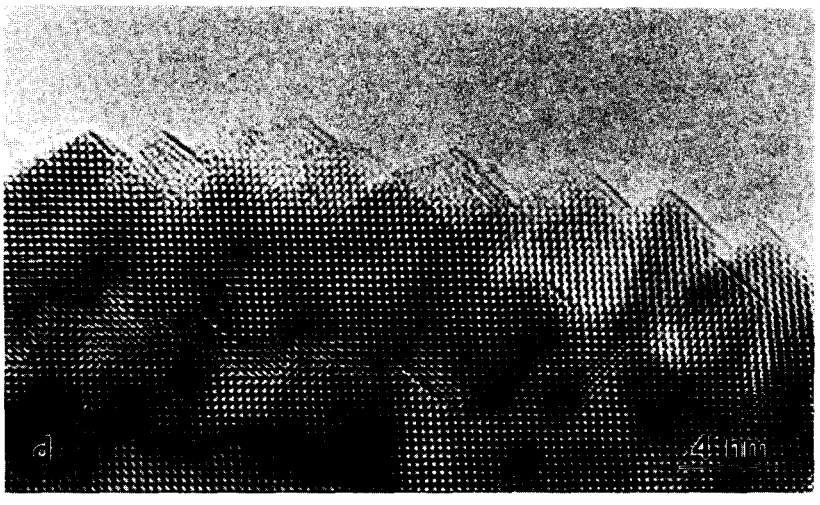

Fig. 1 (continued).

sulting solutions were dispersed on holey films; carbon for the C-HREM and SiO for the UHV-HREM. The Hitachi H9000 HREM used for the C-HREM work had a vacuum of 2×10^{-5} Pa at the specimen while the UHV-H9000 experiments were conducted at a working vacuum of 3×10^{-8} Pa at the specimen. The H9000 microscopes have an accelerating voltage variable from 100 to 300 keV. The flux conditions were measured by means of a Faraday cup in the H9000 and similar conditions were established for use in the UHV-H9000 for comparison.

3. Results and discussion

Specimens of α-alumina were damaged in the C-HREM under low flux (10 A/cm^2) which is typical of the conditions used in HREM. From the onset of observation the faceting phenomenon was observed; that is, in the time necessary to orient a crystal along a specific zone axis (a few minutes) facets had already formed along the surface and thus, in most cases, can be considered a feature of the initial surface. Under prolonged electron irradiation the faceting became more extensive though the facets themselves remained confined to a specific habit plane. Fig. 1 shows a time sequence under constant flux in non-UHV conditions at 300 keV; the faceting is clearly evident. Simultaneous with facet formation, α-alumina suffered from surface roughening, due to ionization damage, resulting in a "quilt" pattern of contrast between thick and thin regions of the crystal. Facet formation was observed for a variety of different crystal orientations (see fig. 1d) and always occurred on those surfaces where "normal" atomic terminations result in planes of either oxygen or aluminum. The damage process also appeared uncorrelated with the crystal orientation. Under conditions of higher electron flux, and lower electron energy, both facet and "quilt" formation accelerated.

We should note that while facet formation occurred along many orientations, the facet itself always appeared in profile, as a "monolayer". Consider, for example, facets along $[2\bar{2}01]$ which form upon $(0\bar{1}14)$ habits. This profile surface, when viewed in plan view, is representative of the $[11\bar{2}0]$ orientation, and assuming the spinel structure of the facets is correct, would give discernibly different HREM images for faceted and unfaceted surfaces. We have not detected such differences in the images implying that the facets form parallel to the electron beam, i.e. top and bottom surfaces of the crystal are unfaceted.

The damage process in α-alumina was accelerated by irradiating with 100 keV electrons, see fig. 2. In the C-HREM the initial surfaces were smooth and very little faceting was present; how-

ever, after irradiation for 90 min (~ 20 A/cm^2) the crystal surfaces had extensive faceting and considerable surface roughening. In the 100 keV regime, ionization processes are favored relative to ballistic processes whereas the opposite is true at higher electron energies. That α-alumina damages, and at a rather fast rate, indicates that an ionization mechanism is responsible for facet formation either as a contaminant-catalyzed or intrinsic process. We should note that the presence of a carbon overlayer seems to locally quench the damage process as in other materials [10].

In contrast to the C-HREM results, crystals of α-alumina irradiated in the UHV-H9000 under similar flux conditions did not exhibit facet formation. Instead, under irradiation the formation of aluminum was detected. Fig. 3 presents the results from the [11$\bar{2}$0] and [2$\bar{2}$01] zone axes, respectively. (PEELS was performed on these specimens and indicated that the O K-edge intensity decreased during the irradiation process, though the structure of the Al $L_{2,3}$-edge could not be well resolved.) These results indicate that facet formation is controlled by the ambient vacuum environment of the the microscope. Whereas the C-HREM can be expected to have a relatively "dirty" vacuum of 10^{-5} Pa with molecular oxygen and residual hydrocarbons from pumps present, the UHV-H9000 represents a clean, dry environment of 10^{-8} Pa where the probability of surface reac-

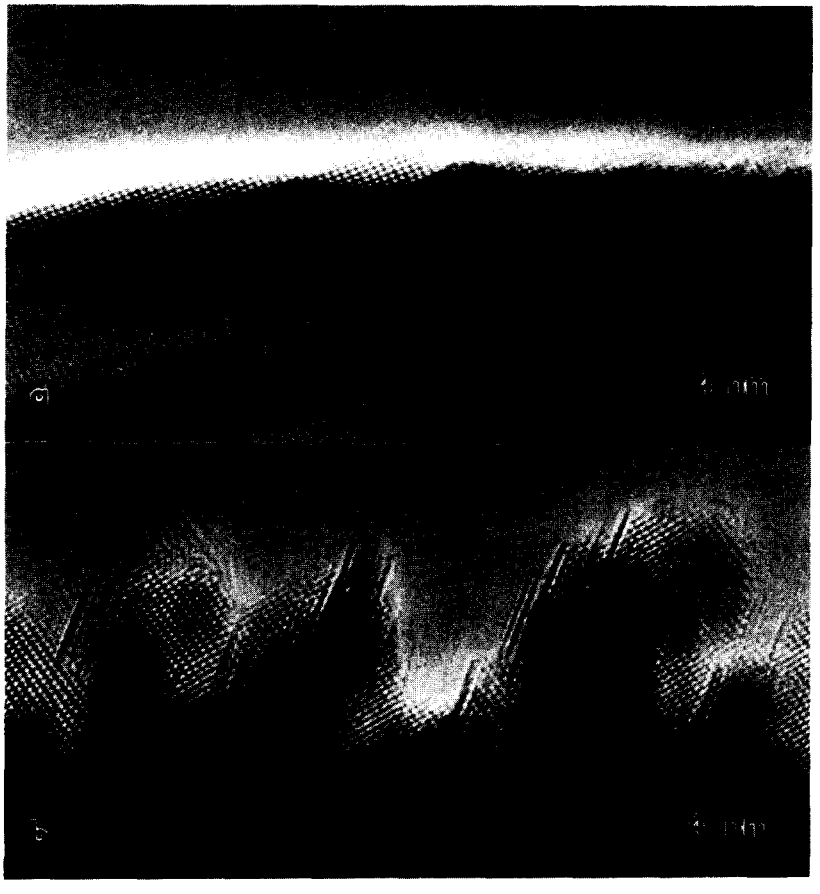

Fig. 2. Irradiation of α-alumina at 100 keV in C-HREM accelerates the damage process. The initial surface (a) of a thick crystal along [11$\bar{2}$0] shows no faceting and a smooth surface. After 90 minutes (b) of moderate flux (20 A/cm^2) irradiation the surface shows extensive faceting and surface roughening.

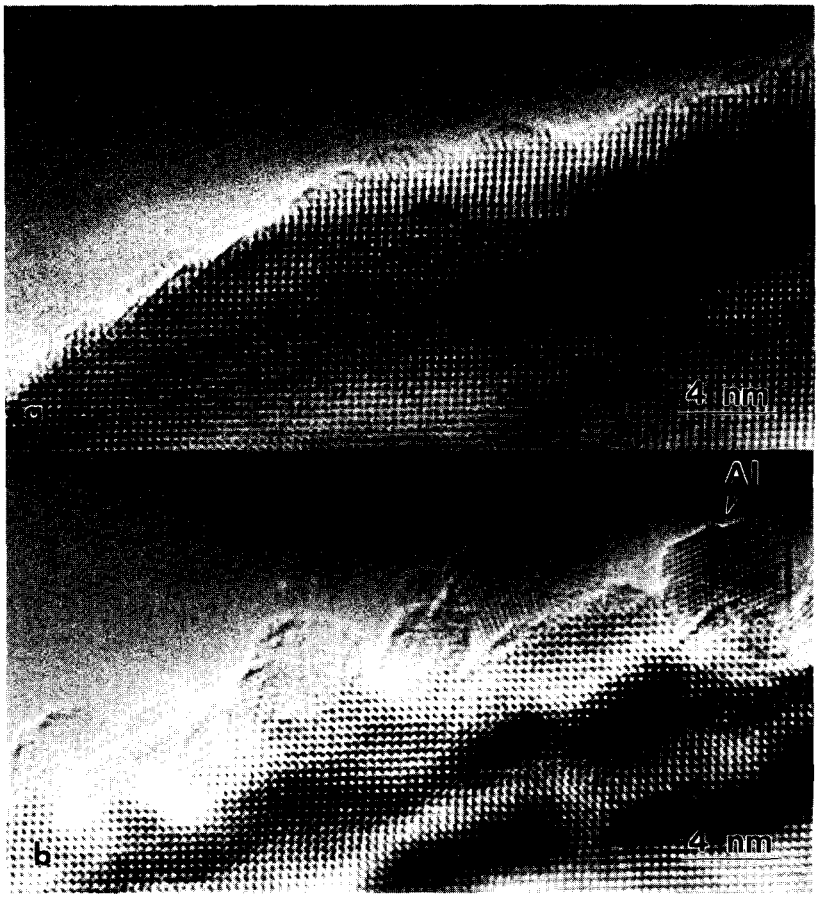

Fig. 3. Irradiation of α-alumina under UHV conditions does not produce facets. Typical results of the [2$\bar{2}$01] zone; the initial surface (a) develops small crystallites of aluminum after 1 hour (b) of moderate flux (20 A/cm^2) damage.

tions is strongly reduced. In addition, the alumina specimens were baked at 200 °C in the specimen transfer chamber before insertion in the UHV microscope. This procedure, not typical of C-HREM experiments, also minimizes any surface contaminants.

4. Conclusions

As mentioned previously, the damage process in alumina in the case of hole drilling has been attributed to the Knotek–Feibelman (KF) oxygen ion desorption mechanism [6,7]. Although the KF mechanism is an attractive candidate for the damage process, this and earlier electron microscope studies cannot determine unambiguously whether KF or another ionization process, see e.g. ref. [11], is responsible. From our results it is clear that the surface faceting phenomenon is a representative artefact of a "dirty" microscope vacuum that typifies most C-HREMs. That is, during irradiation alumina preferentially ejects oxygen from the surface and the "dirty" vacuum re-oxidizes the aluminum that would otherwise be left on the surface. In more recent results, Tomokiyo et al. [12] irradiated single-crystal α-alumina and observed both facets and hole drilling in specimens prepared by Ar^+ ion milling and hot phosphorus etching, indicating that the ambient vacuum at the specimen plays a greater role in the damage process. In the clean environment

of the UHV-HREM reoxidation of the facets is quenched, allowing the reactive aluminum to remain in its metallic form and grow into stable crystallites. These results suggest that the facet formation in C-HREM is a dynamic balance between the desorption process and the high reactivity of metallic aluminum; one might envision a flux threshold above which the formation of aluminum might be stabilized in even an oxidizing environment.

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