ION IRRADIATION STUDIES OF OXIDE CERAMICS*

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1. INTRODUCTION

Ion implantation is a useful tool for modifying the near-surface mechanical properties of ceramic materials. Depending on the implantation conditions, the near-surface region may become hardened or softened (amorphized) relative to the substrate (1). This may in turn exert a strong influence on the fracture toughness, strength, and wear resistance. It is now established that many ceramics can be made amorphous if the lattice damage exceeds some critical level (1-3). Burnett and Page (1) have shown that the near-surface hardness of ceramics typically increases with dose during the initial stages of implantation, then peaks and eventually shows softening due to the formation of an amorphous layer. The conditions for amorphization are material-dependent. For oxide ceramics such as MgO and Al₂O₃, amorphization has been observed in some cases when the damage energy level exceeds a value of ~5 keV per substrate atom for a room-temperature implantation (1,2). However, it is also established that chemical effects associated with the implanted ion species can have a large effect on the critical dose required for amorphization (2). The specimen temperature is also very important. The ion dose required for amorphization increases with increasing temperature. It is uncertain whether any ceramic can be amorphized if the implantation temperature is significantly higher than room temperature.

The fundamental processes responsible for amorphization are not well understood due to the complex interaction between chemical (implanted ion) effects and radiation damage effects. One approach that may be used to

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separate these effects involves the use of high-energy ions. In this case, the microstructure produced near the peak in the implanted ion distribution may be distinctly separated from the microstructure at shallower depths where only displacement damage effects have occurred. This paper presents the initial results of an investigation of the depth-dependent microstructures of three oxide ceramics following ion implantation to moderate doses. The implantations were performed using ion species that occur as cations in the target material; for example, Mg^+ ions were used for the MgO and MgAl_2O_4 (spinel) irradiations. This minimized chemical effects associated with the implantation and allowed a more direct evaluation to be made of the effects of implanted ions on the microstructure.

2. EXPERIMENTAL PROCEDURE

The starting materials for the implantation study consisted of polycrystalline MgAl_2O_4 (grain size $\approx 30\text{ }\mu\text{m}$), two types of polycrystalline $\alpha\text{-Al}_2\text{O}_3$ (grain sizes of 0.8 and $30\text{ }\mu\text{m}$), and single crystal MgO . The 5 by 10 by 2 mm mechanically polished MgO specimens were implanted at an orientation $\sim 7^\circ$ from (100) in order to minimize ion channeling effects. The MgAl_2O_4 and Al_2O_3 specimens were irradiated as mechanically polished transmission electron microscope specimens (3 mm diam by 0.5 mm thickness) in a 9-specimen array. The irradiations were performed at room temperature and 650°C using the Van de Graaff facility at Oak Ridge National Laboratory (4). Table 1 summarizes the implantation conditions. The alumina implantations were performed with simultaneous beams of Al^+ , O^+ , and He^+ (the 0.2 to 0.4 MeV He^+ beam produced negligible displacement damage). The energies of the Al^+ and O^+ beams were chosen so that the calculated mean range of both ions in alumina was $1.2\text{ }\mu\text{m}$. The spinel and MgO irradiations were performed using 2.4 MeV Mg^+ ions, which have a calculated mean ion range of $1.6\text{ }\mu\text{m}$ in both materials.

Table I. Ion implantation parameters

Material	Implanted Ion	Fluence	Peak Damage (keV/atom)	Irradiation Temperature (°C)
MgAl ₂ O ₄	2.4 MeV Mg ⁺	$1.4 \times 10^{21}/\text{m}^2$	3.5	25, 650
Al ₂ O ₃	2.0 MeV Al ⁺ 1.44 MeV O ⁺	$6.9 \times 10^{20}/\text{m}^2$ $8.3 \times 10^{20}/\text{m}^2$	3.1	25, 650
MgO	2.4 MeV Mg ⁺	$4.1 \times 10^{19}/\text{m}^2$	0.10	25
MgO	2.4 MeV Mg ⁺	$2.1 \times 10^{19}/\text{m}^2$	0.05	650
MgO	2.4 MeV Mg ⁺	$8.1 \times 10^{20}/\text{m}^2$	2.0	650

Transmission electron microscopy (TEM) was performed on cross-sectioned specimens that were prepared by standard techniques (5). The depth-dependent hardness and elastic modulus of the implanted MgAl₂O₄ and Al₂O₃ specimens were measured at room temperature with a specialized micro-indentation ("nanoindenter") hardness tester (6). For comparative purposes, Knoop indentation tests at a load of 0.25 N (25 g) were performed with a Shimadzu microhardness tester on the fine-grained Al₂O₃ specimens. The number of indentation measurements performed for the nanoindenter and Knoop cases was 15 and 8, respectively.

3. RESULTS

3.1 Spinel

Ion irradiation of spinel at 25 and 650°C produced faulted interstitial dislocation loops at intermediate depths (~1 μm) along the ion range. The microstructure near the implanted ion region and damage peak consisted of a high density of dislocation tangles for both temperatures. All regions of the irradiated specimens remained crystalline following both room temperature and 650°C implantation. A detailed description of the irradiated microstructure observed in these specimens is given elsewhere (7).

The cross-section microstructure of spinel following irradiation at 650°C is shown in Fig. 1. The near-surface region was devoid of any observable defects for depths up to ~0.9 μm. The damage microstructure at

intermediate depths of the 650°C specimen is shown in more detail in Fig. 2. The loops exhibit fault contrast for $g = \langle 220 \rangle$ and no fault contrast for $g = \langle 440 \rangle$. An analysis of the nature of the loops (7) revealed a mixture of interstitial loops of the type $a/4\langle 110 \rangle\{110\}$ and $a/4\langle 110 \rangle\{111\}$ which, as explained by Clinard et al. (8), are faulted on the cation sublattice.

The depth-dependent microstructure of spinel following irradiation at 25°C was very similar to that observed for the 650°C case (7), except that interstitial loop formation was also observed in the near-surface region of the specimen implanted at 25°C. The microstructures at intermediate depths and near the peak damage region are compared in Fig. 3. Isolated dislocation loops are visible at intermediate depths whereas the peak damage region is a complex mixture of dislocations with no observable loops. A further inspection of the peak damage region reveals the presence of dislocation tangles along with other unidentified defects that exhibit contrast similar to antiphase boundaries (APBs) in ordered crystals (Fig. 4).

Nanoindenter measurements made on specimens irradiated at the two temperatures showed no significant change (<5%) in the elastic modulus. The hardness at an indent depth of 0.5 μm increased from 8.2 GPa (unimplanted) to ~8.6 GPa (implanted) for both irradiation temperatures as a result of the irradiation (7). The hardness change (implanted vs. unimplanted) of the 650°C specimen showed a gradual increase with increasing indentation depth that could be attributed to the loop-denuded region near the surface and the high defect density at deeper subsurface regions (7). The hardness increase of the 25°C specimen was essentially independent of depth for indent depths between 100 and 600 nm (7).

3.2 Alumina

The microstructure of irradiated alumina consisted of dense arrays of dislocation loops and network dislocations, with no evidence of amorphization at either irradiation temperature. The loops were observed on (0001) and $\{10\bar{1}0\}$ habit planes. There were no obvious microstructural differences

between the fine-grained and coarse-grained alumina specimens. Some preliminary observations of the microstructure of irradiated alumina are described below.

As shown in Fig. 5, the dominant microstructural feature in the midrange region of alumina irradiated at 650°C is a network of dislocations. A low density of dislocation loops with habit planes near $\{01\bar{1}0\}$ were also observed under different diffracting conditions. An example of the loop microstructure observed near the peak damage region of a 650°C specimen is shown in Fig. 6. Edge-on loops lying on the basal plane and on the (0110) plane are visible in Fig. 6, with a loop diameter of ~20 nm. The midrange microstructure of the 650°C specimen suggests that the loop density is significantly less than that found near the damage peak (implanted ion region). The aligned dislocations were not observed in the peak damage region, which suggests that either dose or implanted ion effects may be significant at this temperature.

The midrange microstructure of Al_2O_3 irradiated at 25°C was similar to the 650°C case. Figure 7 shows the typical midrange loop microstructure for alumina irradiated at 25°C. Loops with diameters ~10 nm were observed on (0001) and $\{10\bar{1}0\}$ planes. An example of a loop on the basal plane is arrowed in Fig. 7. Dislocations were observed in both the midrange and peak damage regions along with the loops. An example of the dislocation microstructure observed near the peak displacement region of a 25°C specimen is shown in Fig. 8. A Burgers vector analysis of dislocations suggests that $\mathbf{b} = 1/3\langle 01\bar{1}1 \rangle$. A second set of aligned dislocations were observed with their line vectors nearly perpendicular to [0001], but their Burgers vector has not yet been determined. Contrast similar to that associated with APBs was observed under suitable diffraction conditions (Fig. 9).

Nanoindenter and Knoop hardness measurements were performed at room temperature on the irradiated fine-grained ($d \sim 0.8 \mu\text{m}$) alumina specimens. As shown in Fig. 10, the elastic modulus of Al_2O_3 (as determined from nanoindenter measurements) was unaffected by ion irradiation for indent depths

up to 250 nm. The nanoindenter measurements also indicated that there was no significant (<5%) change in the depth-dependent hardness of Al_2O_3 following ion irradiation at 25°C (Fig. 11). The measurements suggested that the near-surface hardness of alumina following irradiation at 650°C relative to the nonirradiated value was increased by 10 to 20%. For the 650°C specimen, the unimplanted hardness was about 10% less than the 25°C unimplanted hardness; the irradiated hardness for the 25 and 650°C specimens was essentially equal. For comparative purposes, Knoop indentation measurements were made at a load of 0.25 N and the hardness was calculated from the long diagonal of the residual indentation. The indentation depth was $\sim 0.5 \mu\text{m}$. The Knoop hardness measurements were in reasonable agreement with the nanoindenter results.

3.3 Magnesia

High densities of small dislocation loops were formed in MgO during irradiation at a variety of experimental conditions. Irradiation at 650°C to a fluence of $2.1 \times 10^{19} \text{ Mg}^+/\text{m}^2$ produced small ($\sim 10 \text{ nm}$ diam) loops near the peak damage region. The loop density was lower and the mean loop size was larger in the near-surface region compared to the peak damage region. The damage microstructure following irradiation at 650°C to a higher fluence of $8.1 \times 10^{20} \text{ Mg}^+/\text{m}^2$ was qualitatively similar to that observed following the low dose irradiation. The loop density was lower in the near-surface region and the mean loop diameter changed from $\sim 40 \text{ nm}$ at a depth of $0.5 \mu\text{m}$ to $\sim 10 \text{ nm}$ at the peak damage region ($1.6 \mu\text{m}$ depth). Figure 12 shows some loops that were present at a depth of $\sim 1 \mu\text{m}$ from the irradiated surface. There was not a large depth-dependence to the irradiated microstructure for the 25°C implantation. Figure 13 shows a cross-section view of MgO following irradiation at 25°C to a fluence of $4.1 \times 10^{19} \text{ Mg}^+/\text{m}^2$ ($\sim 0.7 \text{ dpa}$ peak damage). An interesting feature observed for this moderate irradiation condition was the appearance of heterogeneous "patches" of small voids (Fig. 14). Small loops with diameters $\sim 10 \text{ nm}$ were also resolvable in the microstructure.

Knoop hardness measurements showed a large increase in hardness for the 25°C case, and slight hardness increases for the two 650°C cases. Complete details of the irradiation microstructure and hardness measurements (including hardness anisotropy measurements) are given elsewhere (9).

4. DISCUSSION

4.1 General Microstructural Features

Amorphization was not detected in any of the implanted specimens. This indicates that the critical damage level required to amorphize spinel or alumina at room temperature by implantation with ions that minimize chemical effects is greater than 3.1 to 3.5 keV/atom. Implantation at damage levels below 3 keV/atom with certain ion species such as Zr has been found to induce amorphization in alumina (2), which shows that chemical effects can be important.

The fraction of defects retained from displacement processes in the form of visible clusters is much lower in spinel compared to MgO and Al₂O₃. In particular, only ~0.05% of the calculated displacements in spinel at an irradiation depth of 1 μm result in visible defect clusters (7). Other researchers have made similar observations (8,10) and have attributed the resistance to damage accumulation in spinel to the structural complexity of forming stoichiometric clusters (a minimum of 7 point defects are required). This implies that higher implantation doses may be needed to amorphize spinel compared to simpler oxide ceramics such as MgO or Al₂O₃.

4.2 Depth Dependence

The peak in the displacement damage profile occurs at a depth that is close to the location of the implanted ions. It is therefore difficult to attribute any depth-dependent microstructural changes solely to implanted ion effects unless additional tests have been made at lower or higher doses. On the other hand, if the observed microstructural features do not show a strong depth dependence then it may be argued that implanted ion and displacement damage dose effects are of secondary importance.

The microstructure of implanted spinel exhibited a strong depth dependence at both irradiation temperatures (Figs. 1-4). Some of the depth dependence may be attributed to differences in the damage level — with increasing dose, the density of loops increases until the close proximity of loops induces interactions that could lead to the formation of a dislocation network. However, the mechanism for this process is uncertain since the loops in spinel contain a cation fault and are therefore not glissile. The microstructure of alumina did not show a strong depth dependence for specimens implanted at room temperature (Figs. 7, 8). Alumina specimens irradiated at 650°C showed a slight microstructural depth dependence, changing from primarily aligned dislocations in the midrange region to aligned dislocations and an array of dislocation loops on (0001) and $\{10\bar{1}0\}$ planes in the peak damage region (Figs. 5, 6). The MgO specimens showed a weak dependence on irradiation depth. The main observation was a decrease in loop size with increasing depth for specimens implanted at 650°C. A similar depth dependence of loop size has been reported for ion-implanted Al_2O_3 (11).

4.3 Temperature Effects

Irradiation at 650°C produced microstructures that were qualitatively similar to the room temperature irradiations. A general observation is that high implantation temperatures appeared to enhance the depth dependence of microstructural features. For example, spinel showed a loop-denuded zone within $\sim 0.9 \mu\text{m}$ of the implanted surface following irradiation at 650°C whereas the 25°C specimen contained loops in the near-surface and midrange regions. Most of the loops ($\sim 70\%$) in spinel had $\{110\}$ habit planes for the 650°C case, whereas the loops were nearly evenly divided between $\{110\}$ and $\{111\}$ for the 25°C implantation (7). Aligned dislocations were observed in the midrange region of Al_2O_3 following implantation at both 25 and 650°C. However, at 650°C there was a greater density of arrays of loops on (0001) and $\{10\bar{1}0\}$ in the peak damage region compared to

the 25°C case. The loop density in MgO was lower for the high-temperature irradiations compared to the 25°C irradiation.

5. SUMMARY AND CONCLUSIONS

Initial microstructural observations have been made on three ion-implanted oxide ceramics. The main microstructural features associated with the implantations are dislocation loops and network dislocations. The effect on the resultant microstructure of implantation with ions that minimize chemical effects is uncertain, but the effect does not appear to be large for room temperature irradiations. Implantations at 650°C produced microstructural changes that were in general qualitatively similar to the 25°C implantation case. The high-temperature implantations appeared to enhance the depth dependence of the microstructure, although the effect was often slight.

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DEPTH-DEPENDENT MICROSTRUCTURE OF SPINEL IMPLANTED AT 650 C

FIGURE 1. Depth-dependent microstructure of spinel implanted with 2.4 MeV Mg⁺ ions at 650°C.

Fig 1

WEAK BEAM MICROSTRUCTURES OF SPINEL IMPLANTED AT 650 C

FIGURE 2. Comparison of the midrange microstructure of spinel implanted at 650°C for two different diffraction vectors. a) weak beam ($g, 4g$), $g = 2\bar{2}0$. b) weak beam ($g, 2g$), $g = 4\bar{4}0$. Note the absence of stacking fault contrast in (b). The same area of the foil is shown for the two different diffracting conditions.

WEAK BEAM MICROSTRUCTURES OF SPINEL IMPLANTED AT 25 C

FIGURE 3. Typical irradiated microstructures of spinel implanted at 25°C. The left photograph shows the weak beam (g,3g) microstructure for damage depths of 1.0 to 1.5 μm . The right photograph shows the weak beam (g,4g) microstructure for damage depths of 1.4 to 1.9 μm . The original irradiated surface lies to the left of both photographs.

WEAK BEAM MICROSTRUCTURE NEAR DAMAGE PEAK IN SPINEL

FIGURE 4. Weak beam (g,4g) microstructure of spinel implanted at 25°C at damage depths of 1.3 to 1.8 μm .

MIDRANGE MICROSTRUCTURE IN ALUMINA IMPLANTED AT 650 C

FIGURE 5. a) Weak beam ($g, 3g$) and b) bright field microstructure of alumina at an intermediate depth ($\sim 0.8 \mu\text{m}$ depth) following irradiation at 650°C .

PEAK DAMAGE MICROSTRUCTURE IN ALUMINA IMPLANTED AT 650 C

FIGURE 6. a) Weak beam ($g, 3g$) and b) bright field microstructure of alumina near the peak damage region ($\sim 1.3 \mu\text{m}$ depth) following irradiation at 650°C .

LOOPS IN Al_2O_3 IRRADIATED AT 25 C

FIGURE 7. Microstructure of alumina at an intermediate depth ($\sim 0.8 \mu\text{m}$ depth) following irradiation at 25°C. The arrow points to a loop on the basal plane.

PEAK DAMAGE MICROSTRUCTURE IN ALUMINA IMPLANTED AT 25 C

FIGURE 8. a) Weak beam ($g,3g$) and b) bright field microstructure of alumina near the peak damage region following irradiation at 25°C.

WEAK BEAM (g,2g) MICROSTRUCTURE OF ALUMINA IMPLANTED AT 25 C

FIGURE 9. Weak beam (g,2g) microstructure of alumina irradiated at 25°C.

Fig. 9

DEPTH-DEPENDENT MODULUS RATIO FOR ION-IMPLANTED POLYCRYSTALLINE Al_2O_3

FIGURE 10. Depth-dependent elastic modulus ratio for ion-implanted Al_2O_3 .

DEPTH-DEPENDENT HARDNESS RATIO
FOR ION-IMPLANTED POLYCRYSTALLINE Al_2O_3 FIGURE 11. Depth-dependent hardness ratio for ion-implanted Al_2O_3 .

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LOOP FORMATION IN IMPLANTED MgO

 $B = [001]$

FIGURE 12. Dislocation loops observed in MgO at a damage depth of $\sim 1 \mu\text{m}$ following irradiation at 650°C .

DEPTH-DEPENDENT MICROSTRUCTURE OF MgO IMPLANTED AT 25 C

FIGURE 13. General cross-section microstructure of MgO following implantation at 25°C.

Fig. 13

ORNL-PHOTO-5725-88

VOID FORMATION IN IMPLANTED MgO

FIGURE 14. Heterogeneous formation of small voids (arrowed) at a depth of $\sim 1 \mu\text{m}$ in MgO irradiated at 25°C .