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STRUCTURAL PROPERTIES OF MgO AND $MgAl_2O_4$ AFTER FISSION NEUTRON IRRADIATION NEAR ROOM TEMPERATURE

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Polycrystalline MgO and $MgAl_2O_4$ samples were irradiated at 430 ± 5 K in HFIR to a fast neutron fluence of 2.1×10^{26} n/m^2, $E_n > 0.2$ MeV, and 4.6×10^{26} thermal n/m^2. Following irradiation, swelling, microstructure and mechanical strength were evaluated relative to control samples. Both materials swelled substantially, 2.6-3.0% in the case of MgO, and 0.8% in the case of $MgAl_2O_4$. The substructure of the MgO was found to contain a dense array of dislocation loops while the spinel showed heavy but unresolved damage. Results of mechanical strength evaluation by diametral compression testing showed significant strengthening for both materials. This result, which has important implications for use of cubic technological ceramics, is discussed in terms of the observed fracture modes and microstructural damage.

1. INTRODUCTION

Applications for ceramic components in fusion power reactors have recently been reviewed;(1,2) requirements for material candidates for these applications are discussed elsewhere in these proceedings.(3) A key material requirement is the ability to withstand high stresses due to thermal and structural loadings. While in general the exact level of expected stresses has not been analyzed for most ceramic components, calculations for selected applications and designs have shown the desirability of designing to high stress levels and hence the importance of understanding the effects of neutron damage on strength.(4) In the case of rf windows, strength of unirradiated candidate materials is likely to be limiting.(5)

Previous studies of the effects of neutron damage on mechanical properties of ceramics have revealed strength reductions in polycrystalline non-cubic materials which result from anisotropic swelling.(6) Recent analysis of this problem has suggested that even the mismatch strains in samples undergoing very small macroscopic swelling can seriously reduce strength in initially high strength materials.(7)

No such direct causative features can be found for strength reductions in single phase cubic materials, regardless of swelling. High purity β-SiC irradiated to 2.8×10^{25} n/m^2, $E_n > 0.18$ MeV, at 900 and 1293 K, has been found not to undergo significant changes in either modulus of rupture or elastic modulus, tested at room temperature. These materials swelled by a small amount (∿ 0.3%) and showed x-ray line broadening which was attributed to dislocation loops.(8) No quantitative date for other cubic materials is available after high-dose irradiation.

MgO and $MgAl_2O_4$ are electrically insulating refractory oxide materials which have not previously been neutron-irradiated to high-dose near room temperature, and may be considered candidates for fusion reactor applications, such as in diverter coils. In this investigation, several small polycrystalline samples of these materials were irradiated to 2.1×10^{26} n/m^2, $E_n > 0.2$ MeV, at 430 K. Post-irradiation microstructure, density, and mechanical properties were examined and compared to the unirradiated properties.

2. EXPERIMENTAL DETAILS

MgO and $MgAl_2O_4$ samples in the form of small cylindrical rods 5-6 mm dia. and 19 mm long were irradiated in the Oak Ridge High Flux Isotope Reactor in aluminum holders. The samples were loaded into recessed compartments with the ends sealed by welded plugs. Calculated temperature during irradiation was 425-435 K and the neutron fluence was 4.6×10^{26} thermal n/m^2 and 2.1×10^{26} n/m^2, $E_n > 0.2$ MeV.

Starting properties of the irradiated materials were characterized by measurement of the macroscopic density, grain size, and purity. Results of these measurements are presented in Table 1. All of the materials were rather porous, especially the MgO. Both types of MgO had similar microstructure, featuring large blocky grains dispersed in a much finer-grained matrix, typified by that shown in Fig. 1, for type-2 MgO. Here the fine-grain size was 14 μm. In the case of type-1 MgO, the matrix grains were not as uniform in size, and varied from the same as seen in type-2, up to the size of the large blocky grains (0.28 mm). The microstructure of the spinel was uniform with pores scattered throughout the grains and at the grain boundaries.

Dimensions of the rods were measured micrometrically before and after irradiation to

Table 1. Characterization of Irradiated Materials

Material	Source	% Full Density	Major Impurities Wt. Percent	Grain Size
MgO-1	Degussa Mg-25	75	.3 Fe, 1.2Ca, 1.7 Si, .8 Al	See Text
MgO-2	Honeywell M-30	79	.08Fe, .3Ca, .08Si, .02Al	See Text
$MgAl_2O_4$-1	American Lava	94	.01Fe, .01Ca, .04Si	10 μm

determine changes in density. Subsequenty, the rods were cut with a diamond saw to produce short cylinders for diametral compression testing, and disks for TEM examination. Diametral compression tests were carried out on samples $\sim$4.5 mm dia. and 4.5 mm long, with a deflection rate of $\sim$0.12 mm/min. The samples were wrapped in aluminum foil which served to contain the fragments and to provide padding. In the case of MgO, 0.12 mm Al was used; in the case of the higher strength $MgAl_2O_4$, 0.05 mm Al wrap and 0.12 mm copper pads were used.

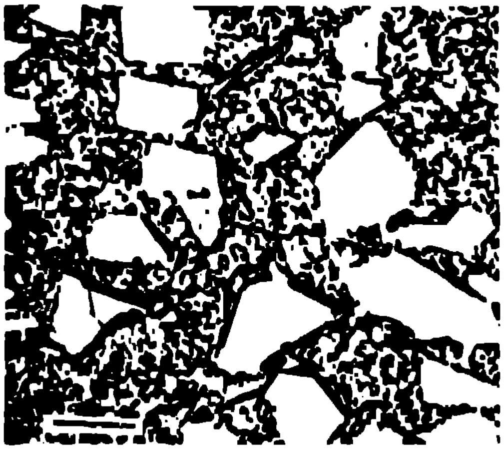

Figure 1: Microstructure of type-2 MgO. Bar = 0.2 mm.

3. RESULTS

All of the irradiated samples were observed to swell, with the magnitudes listed in Table 2.

Table 2.

Material	Vol. Swelling, %
MgO-1	2.6
MgO-2	3.0
$MgAl_2O_4$	0.80

The difference in swelling for the two MgO samples may not be significant. Impurities are known to affect defect production in crystals, including MgO;(9) if a difference is assumed here it might be justified on the basis of the different purity levels of the two materials.

Foils of MgO and of $MgAl_2O_4$ were examined by TEM with representative views as shown in Fig. 2. The features seen are all due to irradiation, and include a high density of small elongated loops in MgO, with a dense array of fine aggregated damage, possibly loops, in the spinel. In addition, note that the grain boundary in Fig. 2b, (spinel) is denuded of damage, also a typical feature.

Diametral compression test results for MgO and $MgAl_2O_4$ are presented in Table 3. The diametral compression test is one in which a cylinder is loaded on its side between parallel plattens. Stress analyses summarized in Ref. 10 show that uniform tensile stress is produced by this configuration along the midplane parallel to the

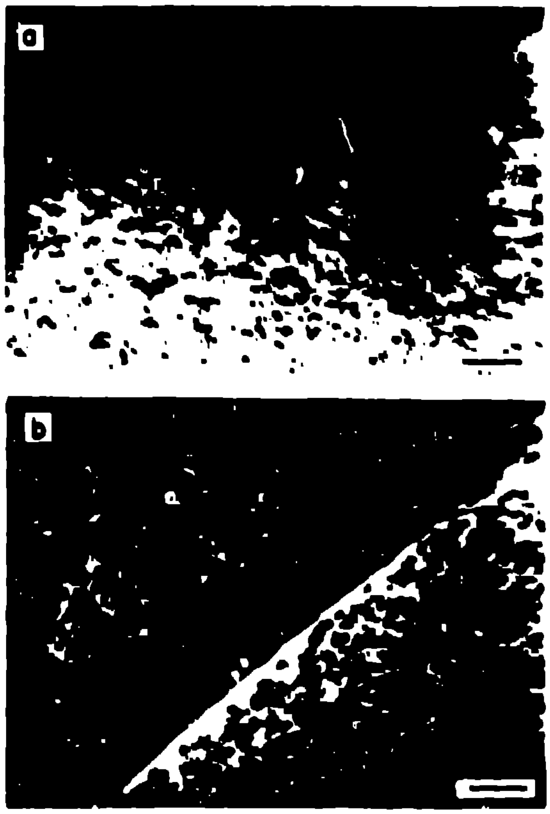

Figure 2: TEM substructure in irradiated MgO (a) and $MgAl_2O_4$ (b). Bar = 0.1 μm.

Table 3. Diametral Test Summary for MgO and $MgAl_2O_4$ Samples Irradiated to 2.1×10^{26} n/m² $E_n > 0.2$ MeV.

Sample	Control, MPa	(No.)	Irradiated, MPa	(No.)	Change, MPa	(%)
MgO-1	23.1 ± 1.0	(6)	25.9 ± 1.1	(3)	+ 2.8	(12)
MgO-2	25.4 ± 1.1	(3)	31.6 ± 0.6	(3)	+ 6.2	(24)
$MgAl_2O_4$	127 ± 4	(6)	152 ±11	(9)	+25	(20)

applied stress. Relative magnitude of this tensile stress to maximum shear and compressive stresses can be controlled by suitable choice of padding materials in order to assure failure in tension.(11) In this case all failures occurred by parting on the midplane, or by triple cleft failure, both accepted as tensile failures.

Fracture surfaces were examined by SEM and by optical microscopy to characterize the fracture processes occurring before and after irradiation. The pair of fractographs in Fig. 3 shows representative areas of irradiated and unirradiated MgO. No differences are observed here; the fracture appears to be virtually completely transgranular in the large grains, and mixed transgranular-intergranular in the matrix material. Cracks which were apparently not involved in the fracture were occasionally seen in the large grains. The location of the fracture origin was not detected by either SEM or optical observation. However, in many cases, large grains which had cleaved were found in the fracture surface, intersecting the tensile surface edge; these were likely sites for machining flaws and suggest themselves as fracture origins.

The pair of fractographs in Fig. 4 reveal the appearance of the $MgAl_2O_4$ fracture surfaces. Here a difference is found. While the fracture in both cases was largely transgranular, a significant occurrence of intergranular failure can be found in the unirradiated material, and is virtually completely missing in the irradiated fracture surfaces. In all of the spinel samples, the fracture origin could be traced to a location at the end surface, suggesting fracture originated at a machining flaw.

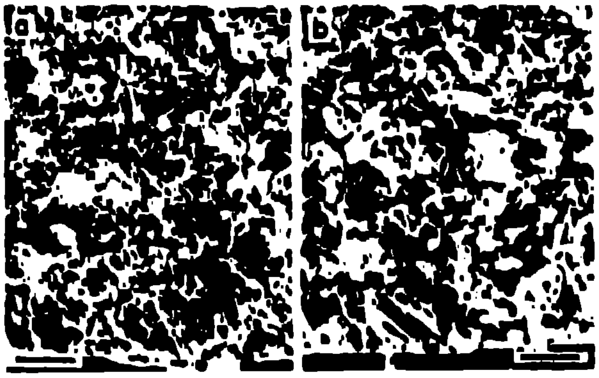

Figure 3: Fracture surfaces of control (a) and irradiated (b) MgO.
Bar = 0.17 mm.

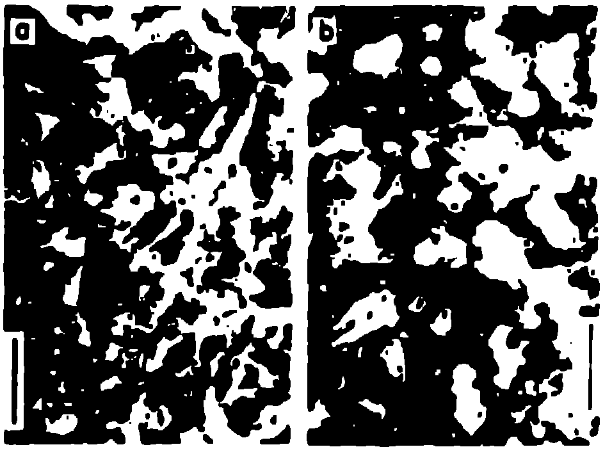

Figure 4: Fracture surfaces of control(a) and irradiated (b) $MgAl_2O_4$.
Bar = 20 μm

4. DISCUSSION

4.1. MgO

Near room temperature neutron irradiation damage in MgO is dominated by large volume swelling and an increase in strength. At similar temperatures and lower fluences (1-5 x 10[illegible] n/m², E_n > 1 MeV) swelling of MgO had previously been reported to show saturation at about 1%.(6) The level of swelling seen in the present work, 2.6-3.0%, is much larger than that seen previously and appears to show that saturation, if it occurs, must be at a much higher level than previously suspected.

This magnitude of swelling can be compared with the behavior of β-SiC which has been found to exhibit swelling as large as 3% when irradiated near room temperature, saturating between 2×10^{24}-10^{25} n/m². TEM examination of such samples shows large number of small dislocation loops lying on (111) planes.(12) However, evidence in the same work shows that the macroscopic expansion is the same as the unit cell expansion as determined by x-ray diffraction measurements. Hence the swelling is viewed as resulting from dilation of the lattice by the irradiation-induced defects.

In a similar manner, the swelling of MgO at low fluence appears to result entirely from lattice dilation (point defects and intersitial loops). The direct confirmation of this correspondence at the high fluences used here is probably not possible since diffuse scattering (see Ref. 13) would be expected to dominate the x-ray diffraction lines. However, no other causes of swelling (e.g., void swelling or microcracking) can be detected in TEM observations. (c.f. Fig. 2a.) This compels the hypothesis that this material must contain an extremely large number of point def[illegible] particularly vacancies. The ratio[illegible] here is that vacancies and intersititials are created by irradiation leading to eventual condensation of interstitials to form loops. If the vacancies find sinks (e.g., vacancy loops, surfaces) no additional swelling results. If the sink is a void, swelling continues, but the voids become visible. With such large numbers of (postulated) vacancies, it would be reasonable to assume some number reductions by their condensation to form, for example, di-vacancies.

Fracture in polycrystalline MgO is far more complicated than in single crystal material for which comparative data are available.(14,15) In the latter case, it is found that dislocation flow aids microcrack growth; reactor irradiation greatly increases the flow stress and leads to microcrack propagation without plastic flow. Thus radiation damage increases the fracture stress in single crystals.

In polycrystalline MgO, room temperature fracture can occur with either positive or negative contribution from plasticity.(16) The effective surface energy for fracture is larger than the thermodynamic value, which is believed to result from flow near the crack tip, which in turn acts to blunt it. If this were the dominant effect in the present material, then irradiation would weaken the material by reducing the fracture energy. Alternatively, as in single crystals, if plastic flow can occur at stresses lower than those to extend pre-existing flaws, then the flow itself initiates fracture. This process would be stopped by irradiation, and would thus increase the fracture strength.

In the current material, inspection of the microstructure and fracture surfaces Figs. 1 and 3a suggests the large crystals as fracture initiation sites, with fracture beginning from machining flaws in these crystals at the surface. Beyond initiation, fracture must proceed through the finer grained, porous matrix, frequently intersecting the larger blocky crystals. The strength-controlling feature of these processes is not clear, but could be re-initiation of the crack effectively blunted by the pore space around the initial flawed grain, or interaction of the crack at subsequent intersection with one of the large grains. It can be seen in Fig. 1 that many of these large grains frequently were found to be separated by porous regions from the fine grained matrix. If either of these interactions involved flow-aided processes, then the irradiation strengthing could be accounted for.

4.2. $MgAl_2O_4$

Phenomenologically, the response of $MgAl_2O_4$ to high dose, near room temperature irradiation was similar to that of MgO, exhibiting substantial (0.8%) though lower volume swelling, and an increase in the mechanical strength. This level of swelling contrasts with the zero swelling observed in single crystals irradiated at high temperature, and moderate swelling seen in polycrystals at the same temperature.(17,18) The significant feature of the microstructure is the denudation of damage along the grain boundaries. Damage in high temperature-irradiated single crystals has been shown to consist of a low density of interstitial faulted loops.(19)

In polycrystalline material, an additional feature is a layer of small voids occuring along the grain boundaries.(20) The void layer probably results from loss of interstitials to the grain boundary sink, with subsequent condensation of the vacancies. In the lower temperature case, interstitials near the grain boundary presumably go to the grain boundary, while agglomerating, in the grain interiors, to give the damage seen in Fig. 2b. Swelling here must effectively be represented by new atom sites occupied by the interstitials going to loops (in grain interiors) or to grain boundaries. Hence, while swelling occurs both in the bulk of the grain and in the grain boundary layers, it may be of a different magnitude in these two regions and thus give rise to strains at the grain boundaries.

The increase in strength observed is particularly interesting since it seems to result from a different cause than in the MgO. The conclusion based on examination of the $MgAl_2O_4$ fracture surfaces (Fig. 3a) is that the partially intergranular nature of the fracture in unirradiated material, is completely absent in the irradiated case. This observation may explain the strength increase in a phenomenological sense since the fracture toughness for mixed-mode transgranular and intergranular fracture in polycrystalline spinel is higher than for intergranular fracture. (21) The direct cause of the changed fracture mode and increased strength cannot be established from this data. The most likely explanation may be related to the denuded grain boundaries. If a stress exists here as a result of a differential swelling effect, it could act to deflect cracks away from the grain boundaries, or in effect, to strengthen them. No effect of reduced potential for plastic deformation is expected since flow is not thought to be involved in room temperature fracture of spinel.(22)

5. SUMMARY

MgO and $MgAl_2O_4$, irradited to 2.1 x 10^{26} fast n/m^2 at 430 K, exhibit substantial volume swelling. In the case of MgO, the volume expanded by 2.6 to 3.0% which is close to the high value observed for SiC near room temperature. $MgAl_2O_4$ swelled 0.8% In both cases, microstructural damage was found by TEM examination suggesting interstitial agglomeration as fine loops. In the case of spinel, denudation in the grain boundaries of agglomerated damage suggests a mechanism for generation of internal strains localized at the grain boundaries. These grain boundary effects in turn may be responsible for the strengthening observed. MgO was also strengthened, possibly by increased resistance to slip, induced by irradiation. The occurrence of strengthening is extremely important as it now demonstrates the usefulness of cubic technological ceramics in load-bearing applications, despite the occurrence of radiation damage.

ACKNOWLEDGMENT

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