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STRUCTURAL PERFORMANCE OF CERAMICS IN A HIGH-FLUENCE FUSION ENVIRONMENT*

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The ceramics MgAl₂O₄, Al₂O₃ (single crystal), Si₃N₄, and a SiC/graphite laminate were irradiated to $\sim 2 \times 10^{26}$ n/m² (E > 0.1 MeV) at 680 and 815K. Spinel exhibited near-zero dimensional change, while Al₂O₃ and Si₃N₄ swelled ~ 3 vol% and 1 vol% respectively. Strength of MgAl₂O₄ was increased, while strength of Al₂O₃ and Si₃N₄ were not greatly altered. The SiC/graphite composite, tested only at 680K, suffered almost complete delamination as a result of swelling of the SiC and densification of the graphite. These results are discussed in terms of microstructural alterations and related to various fusion applications.

1. INTRODUCTION

Ceramics are specified for a number of high neutron dose applications in fusion reactors. Prominent among these are electrical insulators for water-cooled copper magnetic coils, dielectric windows and standoffs for RF heating systems, and near-first-wall structural components or coatings for beam dumps, limiters, armor, and perhaps the first wall itself.^{1,2} Lifetime neutron doses in these applications will often exceed 10^{26} n/m², accumulated near or well above room temperature.³

For those applications where insulating solids are required, as in the first two cited above, ceramics must be used. Here, electrical properties such as resistivity, breakdown strength, and loss tangent are important. However, structural failure is also of concern, as this can lead to loss of insulating properties or wholesale destruction of the component. Where structural integrity is the sole consideration, either ceramics or metals can be used; here, ceramics typically offer such advantages as low activation, low cost, high operating temperatures, low plasma contamination effects, resistance to chemical erosion (compared with

graphite), and immunity to electromagnetic loads (for insulating ceramics). The principal disadvantage of ceramics, their brittle behavior, must be accommodated by careful application of brittle-material design techniques.

Ceramics in intense radiation fields may be subjected to swelling stresses as well as those from external loading. Thus radiation-induced changes in density and strength are of major concern, and these properties are discussed in this paper. The work described here is from an ongoing program to evaluate temperature and fluence-dependence of changes in physical properties of ceramics appropriate for fusion reactor applications. In this paper we report initial results on materials irradiated to $\sim 2 \times 10^{26}$ n/m² (E > 0.1 MeV) at 680 and 815K. Test ceramics were MgAl₂O₄, Al₂O₃, and Si₃N₄, as well as a SiC/graphite laminate. The first three materials are candidates for magnet and RF system insulators, while the last two are appropriate for near-first-wall structural applications (the laminate being representative of a low-Z protective coating on a candidate substrate material). Swelling and strength results obtained here are compared with earlier obser-

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vations of swelling, strength, fracture toughness, thermal diffusivity and microstructural changes after irradiation to similar doses at temperatures both above and below 680 and 815K. In this way a unified picture of structural behavior of these ceramics in a high-fluence neutron environment can be assembled.

2. EXPERIMENTAL PROCEDURE AND RESULTS

2.1. Swelling

All irradiation tests reported here were carried out in the EBR-II fission reactor. Monolithic samples were held in an inert atmosphere during irradiation to $2.2 \pm 0.4 \times 10^{26}$ n/m² ($E > 0.1$ MeV) at 680 and 815K. Control samples were held at the same temperature for a period of time characteristic of the reactor exposure.

Most swelling measurements were carried out by an immersion density technique.⁴ Volumetric changes were determined to an accuracy approaching ± 0.01 vol% by comparison of results with those from control samples. Swelling of Si₃N₄ was calculated from micrometric measurement of changes in length of bend bar samples; accuracy of these results is estimated to be ± 0.1 vol%. The SiC/graphite laminate was irradiated only at 680K. Volumetric change for the SiC component was measured by immersion after separation from the substrate, and that for the graphite by a difference method involving both immersion and micrometric measurements of composite samples. Swelling results for all test materials are given in Table I.

Transmission electron microscopic (TEM) examination has to date been carried out for single-crystal MgAl₂O₄ irradiated at both 680 and 815K, and is described elsewhere.⁵ The damage microstructure after irradiation at 815K consisted of faulted 1/4-110-(110) and 1/6-111-(111) dislocation loops. A similar but finer loop distribution was observed after 680K irradiation.

2.2. Strength

Four-point bend bar samples were employed to evaluate strength changes at room temperature. Irradiation test conditions were identical to those described earlier. Samples were of dimensions 0.5 x 1.5 x 22 mm, and a support span of 19 mm was used. Rate of deflection was 10^{-3} mm/s. Test bars were cut to shape with a diamond saw, so that surface condition was optimal for highest strength but was consistent from sample to sample. Results of strength tests are given in Table I.

Interlaminar strength of the SiC/graphite composite was reduced to a near-zero value by irradiation at 680K. Samples were visibly bowed after removal from the reactor, and metallographic examination showed that the composite had almost totally delaminated as a result of differential swelling (Fig. 1).

3. DISCUSSION

The swelling and strength results for MgAl₂O₄ irradiated at 680 and 815K show excellent radiation resistance for this ceramic. It is in-

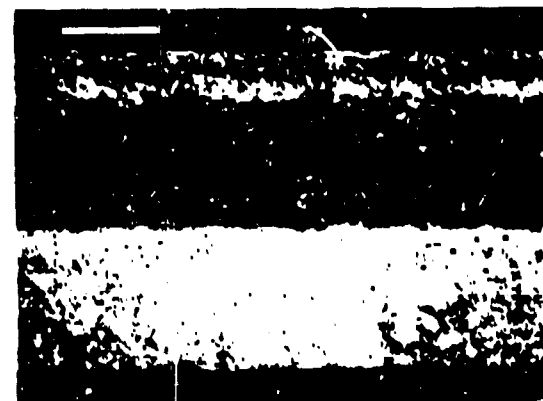


FIGURE 1
Microcracking at the interface between SiC (top) and graphite after irradiation at 680K. Bar 300 μ m.

TABLE 1
Swelling and strength changes after irradiation to $2.2 \pm 0.4 \times 10^{26}$ n/m²
(E > 0.1 MeV) at 680 and 815K

Material	Condition/ Irradiation Temperature, K	Volume Change, % [†]	Number of Bend Bar Samples	Strength, MPa and [Standard Deviation]	Strength Change, %
MgAl ₂ O ₄ ¹⁾ (sc) ^{††}	control	--	5	145 [18]	--
	680	0.05	4	279 [28]	+92
	815	-0.11	4	254 [20]	+75
MgAl ₂ O ₄ ²⁾ (pc) ^{††}	control	--	3	129 [2]	--
	680	-0.19	6	178 [14]	+38
	815	-0.35	4	173 [16]	+34
MgAl ₂ O ₄ ³⁾ (pc)	control	--	5	112 [12]	--
	680	-0.39	3	156 [12]	+39
	815	-0.31	3	137 [17]	+22
Al ₂ O ₃ ⁴⁾ (sc)	control	--	8	273 [80]	--
	680	3.54	4	290 [43]	+ 6
	815	3.37	4	333 [40]	+22
Al ₂ O ₃ ⁵⁾ (sc)	control	--	7	302 [68]	--
	680	3.52	4	330 [22]	+ 9
	815	3.28	4	286 [124]	- 5
Si ₃ N ₄ ⁶⁾ (pc)	control	--	7	234 [20]	--
	680	1.1	4	195 [12]	-1*
	815	1.0	4	219 [7]	- 6
SiC/graphite ⁷⁾	At 680 K, SiC swelled 1.47 vol% and graphite densified ~7 vol %, resulting in nearly-complete delamination.				

[†] The negative sign represents densification.

^{††} (sc) = single crystal, (pc) = polycrystal.

Sources, impurity contents in wt ppm and other characteristics of test materials are:

- 1) Linde Division, Union Carbide Corp.; 100 Si, 20 Fe, 8 B.
- 2) Ceradyne Inc.; 1000 Li, 200 Fe, 70 Ca, 60 Ba; ~99% dense.
- 3) Coors Porcelain Co.; 1500 Li, 150 Fe, 40 Si, 30 Ca; grain size ~200µm; ~100% dense; ~1% Al₂O₃-rich.
- 4) Tycos Laboratories Inc.; 100 Nb, 80 Fe, 15 Ni.
- 5) Linde Division, Union Carbide Corp.; 60 Fe, 50 Nb, 40 Mo.
- 6) Ceradyne Inc.; 20,000 Mg, 2000 Al, 300 Fe, 200 B, 200 Ca; beta phase, with MgO present. This ceramic was an experimental material made from powders ball-milled with Al₂O₃ balls to reduce residual radioactivity. No attempt was made to optimize strength or control boundary phases.
- 7) Materials Technology Corp.; chemically vapor-deposited stoichiometric β-phase SiC on isotropic graphite of 18 µm grain size and density 1.80 g/cc.

structive to consider the irradiation response in the context of earlier results obtained at 925-1100K and at 430K. Irradiation to similar doses at 925-1100K revealed that this ceramic in single-crystal form exhibited no discernable swelling⁴ and little change in fracture toughness.⁶ The microstructure after 925K irradiation was characterized by rosettes of ~200nm dia faulted Frank interstitial loops of type $1/4\langle 110 \rangle \langle 110 \rangle$, along with a lesser number of smaller $1/6\langle 111 \rangle \langle 111 \rangle$ loops. At 1100K only the former loops were present, and these had grown to micron dimensions.⁷ Calculations based on loop concentration and size showed that ~99.99% of displaced atoms had not formed visible aggregates, but had either recombined with their complementary vacancies or were present in submicroscopic form. However, submicroscopic defects can induce swelling⁴ and reduce thermal conductivity by scattering short wavelength lattice vibrations which dominate heat transfer near room temperature.⁸ Since swelling was near zero and thermal diffusivity was not degraded⁹, it may be concluded that the vast majority of displaced atoms were annihilated by recombination. Polycrystalline $MgAl_2O_4$ showed a different damage response⁴, characterized by formation of $1/4\langle 110 \rangle \langle 110 \rangle$ loops as before but in addition by 5 nm dia voids (after 1100K irradiation) arrayed 6 nm on either side of grain boundaries. A similar but finer distribution of voids was observed after 925K irradiation. These voids are thought to have been formed as a result of a vacancy bias following preferential annihilation of interstitials at boundaries. The accompanying swelling (~1 vol%) is attributed at least partially to this void concentration, as is the reduction of thermal diffusivity.⁹ By contrast with these high-temperature results, polycrystalline $MgAl_2O_4$ irradiated to 2.1×10^{26} n/m² ($E > 0.1$ MeV) at 430K exhibited a dense array of small (<5 nm) defect clusters

(possibly loops) and near-grain boundary regions denuded of visible aggregates.^{4, 10} Swelling of 0.6 vol% was observed, and is thought to have resulted from a high concentration of fine (perhaps unresolved) defects.

The present swelling results can be interpreted in terms of the observed defect structure⁵ and earlier results. The damage microstructure is again characterized by $1/4\langle 110 \rangle \langle 110 \rangle$ and $1/6\langle 111 \rangle \langle 111 \rangle$ faulted interstitial loops, of a size and concentration intermediate between those observed at 925K and the aggregates formed at 430K. Calculations show that the fraction of displaced atoms accommodated in loops is on the order of that observed at the higher test temperatures. The near-zero volumetric changes imply that once again most point defects have disappeared through recombination. The observed slight densification of single-crystal $MgAl_2O_4$ at 315K (which has been confirmed by direct comparison of densities of control and irradiated samples in the same immersion experiment⁵) may be attributable to rearrangement of Al and Mg atoms on cation sites. The same alteration could have occurred in the polycrystalline samples, which also densified slightly.

The large increases in strength observed for single-crystal $MgAl_2O_4$ may have resulted from impedance of crack propagation by the damage microstructure. TEM studies have shown that such an effect leads to a doubling of fracture toughness in Al_2O_3 irradiated at 1100K¹¹; here the enhancement apparently results from interaction of the crack front with the void field. In the absence of voids (the present case), it can be postulated that crack propagation is impeded by strain fields surrounding the dislocation loops or perhaps by jogging of an atomically-sharp crack front as it moves through the array of radiation-induced defects. The 20% strength increase measured in polycrystalline

MgAl₂O₄ after irradiation at 430K¹⁰ may be explained by a similar argument. Alternatively, it has been suggested¹² that the principal strengthening effect of irradiation may be the blunting of sharp tips of pre-existing flaws (i.e., alteration of the crack initiation rather than propagation step). It does not appear necessary to invoke such a model to explain the toughening of Al₂O₃ described above, but this explanation could apply to the present results.

The observation that strengthening is less pronounced in polycrystalline than in single-crystal spinel suggests that damage effects in grain boundaries can be deleterious. Earlier results have shown that irradiation at 925-1100K and at 430K both introduce near-boundary heterogeneities (voids in the former case⁴, denudation in the latter¹⁰). Interpretation of strength changes in polycrystalline MgAl₂O₄ after irradiation at 680 and 815K in terms of grain boundary effects must await the results of further TEM examinations.

The two forms of single-crystal Al₂O₃ studied here exhibited swelling in the narrow range of 2.28-3.54 vol%, with the higher values corresponding to the lower irradiation temperature. Although voids form readily in this material at 925-1100K (and are accompanied by ~4 vol% swelling)⁴, such aggregates are at the limit of resolution for conventional TEM (~2 nm dia) after irradiation at 875K, and only a fine dispersion of unresolved damage is observed after 650K irradiation.¹³ Nevertheless, large amounts of swelling were observed here, and have also been reported for other ceramics after low-temperature irradiation: MgO swells 2.6-3.0 vol% at 430K as displaced atoms are accommodated in a dense concentration of loops or a dislocation network^{4, 10}, and SiC swells 3 vol% at 300K apparently by retention of a high concentration of point defects or small clusters.¹⁴ It has been postulated⁴ that barriers to defect

recombination can enhance low-temperature swelling of ceramics; such an effect could explain the behavior of these three materials as well as the temperature-dependence of swelling observed here for Al₂O₃. Thermal diffusivity of single-crystal Al₂O₃ is significantly reduced after irradiation at 925-1100K.⁹ Calculations have shown that less than half of the reduction results from the void content, with the remainder attributed to a point defect (or unresolved cluster) content of ~1%.⁸ Thus recombination is not so strong a factor in Al₂O₃ as in MgAl₂O₄, and the retained fine-scale damage could represent a significant source of swelling.

It might be anticipated that the damage microstructure of the Al₂O₃ tested here would cause an increase of strength. Unfortunately, the results in Table 1 show extensive experimental scatter, so that it can only be concluded that major changes (either positive or negative) did not occur. It should be pointed out that this ceramic is subject to anisotropic swelling, especially at higher temperatures, which in polycrystalline material can lead to grain boundary separation and severe structural degradation.⁴

The ~1 vol% swelling observed here for Si₃N₄ is essentially the same as that measured after irradiation at 925 and 1100K (also ~1 vol%).¹⁵ After those exposures the defect microstructure was characterized by dislocation loops (denuded near grain boundaries) and extensive damage to a glassy grain boundary phase.^{15, 16} The swelling results and the large reduction of thermal conductivity⁹ imply that a high concentration of unresolved defects is additionally present.

The non-cubic (trigonal) crystal structure of Si₃N₄ or the presence of the grain boundary phase could lead to anisotropic or differential swelling and loss of strength. Nevertheless, strength after irradiation at 680 and 815K was only slightly reduced (perhaps not signifi-

cantly so at the higher temperature). Thus it appears that the effects of anisotropic and/or differential swelling were not large under the conditions utilized here.

The consequences of a severe swelling mismatch are graphically illustrated by the almost complete separation of SiC from graphite in that composite (Fig. 1.). Delamination was induced primarily by the ~7 vol% shrinkage of the graphite substrate, a dimensional change consistent with observations by others at this temperature and dose¹⁷. Swelling response of graphite is strongly dependent on starting material as well as temperature and fluence, so that somewhat better matching of volumetric changes with SiC should be possible. However, the fluence-dependence of swelling as well as the magnitude of the mismatch at a given dose must be considered. By this measure a SiC/graphite system is subject to particular difficulties: graphite typically undergoes only slight (sometimes negative) swelling at low fluences followed by extensive growth at high doses.¹⁷ By contrast, SiC swells rapidly at low fluences but then saturates at a comparatively modest dose below 1275K.¹⁴ (The swelling value of 1.47 vol% observed here after irradiation to 2.2×10^{26} n/m² at 680K agrees closely with the 1.6 vol% value reported after a dose of $\sim 2 \times 10^{24}$ n/m² at that temperature).¹⁴ The greater part of the swelling mismatch reported here could likely be avoided by use of another substrate material; however, differential growth of ~1.5 vol%, which may be sufficient to cause structural degradation, seems unavoidable at this test temperature.

4. CONCLUSIONS

MgAl₂O₄ spinel exhibited excellent resistance to structural degradation under the irradiation conditions utilized here. Results to date indicate that, insofar as fission neutrons accurately simulate fusion neutrons, this ceramic

should perform satisfactorily as an insulator for magnetic coils and as an RF window material. However, a slight amount of swelling may have to be accommodated at lower temperatures. Efforts should be made to develop stronger forms of spinel so as to extend its usefulness.

Al₂O₃ showed significant swelling but no major strength change after irradiation. The large amount of growth presents a design constraint, and in polycrystalline forms can lead to structural failure from anisotropic swelling. Nevertheless, this highly-developed ceramic will likely be used in various fusion applications to the limit of its radiation tolerance.

Si₃N₄ exhibited modest swelling and, despite its propensity for anisotropic growth, only slight reduction of strength. Its already promising performance with respect to such applications as magnet insulators, RF windows and near-first-wall components could be enhanced by materials development directed toward optimization (or perhaps elimination) of the grain boundary phase.

The SiC/graphite layered composite was severely damaged by differential swelling. Although better performance for a coating/substrate system could be attained by minimization of the swelling mismatch, greater structural stability in first-wall and other applications will be achieved by use of monolithic materials.

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