Received by OSTI

APR 07 1986

CCVI-560421--8

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

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TITLE: SWELLING OF SPINEL AFTER LOW-DOSE NEUTRON IRRADIATION

LA-UR--86-1048

DE86 008753

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SUBMITTED TO: The Second International Conference on Fusion Reactor Materials,
April 13-17, 1986 in Chicago.

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SWELLING OF SPINEL AFTER LOW-DOSE NEUTRON IRRADIATION

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ABSTRACT

Swelling was determined in samples of single-crystal MgAl_2O_4 spinel, irradiated to doses as high as $8 \times 10^{22} \text{ n/m}^2$ ($E > 0.1 \text{ MeV}$) at $\approx 50^\circ\text{C}$ in the Omega West Reactor. Swelling effectively saturated at $\approx 2 \times 10^{22} \text{ n/m}^2$ which corresponds to a damage level of only $\approx 2 \times 10^{-3} \text{ dpa}$. In addition subsequent measurements after irradiation have revealed that the samples continued swelling for several weeks. These results imply that irradiation defects begin to interact by recombination and aggregation at low damage levels in this material at 50°C and perhaps continue to cluster at room temperature after irradiation. Rate equations have been employed to determine defect concentrations at saturation. Results to date show that the observed swelling is consistent with the number of surviving defects if swelling per Frenkel defect pair is taken to be one atomic volume.

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I. INTRODUCTION

Ceramics are required in magnetically confined fusion power systems for a number of applications including insulators, waveguides, and dielectric windows¹. These various applications use one or more of the properties unique to ceramics and many of them expose the ceramic to high temperatures and significant neutron fluences. MgAl_2O_4 spinel is a prime candidate ceramic for several of these applications because of its low swelling²⁻⁴, enhanced strength³, and increased fracture toughness⁵ after high-dose fission neutron irradiation over a wide temperature range. Progress has been made in explaining these observations in terms of generation, recombination, and aggregation of irradiation-induced defects,⁶ but data are needed at lower doses to more fully understand defect behavior.

A very precise measurement of swelling of single crystal spinel after low dose fission irradiation was undertaken to further understand defect production, annihilation, and agglomeration. Because of the extreme sensitivity of this measurement, the expansion of the crystal lattice resulting from the accumulation of point defects has been measured for the first time. As radiation continued the point defect concentration saturated as did the swelling. Defects appeared to continue to diffuse and agglomerate after irradiation ceased leading to continued swelling as the crystals were stored at ambient temperature.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The fission irradiation of the crystals was done in the Omega

West Reactor at Los Alamos National Laboratory. We originally planned to measure swelling after fission neutron exposures of $\approx 2 \times 10^{22}$ n/m². It first appeared that these measurements would be impossible because previous measurements in spinel after high-fluence fast neutron irradiations at 157°C showed only 0.8 volume percent swelling after 2.1×10^{24} n/m² ($E > 0.1$ MeV)⁶. Some previous measurements in Al₂O₃ offered more encouragement.⁷ First, alumina swells faster at 150°C than at 650°C, and our measurements were planned near the lower temperature. Second, the swelling rate was higher at low dose. Extrapolation of these data to low doses suggested that swelling of about 0.1 volume percent may be expected at a fluence of 2×10^{22} n/m². The experiment was initially designed to measure swelling as low as 0.03 volume percent.

One-centimeter cubes were cut from a single crystal of MgAl₂O₄ obtained from Linde Division of Union Carbide Corporation. The spinel contained the following impurities (in wppm): 200 Fe, 100 Si, 50 Ti, 40 Cr, 14 Co, and 15 Ni. A one-centimeter thick slice was cut from the crystal with care taken to insure uniform thickness. As a result the cubes cut from the slice were very nearly the same height. The relative height of the cubes was determined before and after irradiation by comparison with an unirradiated cube using a gage block comparator located in a temperature controlled room (20±0.1°C). The gage block comparator has a sensitivity of 0.05 µm. Repeated measurements resulted in experimental measurements of height precise to ±0.1 µm. This error represents an error in swelling of 0.003 volume percent.

The crystals were wrapped in Al foil and placed along with

dosimeter wires in Al cans which were inserted in a hydraulic rabbit tube for irradiation. The rabbit tube allowed easy insertion and removal of the capsules from the reactor core. Thermal contact with the cooling water surrounding the cans was enhanced by packing Al-foil around the samples. The cans irradiated at the four highest fluences contained two crystals. In each case the face of one of these crystals was in contact with the bottom of the can. No systematic differences in swelling were observed for the two crystals. The irradiation temperature was $\approx 50^{\circ}\text{C}$ which was calculated to be no more than 7°C above that of the cooling water.

The crystals were irradiated to six fluences between 4.7×10^{21} and 7.9×10^{22} n/m² ($E > 0.1$ MeV) representing exposures of from 2 to 31 hours. Since the reactor is operated for $\approx 7\frac{1}{2}$ hours per day, the four highest fluences represent exposures of from one to four days with the samples remaining in the reactor between daily irradiations. The storage conditions were about 50°C under a very low neutron flux. These samples were irradiated during two consecutive weeks insuring no changes in reactor operating parameters or in fuel loading. A dosimeter package consisting of eight wires was placed in the capsule exposed for one day. The package was similar to one that was used in a previous measurement to determine the flux spectrum in the reactor.² The previous measurements were made in a vacant fuel rod position while the present measurements represent the spectrum in the rabbit tube in the core. The measured spectrum is shown in Fig. 1. The calculated exposure was 59.61 MWH with an average power level of 7.9 MW over a 7.55 hour period. A summary of the resulting flux and fluence values calculated for an eight hour period are given in

Table I. These values represent a fast flux that is about 15 percent higher than that measured in the vacant fuel rod position and a thermal flux nearly twice that measured previously. The measurements seem reasonable because the previous measurement position was adjacent to a control rod which would be expected to absorb a large number of thermal neutrons. Taking the gamma heating rate to be 5 W/g, the gamma dose under these conditions was 1.36×10^4 Gy. Adding to this the ionizing fluence from neutrons of 4×10^4 Gy, the total ionizing dose was 1.40×10^4 Gy. Fluence values for irradiations of the higher dose irradiations were based on these measurements. The fluences for the two lowest values, which were irradiated about six weeks later, were determined by measuring two nickel dosimetry wires which were irradiated with the crystals. The spectrum was normalized to that measured previously using the more complete dosimetry package.

The possibility was considered that dimensional changes might result from changes in electronic state of impurities present in the test material. Accordingly, a cube of spinel was exposed to an ionizing dose of 5.06×10^4 Gy from a ^{60}Co source at Los Alamos over a period of 65 hours.

Threshold displacement energies for the atomic components of MgAl_2O_4 are not well known. Dell and Goland⁹ calculated radiation damage parameters in spinel using displacement threshold energies of 86, 77, and 130 eV for Mg, Al, and O, respectively. These values were obtained from an abstract by Crawford et al.¹⁰. In a later paper, Summers et al.¹¹ discuss the complicated damage states observed in the electron irradiation of spinel. They report a

TABLE I: Flux and Fluence Values for the OWR Rabbit Tube
Normalized to 8 MW -- Fluence is that for 59.6 MWH

ENERGY	FLUX	FLUENCE
	($\times 10^{17}$ n/m ² -s)	($\times 10^{22}$ n/m ²)
Total	28.0	7.50
Thermal (<.5 eV)*	16.0	4.29
0.5 eV - 0.1 MeV	5.61	1.51
>0.1 MeV	6.35	1.71

*The 2200 m/s flux is about 25% lower.

TABLE II: Calculations of Displacement per Atom and H and He
Generation in MgAl₂O₄

MATERIAL	DPA*	H, appm	He, appm
	($\times 10^{-3}$)	($\times 10^{-3}$)	($\times 10^{-3}$)
Mg	2.51	1.24	3.24
Al	2.19	1.54	0.70
O	1.77	0.029	9.67
Spinel	2.00	1.49	6.19

*SPECTER assumes displacement energies of 25, 27, and 30 eV for Mg, Al, and O, respectively; the same values were also assumed for spinel.

value of 59 eV for the displacement threshold of oxygen at 77 K and conclude that 130 eV is required to form a stable defect containing both the interstitial and the vacancy. Nothing is mentioned about the energies required to displace Mg and Al atoms. In a later paper, Matzke¹² reported a value of 56 eV for the oxygen displacement energy. If one assumes the default values of 25, 27, and 30 eV in the SPECTER¹³ code, the dpa levels as well as transmutation generated H and He concentrations are those shown in Table II. Since the displacement energies used are lower than those reported for spinel, the displacement rates in Table II should be considered maximum values.

Swelling results are shown in Fig. 2. Two samples were irradiated at each of the four highest doses, with each sample being measured three times between approximately one and two months after irradiation; the error bars around each average value represent the standard deviation for the six readings. Single samples were used for the two lowest neutron doses and for the gamma irradiation; single readings were taken from the low-dose neutron samples while two readings, which were identical, were obtained from the gamma sample.

During the course of the continued measurements of the irradiated crystals it became clear that the swelling was continuing during storage. This surprising result is illustrated in Fig. 3 which shows the time dependence of swelling for the samples irradiated to the four highest fluences. These were chosen because more measurements had been made on these samples.

III. DISCUSSION

The swelling results in Fig. 2 show rapid initial growth. This growth appears to stop suddenly after only $2 \times 10^{22} \text{ n/m}^2$. This apparent saturation at low fluence is expected to be temporary and swelling will continue if voids or other volume producing defect clusters form at higher fluence. However voids have not been seen in irradiated single crystal spinel. We expect small defect clusters and dislocations to be the dominant sinks in this material. At these low doses we expect to find that irradiation has formed only single defects and small defect clusters. The swelling that is observed is consistent with a saturation of the defect concentrations. The following argument is presented to support this contention. In this argument we use the terms "vacancy" and "interstitial" as if only one kind of each existed. There are many kinds of each defect because of the various sub-lattices and charge states in spinel. However, little is known about the diffusion properties of each kind. In our arguments we will assume that some kind of interstitial defects remain at 50°C and that one of the vacancies will diffuse with an activation energy less than that of the others. It appears that most of the vacancy diffusion occurs on the cation sub-lattices since Sonder¹⁴ has reported activation energies of 1.6, 2.3, and 2.8 eV for cation diffusion in spinel depending on the temperature range. Diffusion of oxygen is more difficult with an activation energy of 4.6 eV reported by Ando and Oishi¹⁵. Such defects are not expected to migrate at the irradiation temperature of 50°C.

When a material is placed under irradiation the defect concentration increases rapidly. As vacancy and interstitial

concentrations increase, these defects begin to annihilate each other by mutual recombination. In the absence of other defect sinks, $(1-1/e)$ of the saturation¹⁴ will be achieved in a time,

$$t_+ = (G/R)^{-1} \quad (1)$$

where G is the production rate of defects that survive the initial damage event. The quantity $R = 4\pi r_0(D_i + D_v)/\Omega$ where r_0 is the vacancy-interstitial recombination radius, D_v and D_i are the diffusion coefficients of vacancies and interstitials respectively, and Ω is the atomic volume. In most cases one of the defects will diffuse much more rapidly than the other and will dominate this calculation so $R \approx 4\pi r_0 D_+/\Omega$ where D_+ is the diffusion coefficient of the fastest diffusing species. We now use the symbols s and f denoting "slow" and "fast" to replace the subscripts i and v . As irradiation continues, defects diffuse to sinks and will establish steady state defect concentrations that depend on the sink strength for the slower diffusing species. At low temperatures this steady state may not be reached in a reasonable time. Where dislocations are the only sinks, the time required is given by

$$t_- = (D_- Z_- L)^{-1} \quad (2)$$

where D_- is the diffusion coefficient for the slower diffusing species, Z_- is the capture efficiency (≈ 1) of the dislocations for the slower diffusing defect, and L is the dislocation density. The defect concentrations for these cases are

$$C_+ = C_- = (G/R)^{-1}, \quad (3)$$

for $t = t_+$, and

$$C_+ = G/(D_+ Z_+ L) \quad (4)$$

$$C_- = G/(D_- Z_- L), \quad (5)$$

for $t = t_0$. Equation (3) gives the metastable concentration achieved initially. This concentration eventually decays to that given by eqs (4) and (5) which corresponds to the quasi-steady state values. These values will change if continued irradiation changes the dislocation density or produces new sinks such as voids.

In this experiment it appears that the build-up to the initial defect concentration corresponds to the initial build-up of the swelling which occurs during the first 1.5×10^{-4} s. From Table 2 the production rate of diffusing defects is $7.4 \times 10^{-22} \beta \text{ s}^{-1}$ where β is the fraction that survive the initial damage event. Using this value for G and combining eqs (1) and (3) to eliminate R , the concentration of defect pairs will be $1.5 \times 10^{24} \beta \text{ m}^{-3}$. If each defect pair contributes one atomic volume, Ω , a swelling fraction of 0.0004 represents a concentration of $4.25 \times 10^{28} \text{ m}^{-3}$. Equating the two values leads to $\beta = 0.28$ which is a reasonable value for the surviving fraction of defects. If we continue along these lines and assume that the recombination radius for these defects is about equal to the lattice parameter, 0.808 nm, the diffusion coefficient of the fast diffusing defect is $2 \times 10^{-22} \text{ m}^2/\text{s}$. For $T = 50^\circ\text{C}$, this diffusion coefficient represents an activation energy between 1.1 and 1.4 eV for values of D_0 between 1 and $10^{-4} \text{ m}^2/\text{s}$. These values depend on the calculated damage rate and the extra volume contributed by each pair of defects; however, the resulting values for the activation energy will not be far from this range. Since this value is lower than the values cited before for vacancy diffusion, we conclude that an interstitial defect is responsible for the defect saturation. The time required to achieve the quasi-steady state

concentration will depend on the slower diffusing defects and the dislocation density. These slower defects will most probably be oxygen vacancies and will have activation energies for motion greater than 2.5 eV. More than 10^4 years would be required to achieve steady state concentrations. Since steady state defect concentrations were not achieved, we conclude that dislocations did not play an important role in this experiment.

A small amount of swelling apparently resulted from gamma irradiation to 5.06×10^4 Gy (Fig. 2). Although this dose is much lower than that experienced by the crystals in the reactor, it is expected that it was high enough to saturate the changes in electronic state of the impurities since previous irradiations have show saturations of a number of optical transitions¹⁷. In gamma irradiations only a few defects are created by high energy secondary electrons. As a result the observed swelling is thought to be due to Coulomb interactions of the charged defects. Perhaps further optical studies of these materials could be done to clarify these observations.

Finally, there are many questions raised by the observation of continued swelling during storage of the samples at ambient temperature ($\approx 20^\circ\text{C}$). An obvious explanation blaming the expansion on the absorption of water in the crystals does not appear to be valid since the increase in height is found by comparing the irradiated crystals with an unirradiated one. All the crystals were stored together and should have absorbed the same amount of water vapor. We believe the only reasonable explanation involves continued diffusion and clustering of interstitial defects. If single interstitial

defects had a volume of less than one atomic volume, the combination of these defects with small dislocation loops would increase the total volume of the crystal. Attachment to a dislocation loop would effectively convert the defect to a lattice site. The diffusion of the same interstitials responsible for defect saturation after one day in the reactor at $\approx 50^\circ\text{C}$ might be expected to cause changes at 20°C during a period of weeks. Several attempts to model this process using rate equations have produced clustering that will show continued swelling but have not yet been able to predict the observed magnitude of total swelling and continued swelling simultaneously. More theoretical work is continuing to obtain a satisfactory explanation.

IV. CONCLUSIONS

Single-crystal spinel exhibits effective saturation of swelling at damage levels of $\approx 2 \times 10^{22} \text{ n/m}^2$ ($E > 0.1 \text{ MeV}$) at $\approx 50^\circ\text{C}$. These results imply that irradiation-induced defects begin to interact either by recombination, aggregation, or a combination of these processes at low damage levels in this material. The magnitude of the observed swelling is consistent with the number of surviving defects if swelling per Frenkel pair is taken to be approximately one atomic volume. The defect responsible for the saturation has an activation energy for motion less than the values reported for vacancy diffusion in spinel. We therefore conclude that an interstitial defect appears responsible for the recombination leading to the saturation effect.

In addition continued swelling during storage of the irradiated

samples is observed which also appears to be associated with diffusion and agglomeration of interstitial defects. A complete model for this phenomenon has not been achieved.

ACKNOWLEDGEMENTS

The authors would like to thank L. W. Hobbs for helpful discussions concerning the effects of gamma irradiation. We would also like to thank L. K. Mansur for discussions concerning the saturation of defect concentrations and for reviewing our manuscript. We also appreciated the help of A. Gauler and E. Fisher for the measurements of the radioactive crystals in the constant temperature precision measurements laboratory. Their help in meeting our time schedule was greatly appreciated.

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FIGURE CAPTIONS

FIGURE 1: The neutron energy spectrum for the rabbit tube in the core of the Omega West Reactor at Los Alamos National Laboratory. The spectrum of the fusion neutrons in RTNS-II is also plotted for reference. The ordinate is $d\bar{\phi}/d \ln E$ where $\bar{\phi}$ is the flux and E is the neutron energy.

FIGURE 2: Swelling of single-crystal MgAl_2O_4 spinel after irradiation in OWR at $\approx 50^\circ\text{C}$.

FIGURE 3: Swelling as a function of storage time after removal from the reactor for four fluences.