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DAMAGE TO MACOR GLASS-CERAMIC FROM HIGH-DOSE 14 MeV NEUTRONS

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ABSTRACT

Macor machinable glass-ceramic was irradiated to fluences up to 1×10^{23} 14 MeV n/m^2 at room temperature. Post-irradiation measurements were carried out to determine changes in high-frequency electrical conductivity, hardness, and density. It was found that neutron damage caused slight increases in conductivity and hardness. The major change noted was in density, where a fluence of 4×10^{22} n/m^2 caused swelling of 1.55 vol% while a dose of 1×10^{23} n/m^2 resulted in a lower swelling value (0.82 vol%). This unusual behavior is explained by a model involving expansion of the mica phase of Macor and contraction of the glassy phase. Implications of the present results for engineering performance of Macor at these and higher fluences are discussed.

Key words: Macor, mica, glass, irradiation, fusion neutrons, electrical conductivity, hardness, swelling

1. Introduction

Macor machinable glass-ceramic (code 9658; a product of Corning Glass Works, Corning, NY) is a material of great usefulness for fusion applications where there is a need for a small number of insulator components, or where grinding conventional refractory ceramics to shape would be prohibitively expensive. Applications for which Macor has been considered or actually employed include insulators for neutral beam injectors, RF heating systems, and diagnostic components.

The microstructure of Macor consists of 1-10 μm flakes of crystalline fluorophlogopite mica precipitated in a borosilicate glass matrix [1]. In its final form the material consists of approximately 50 vol% of each phase. The combination of these two phases renders the Macor machinable using conventional metalworking tools [2]. Silicates are typically sensitive to radiation damage [3], undergoing alterations in degree of atomic order which depend on starting condition [4]. If the two phases of Macor are prone to low-dose damage or undergo density changes at different rates, the result can be generation of destructive internal stresses.

In earlier work [5] changes in density, electrical conductivity, thermal diffusivity, flexural strength, and microstructure were measured on samples exposed to 1×10^{20} and 1×10^{22} 14 MeV n/m² at room temperature. Irradiations were carried out at RINS-II, the rotating target neutron source at Lawrence Livermore National Laboratory. Results showed little change in any of these properties, but transmission electron microscopic examination revealed the presence of

fine-scale mottled damage after the higher dose. This finding suggested that at higher fluences significant damage might be observed, and so irradiations up to $1 \times 10^{23} \text{ n/m}^2$ were carried out with the results reported here.

2. Experimental procedure and results

Eight Macor disks 16 mm dia by 0.55 mm thick were machined from the same block of Macor that was used for the earlier study, and irradiated at room temperature using the RTNS-II 14 MeV neutron source. The disks were stacked and periodically exposed to the neutron flux over a time period on the order of one year, with the result that the lowest-dose sample received $4 \times 10^{22} \text{ n/m}^2$ while the highest-dose sample received $1 \times 10^{23} \text{ n/m}^2$. Because the stack of disks was always located behind other experiments and therefore well away from the neutron source, the flux gradient across the face of each disk was small and is not considered here.

Some of the disks were fractured by the frequent handling that resulted from repeated exposures at RTNS-II, and others were damaged by attempts to remove radiation-damaged Kapton tape that had been used to hold the assemblage together during irradiation. As a result, measurements reported here were carried out on fewer than the full complement of eight disks. In all cases data were obtained at room temperature.

Electrical conductivity measurements were carried out over a frequency range of 5×10^4 to $5 \times 10^7 \text{ Hz}$, using a Hewlett Packard 4342A Q-meter. Results are shown in Fig. 1, along with those reported earlier by Fowler et al. [5]. In the

earlier work conductivity was measured by using a capacitance bridge; this difference in technique may explain the small differences in results observed in the overlap frequency range. It can be seen that irradiation caused only a small increase in electrical conductivity of Macor.

Hardness measurements were carried out on two irradiated samples plus a control sample, all of which were mounted edge-on in epoxy and polished prior to testing. Several Vickers hardness indentations were made in each sample using a Leitz Wetzlar Miniload tester and employing 10g and 35g loads. Average values obtained are shown in Fig. 2. Dimensional measurements from which hardness values were obtained were difficult to carry out because of the transparency of the test material, and considerable scatter in hardness resulted from the fact that size and spacing of mica flakes was on the order of indentation sizes; as a result the average values reported show a relatively large standard deviation for such measurements. No cracks were seen to emanate from the microhardness indentations, so that fracture toughness could not be calculated for either the control or the irradiated samples.

Density measurements were carried out on samples in the unirradiated condition and after irradiation to 4×10^{22} and 1×10^{23} n/m², using the technique employed by Fowler et al. [5]. In brief, small pieces of material were levitated in aqueous solutions of thallium salts and the densities of the solutions were then measured using a Mettler DMA 45 density meter. The density of the control sample was 2.539 Mg/m³, which compares well with the value of 2.52 Mg/m³ reported by Corning [2]. The irradiated samples exhibited swelling

values of 1.55 vol% at the lower fluence and 0.82 vol% at the higher dose; these results are presented graphically in Fig. 3.

3. Discussion and conclusions

The absence of a significant change in electrical conductivity (Fig. 1) is consistent with the results of Fowler et al. [5], and indicates that the atomic rearrangements which led to the significant density changes that were observed here are insufficient to cause major changes in electrical behavior. It is important to note, however, that electrical resistivity of ceramics during irradiation is typically quite sensitive to the absorbed flux of ionizing radiation [cf. reference 6]. Data on in-situ electrical properties is therefore needed before a final judgment can be made as to the performance of Macor in a fusion environment.

The observed increases in microhardness are near the limit of significance, considering the large standard deviations in the results. Nevertheless the data of Fig. 2 show that, as is argued above for electrical conductivity, the atomic rearrangements that resulted from neutron damage are insufficient to degrade the hardness. Similarly, the absence of microcracks emanating from indentations in the irradiated material indicates that gross weakening of Macor on a microscopic scale has not occurred.

The unusual swelling results shown in Fig. 3 are qualitatively consistent with two competing processes: swelling of one of the two phases present and densification of the other. Mica is not a particularly important material in

the nuclear field; as a result, there has been little research on radiation effects in this material. Bopp et al. [7] irradiated muscovite mica to a fluence of $2 \times 10^{24} \text{ n/m}^2$ and found swelling values of from 2.8 to 13.1 vol%. This study was carried out to investigate the release of water from mica, which causes shrinkage, so that the intrinsic swelling of the forms of mica tested should be larger than these values.

Crystalline silica swells about 15 vol% as a result of irradiation to $2 \times 10^{24} \text{ n/m}^2$ [8], while vitreous silica densifies about 3 vol% after irradiation to the same dose [9]. These two forms of SiO_2 approach the same density and state of disorder (the so-called metamict state [4]) at saturation. Thus it would seem that the results reported here are best explained by swelling of the mica crystals and densification of the glass matrix, rather than the reverse.

A simple model for the swelling behavior of Macor has been developed based on the limited data in the literature. Both phases, mica and glass, are assumed to begin to change in density after some incubation period, and to swell or densify exponentially to a steady-state value. The density D is given by

$$D = D_i + a \exp(-b/[n-c]), \quad (1)$$

where D_i is the initial density of the phase and n is the fluence of 14 MeV neutrons in units of $1 \times 10^{22} \text{ n/m}^2$. The constant a is the limiting density change, and the constant c is the incubation fluence. The constant b controls the rate of swelling.

The glass phase of Macor is assumed to demonstrate the same limiting value of densification as is observed for vitreous silica (that is, 3 vol%). A starting density of 2.32 Mg/m^3 , which is that for the similar glass Pyrex, is used. The resulting value for the constant a is 0.072 Mg/m^3 . Given this starting density for the glass, the density of the mica can be estimated from the measured density of the composite and is found to be 2.76 Mg/m^3 .

The remaining five constants must be determined from the experimental density values for the composite: 2.54 , 2.50 , and 2.52 Mg/m^3 at fluences of 1×10^{22} , 4×10^{22} , and $10 \times 10^{22} \text{ n/m}^2$ respectively. There are not enough data to determine a unique set of values for these five constants; however, the experimental points can be fit with values near the following: for the glass phase, $b = 4.45$ and $c = 2.5$ fluence units, and for the mica phase, $a = 0.107 \text{ Mg/m}^3$, $b = 0.25$, and $c = 0.9$ fluence units. These values were found by maximizing the constant b and minimizing c for the glass. The limiting density change for mica of 0.107 Mg/m^3 implies swelling for that phase of 4.0 vol%. The resulting fluence dependencies of densities for mica, glass, and Macor are presented in Fig. 4, and Fig. 5 shows the calculated swelling for Macor.

A comparison of Figs. 3 and 5 demonstrates that the model developed here correctly predicts the main features of the swelling behavior of Macor: the incubation period, a rapid increase with fluence to a peak value of $\approx 1.5 \text{ vol\%}$ at about $4 \times 10^{22} \text{ n/m}^2$, and a more gradual decrease at higher doses. Further, the model predicts a limiting value for swelling of Macor of less than 0.5 vol%, a number that could prove valuable for high-dose applications.

It is known that differential swelling of two phases can lead to reduction of strength [10], and ultimately to separation of the phases and total destruction of the material [11]. Further testing of Macor is needed to determine to what extent this glass-ceramic is structurally degraded by the test fluences employed here, and by higher neutron doses.

Acknowledgments

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FIGURE CAPTIONS

- Fig. 1. Electrical resistivity as a function of neutron dose. The data bar for irradiated Macor (this work) encompasses results from samples irradiated at 5.9×10^{22} , 6.7×10^{22} , 7.5×10^{22} , and 8.4×10^{22} n/m^2 . Results from Fowler et al. [5] include data from unirradiated and irradiated samples (1×10^{22} n/m^2), which are indistinguishable on the scale used here.
- Fig. 2. Vickers hardness as a function of neutron dose, tested at two indentation loads. Standard deviation for the data points is 25 Vickers hardness numbers.
- Fig. 3. Swelling of Macor as a function of neutron dose.
- Fig. 4. Calculated changes in density of Macor and its two component phases as a function of neutron dose.
- Fig. 5. Calculated swelling of Macor as a function of neutron dose.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5