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14 MeV NEUTRON IRRADIATION EFFECTS IN MACOR GLASS-CERAMIC

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Samples of MACOR machinable glass-ceramic were irradiated at room temperature to fluences of 10^{20} and 10^{22} n/m^2. No significant volume changes or deterioration in thermal conductivity were detected, while strength appeared to increase slightly. A slight increase in electrical conductivity, which disappeared with annealing, was noted for the higher fluence. Examination of ion-thinned samples by TEM showed only minor damage from the high-fluence neutron irradiation, where ionizing doses are estimated to be 10^7 Gy. Exposure to higher doses from 200-KeV electrons in the TEM caused the formation of pore-like aggregates.

1. INTRODUCTION

Because of its fabricability, MACOR (Code 9658)[1] machinable glass-ceramic is a candidate material for neutral beam injector and magnetic coil insulators in fusion devices. The structure of MACOR consists of a set of interlocking but non-contiguous fluorophlogopite mica crystals embedded in a borosilicate glass matrix.(1) Its machinability is comparable to that of a soft metal. The phase composition is given in Table 1 and a replica electron micrograph of the microstructure is shown in Fig. 1.

Since both glass and mica may undergo radiolysis (bond-breaking by absorption of ionizing energy), an enhanced damage rate in MACOR is possible. Radiolysis can result from irradiation by photons, electrons, ions, or neutrons; in the last case deposition of ionizing energy by knock-on atoms is responsible. The resulting alterations in structural, electrical, or thermal properties might render the material unsuitable for some fusion system applications. In order to determine fusion environmental effects on the above properties, MACOR samples were irradiated at room temperature to fluences of 10^{20} and 10^{22} 14 MeV n/m^2 at RTNS-II for subsequent physical property measurements. In addition, samples were irradiated to an ionizing dose of 10^{10}-10^{11} Gy by 200 KeV electron bombardment in the electron microscope.

2. RESULTS OF MEASUREMENTS

2.1 Electrical Properties

A set of disks 17 mm in diameter by 0.5 mm thick was cut from a block of MACOR, all disks being cut with the same orientation relative to the block geometry in order to minimize any possible effects of anisotropy.

Upon return from RTNS-II it was noticed that the low-dose (10^{20} n/m^2) disks were slightly pink, and the high-dose (10^{22} n/m^2) disks were a somewhat darker shade of pink in contrast to the pure white color of the unirradiated disks. This color gradually annealed out during high-temperature measurements of these disks.

Table 1. Composition of MACOR Glass-Ceramic (wt.%)

Compound or element	Mica	Glass
SiO_2	42.8	50.7
Al_2O_3	13.7	19.4
MgO	27.3	4.5
K_2O	10.7	8.5
F	8.1	4.4
B_2O_3	0.8	14.4

Prior to measurement but after irradiation the disks were either coated by vapor deposition in vacuum or by silk-screening with a standard three-electrode configuration consisting of guard and guarded electrodes on one side and a single electrode on the other side. Results from both types of disks were mutually consistent.

Direct current data were taken with either a Keithley 616 electrometer in the current mode or a Keithley 415 picoammeter connected in series with the guarded electrode of the sample. Circuit voltage was provided by a battery. This voltage varied between 317 volts at the lowest measured conductivity and 3 x 10^{-2} volts at the highest conductivity. The aim was to keep the

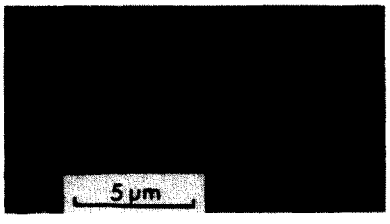


Figure 1. Microstructure of MACOR.

circuit current sufficiently above the noise but low enough to avoid mass transport or heating effects. At about 400 K the current-voltage relationship was approximately linear for voltages between 1.5 and 317 volts.

Data for alternating current measurements were obtained with a General Radio type 716C Schering capacitance bridge with three-terminal adapter. The driving voltage into the bridge was limited to ten volts rms. Standard formulas were used to obtain the conductivity from the measured capacitance and dissipation factor. Some of the A. C. data at high temperatures were taken by using a lock-in amplifier to measure the quadrature components of the voltage drop across a resistor in series with the sample. This method was used above about 600 K to corroborate the D. C. data.

The experimental results of conductivity measurements are shown in Fig. 2. The solid lines are least-squares fits to the data for the unirradiated samples and the points are experimental data for the sample irradiated to 10^{22} n/m^2. Data for the samples irradiated to 10^{20} n/m^2 were not significantly different from those for the control samples and thus are not shown.

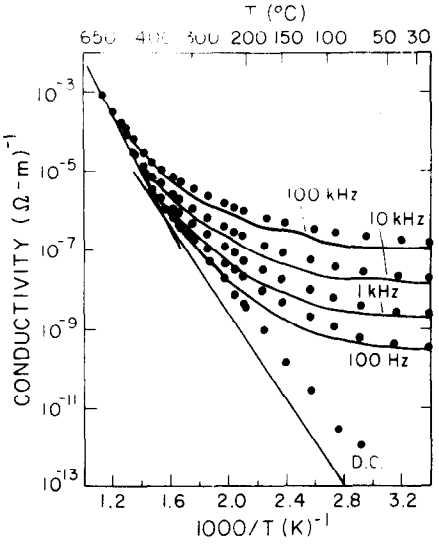


Figure 2. Electrical conductivity of MACOR. Lines are fits to controls; points are data for samples irradiated to 10^{22} 14 MeV n/m^2.

From the figure it can be seen that the D. C. data exhibit Arrhenius-type behavior over two distinct temperature ranges, meeting at about 660 K. Values for the pre-exponential factor σ_o and activation energy Q are listed in Table 2 for least-squares fits of the D. C. data to the Arrhenius equation

$$\sigma = \sigma_o \exp(-Q/kT).$$

In the higher temperature range it was observed that the D. C. current would drop rapidly upon completing the circuit. Such behavior is indicative of blocking of an ionic charge carrier at an electrode. Usually in glass this is an alkali ion. The most likely candidates for MACOR are potassium and sodium; the latter was present at 0.3 per cent by weight. The activation energy for conductivity in MACOR above 660 K (2.2 to 2.4 x 10^{-19} J from Table 2), agrees quite well with that for potassium ions in fused silica (2.28 x 10^{-19} J). (2)

Table 2. Electrical conductivity parameters.

Dose (n/m^2)	T (K)	$\sigma_o(\Omega\text{-m})^{-1}$	Q x 10^{19} (J)
0	345-660	81.9	1.66
0	680-980	1.98 x 10^5	2.36
10^{20}	365-660	77.4	1.65
10^{20}	750-870	3.91 x 10^4	2.15
10^{22}	340-640	17.5	1.46
10^{22}	680-885	1.06 x 10^5	2.25

In an attempt to identify the conducting species, a sample of MACOR was heated to 1000 K with a potential of 24 volts applied across the faces. The sample was then cooled and the voltage removed. The sample was sliced and submitted for ion microprobe analysis of possible current-induced chemical gradients, but none were found.

There was an annealing effect on data from the high-dose sample. The data as shown represent the initial measurement at a given temperature the first time it was reached. This was reproducible until this temperature was exceeded. Subsequent measurements after annealing at higher temperatures gave results which were much closer to the unirradiated data. Eventually there appeared to be no difference between this sample and the others. This disappearance of the irradiation-enhanced conductivity was simultaneous with the disappearance of the discoloration of the sample.

2.2 Swelling

Swelling was investigated by density measurements in which the densities of the irradiated samples were compared with those for a set of unirradiated control samples. The density measurements were carried out by submerging the sample in an aqueous solution of thallium formate, then adjusting the density of the solution by appropriate additions of water or dense solution until the sample remained stably in suspension in the middle of the column of liquid. Density of the liquid was then measured directly in a Mettler DMA 45 density meter.

Density for control samples and those irradiated to 10^{20} and 10^{22} n/m^2 are reported in Table 3. Since the absolute density is not the significant quantity here, these results are reported normalized by the median value for the control

material (2.542 g/cm^3). Only the higher fluence gave results showing evidence of a change, with an apparent compaction of 0.05 to 0.1 per cent. No independent measurements of density changes for the component phases of MACOR are avaliable. Volume expansion for an unidentified mica has been reported after exposure to 4 x 10^{23} n/m^2(3), while detectable shrinkage is observed in silica and other glasses after fluences of 10^{22} n/m^2(4,5) or greater. In the present case, it appears that the dominant effect is the beginning of compaction of the glassy phase, at the higher fluence. This would be expected to affect the distribution of internal stresses and the strength.

Table 3. Density changes in irradiated MACOR.

Sample fluence (n/m^2)	Number of samples	Normalized density range	Density change,%
control	3	1±.00008	------
10^{20}	2	0.9999 - 1.0002	------
10^{22}	2	1.0005 - 1.0010	+0.05 - +0.1

2.3 Strength

The mechanical strength of MACOR was evaluated by means of four-point bend tests on control samples and on samples irradiated to 10^{20} and 10^{22} n/m^2. Test samples had nominal dimensions of 1.0 x 0.5 mm cross-section and load was applied across a 12.7 mm (0.5 in.) gauge length. Strain rate was approximately 12 x 10^{-6}/s.

Results of these tests and parameters of the Weibull distributions are given in Table 4, and the Weibull cumulative distribution functions are plotted in Fig. 3. While these results are all close together, the differences between the control and either set of irradiated samples are significant and show a small increase in strength after irradiation.

The strength of brittle materials depends on the size of pre-existing flaws and on the fracture toughness. Hence changes in strength can occur if treatment of the material changes either the size of the flaws or the fracture toughness. In the case of room temperature irradiation followed by a strength increase, we would not suspect a decrease in flaw size; an increase in fracture toughness could account for increased strength. Enhanced fracture toughness has been observed in neutron-irradiated Al_2O_3.(6) Another effect which can affect strength in ceramics is the internal stress distribution. In the case of internal stress generated by a phase transition, the fracture criterion is satisfied when the applied stress added to the effective internal stress reaches a critical value.(7) Reduction of internal stress would therefore result in a strength increase as measured in a mechanical test. Internal stress can also increase strength, if the stresses generated act to inhibit crack propagation in the strength-controlling phase of a multi-phase material.(8) This latter effect has been concluded to dominate fracture in some glass-ceramic compositions.(8)

Table 4. Flexure strength test results for MACOR.

Sample fluence (n/m^2)	MOR* (MN/m^2)	No. of samples	Standard deviation (MN/m^2)	Weibull m	Weibull σ_o
control	104	24	3.7	27.7	107
10^{20}	107	13	4.0	24.9	110
10^{22}	109	14	4.0	28.0	110

*MOR=Modulus of Rupture

The strength of MACOR has been shown to result from a high fracture energy which follows the interaction of cracks with the microstructure.(9) The irradiation effects on the microstructure in the present investigation were small and appear unlikely to have affected the fracture energy (toughness). It is most likely that changes in internal stress are responsible for the change in strength. X-ray diffraction traces of irradiated MACOR disclosed an apparent small broadening of the high angle peaks which would support, along with the swelling results, the expectation of internal stress changes. However, the lines which were broadened were too weak to analyze quantitatively.

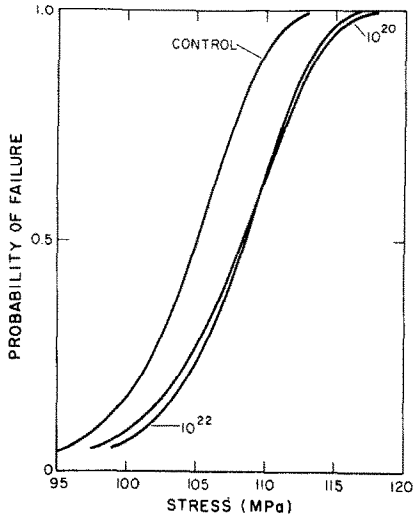


Figure 3. Weibull cumulative distribution functions for MACOR.

2.4 Thermal Diffusivity

Thermal diffusivity was determined by means of the flash diffusivity technique. Temperature rise at the rear of the sample was measured by pressing the separate legs of the chromel-constantan thermocouple against a thin metallized layer which had been evaporated onto the sample.

Results of the measurements are given in Table 5

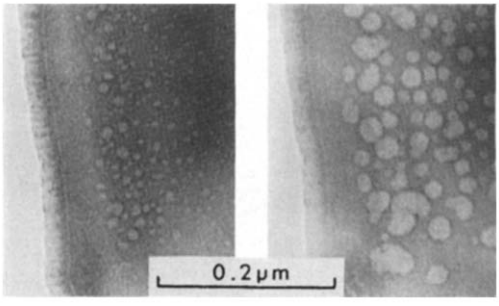
and show that the changes, if any, are small. The starting value, 4.5 x 10^{-7} m^2/s, is similar to values for this material in the literature.(10) The latter showed that thermal diffusivity varied with the heat treatment which controlled the microstructure. The crystalline phase produces a small improvement in thermal diffusivity and some reduction would be expected from the microstructural damage resulting from neutron irradiation.

Table 5. Thermal diffusivity changes in MACOR.

Sample fluence (n/m^2)	Number of samples	Thermal diffusivity (normalized)
Control	5	1 (4.5 x 10^{-7} m^2/s)
10^{20}	4	0.998
10^{22}	2	0.978

2.5 Microstructural Changes

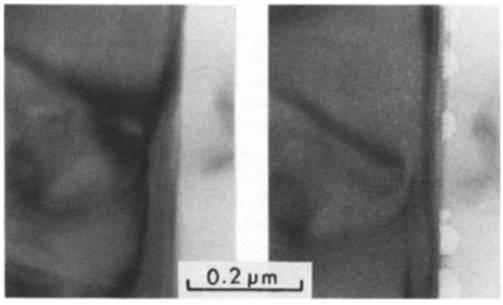
MACOR which had been irradiated to 10^{22} n/m^2 was ion-thinned and examined for structural changes in the transmission electron microscope, along with unirradiated control samples. Other as-received material was thinned and irradiated with 200 keV electrons in the microscope. In the latter study, ionizing doses used were those necessary to generate visible damage. It was found that damage clusters were formed in a finely-distributed crystalline phase (probably a minor constituent) after about one minute of beam irradiation at a dose rate of 10^{10} - 10^{11} Gy/min. At approximately the same dose, pore-like aggregates were formed in the glassy phase (Fig. 4a and b). After several minutes' exposure, other pore-like aggregates appeared in the mica phase and in the glass at the



(a) (b)

Figure 4. Electron beam damage in the glassy phase of MACOR after (a) 1 min, (b) 2 min.

interface with the mica (Fig. 5 a and b). It has been suggested that such defects in electron-irradiated borosilicate glass are oxygen bubbles.(11) In contrast, the high-dose neutron-irradiated material showed only a slight change, in the form of occasional areas of barely-visible mottled damage in the mica phase (Fig. 6). In view of this, the 10^{20} n/m^2 samples were not examined.



(a) (b)

Figure 5. Electron beam damage in the glassy and mica phase of MACOR after (a) 1 min, (b) 5 min.

The ionizing dose from neutron irradiation was estimated from the work of Dell et al.(12) It was shown in calculations for Al_2O_3 in two neutron spectra that the correlations are approximately

$$1.7 \times 10^{15} \text{ 14 MeV } n/m^2 \rightarrow 1 \text{ Gy, and}$$

$$2.4 \times 10^{16} \text{ fast fission}^2 \text{ } n/m^2 \rightarrow 1 \text{ Gy.}$$

Since Al_2O_3 has relevant parameters similar to those of the two phases in MACOR, these correlations are roughly applicable to the present study and are used here.

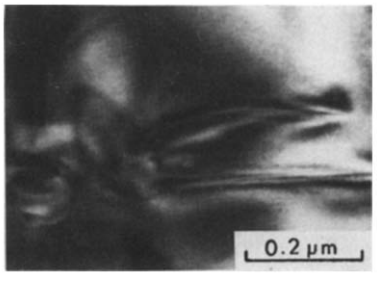


Figure 6. Neutron damage in the mica phase of MACOR.

Damage to the principal phases of MACOR from electron and neutron irradiation is compared in Table 6. Results are also given for a fission neutron irradiation study of muscovite mica by Bopp, Sisman, and Towns.(13) It may be seen that mica is perhaps four orders of magnitude more sensitive to neutron-induced ionizing doses than to such doses from electrons. A comparison of this type can also be made for crystalline SiO_2, which likewise suffers radiolytic damage, by reference to the literature. Wittels and Sherrill (14) found that a fast fission neutron dose of $\sim 10^{24}$ n/m^2 (equivalent to $\sim 4 \times 10^7$ Gy) caused amorphization of this

Table 6. Damage effects in irradiated MACOR and mica.

Material and source	Particle	Dose, Gy	Result
Glassy phase in MACOR (this work)	200 keV e	10^{10}-10^{11}	Pore-like aggregates; no evidence of swelling
Mica phase in MACOR (this work)	200 keV e	$\sim 10^{11}$	Same
MACOR (this work)	14 MeV n	$\sim 6 \times 10^{6}$	Minor microstructural damage in mica phase only
Mica (Bopp, Sisman and Towns)	fission[3] n	$\sim 2 \times 10^{7}$	4% swelling

ceramic, while Hobbs and Pascucci (15) have shown that $\sim 10^{12}$ Gy is required to achieve a similar level of damage in the electron microscope. Thus the factor of roughly four orders of magnitude difference is again seen. The reason for the vastly greater damage effectiveness of neutrons is not clear, but may be related to the more intense, localized nature of energy deposited by these particles.

3. CONCLUSIONS

These studies show that there exists no permanent degradation in measured mechanical and electrical properties of MACOR at doses as large as 10^{22} 14 MeV n/m^2. Use of MACOR in fusion systems is acceptable at or below this lifetime dose.

It should be pointed out that a dose of 10^{22} fusion n/m^2 in a material system would be less damaging than the same dose at 14 MeV because of degradation of the energy spectrum.

ACKNOWLEDGMENTS

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FOOTNOTES

[1] MACOR is a product of the Corning Glass Works, Corning, NY.

[2] EBR-II reactor, row 7.

[3] Converted to Gy from a fast fission fluence of 4 x 10^{23} n/m^2.

REFERENCES

[1] Beall, G. H., Chyung, K., Grossman, D. G. and Smith, G. P., Machinable Glass-Ceramics: New Materials for Electrotechnical Applications, presented at the World Electrotechnical Congress, Moscow, USSR (June 1977).

[2] Clausen, E. M., Alkali ion conductivity in fused silica, in Cooper, A. R. and Heuer, A. H. (eds.), Mass Transport Phenomena in Ceramics (Plenum, NY, 1975).

[3] Wullaert, R. A., Buriar, R. J., Melehan, J. B., Kangilaski, M. and Gates, J. E., Effects of Radiation on Ceramic Materials, in Kircher, J. F. and Bowman, R. E. (eds.), Effects of Radiation on Materials and Components 386, (Reinhold, NY, 1964).

[4] Primak, W., Fuchs, L. H. and Day, P., Effects of Nuclear Reactor Exposure on Some Properties of Vitreous Silica and Quartz, J. Am. Ceram Soc. 38 (1955) 135-9.

[5] Wullaert, R. A., Buriar, R. J., Melehan, J. B., Kangilaski, M. and Gates, J. E., op. cit. ref. 3, 370-4.

[6] Hurley, G. F. and Youngman, R. A., Los Alamos National Laboratory, Los Alamos, NM, to be published.

[7] Pohanka, R. C., Rice, R. W., and Walker, B. E. Jr., Effect of Internal Stress on the Strength of $BaTiO_3$, J. Am. Ceram. Soc. 59 (1976) 71-4.

[8] Borom, M. P., Dispersion Strengthened Glass Matrices - Glass-Ceramics, a Case in Point, J. Am. Ceram. Soc. 60 (1977) 17-21.

[9] Chyung, K., Fracture Energy and Thermal Shock Resistance of Mica Glass-Ceramics, in Bradt, R. C., Hanselman, D. P. H., and Lange, F. F. (eds.), Fracture Mechanics of Ceramics, Vol. 2, 495-507 (Plenum, NY, 1974).

[10] Siebeneck, H. J., Chyung, K., Hasselman, D. P. H. and Youngblood, G. E., Effect of Crystallization on the Thermal Diffusivity of a Mica Glass-Ceramic, J. Am. Ceram. Soc. 60 (1977) 375-6.

[11] DeNatale, J. F. and Howitt, D. G., Radiation Damage in Nuclear Waste Glass, Am. Ceram. Soc. Bull. 60 (1981) 368.

[12] Dell, G. F. and Goland, A. N., Brookhaven National Laboratory, Radiation Damage Parameters in Non-Metals for Fusion Reactor Applications, submitted for publication.

[13] Bopp, C. D., Sisman, O. and Towns, R. L., The Effect of Irradiation on the Thermal Stability of Muscovite Mica, Oak Ridge National Laboratory Solid State Division Annual Progress Report for Period Ending August 31, 1960, ORNL-3017, 98-100.

[14] Wittels, M. and Sherrill, F. A., Radiation Damage in SiO_2 Structures, Phys. Rev. 93 (1954) 1117-8.

[15] Hobbs, L. W. and Pascucci, M. R., Radiolysis and Defect Structure in Electron-Irradiated Alpha Quartz, J. de Physique 41 (C6) (1980) 237-242.