CONF-760355-1

LA-UR -76-1131

MASTER

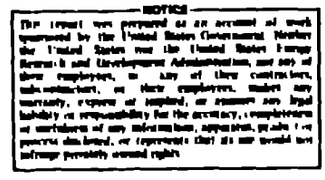
TITLE: STRUCTURAL EFFECTS IN NEUTRON IRRADIATION OF INSULATING CERAMICS

AUTHOR(S): George F. Hurley

SUBMITTED TO: Presentation at CTR Electrical Insulator Meeting, LASL, May 17-19, 1976

Proceedings to be published.

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544



Form No. 836
St. No. 2629
1/75

UNITED STATES
ENERGY RESEARCH AND
DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

STRUCTURAL EFFECTS IN NEUTRON IRRADIATION OF INSULATING CERAMICS*

by

George F. Hurley
University of California
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

ABSTRACT

A vacuum gap irradiation capsule was desigred and built to maintain a temprature of 740°C during 6 weeks irradiation at EBR-II. Sixty-eight samples of 15 ceramic or metal-ceramic combinations were irradiated to a fluence of approximately 3×10^{21} neutrons/cm^2, E > 0.1 MeV. Measurements of sample dimensions before and after irradiation were used to determine volume swelling. This parameter and the physical appearance of the samples are discussed.

A primary application of insulating ceramics in proposed fusion powder devices is the first wall insulating lining in the RTPR reactor. A satisfactory material for this application must bear substantial thermal stresses in cyclical fashion. Calculated values of pertinent parameters are presented and compared for several of the irradiated materials in non-irradiated form. Work to prepare apparatus for the measurement of thermal and mechanical properties of these materials following neutron irradiation is described.

Silicon nitride is representative of a class of refractory ceramics distinguished by its high thermal conductivity, resistance to thermal shock, and elevated temperature strength retention. Recent work has suggested that Si_3N_4 hot pressed with additions of Y_2O_3, rather than the usual MgO, may offer improved high temperature strength. A project to prepare samples of this material with optimized Y_2O_3 concentration and pressing conditions is described. Samples of Si_3N_4 hot pressed with 0, 5, 10, 15, and 20 w/o Y_2O_3 additions have been prepared for an irradiation experiment being carried out by ORNL at EBR-II.

*Work performed under the auspices of the USERDA.

INTRODUCTION

Many ceramic materials bear particular potential for elevated temperature service including load-bearing applications due to their typical high modulus, resistance to deformation, and relatively inert behavior in many adverse environments. In addition, many ceramics are also electrical insulators and this combination of properties make such materials promising for several fusion reactor applications.

The Reference Theta Pinch Reactor (RTPR) requires an insulating first wall to prevent energy dissipation by induced electrical currents during implosion heating of the plasma. In this application, an insulator conducts heat out from the plasma, undergoes cyclic thermal stresses, and is also cyclically bombarded by neutrons. This application is possibly the most severe of several envisaged for this class of materials.

In this part of the insulator program the major areas of investigation are the effect of neutron irradiation on dimensional stability (swelling), thermal conductivity, and mechanical behavior, and the relationship of these properties and their changes to structure and composition.

IRRADIATION OF CANDIDATE INSULATING CERAMICS

A third irradiation capsule was designed to provide preliminary data on the same materials being prepared for irradiation for a 1 yr period. The new capsule was designated KA-3, with a design temperature of 740°C, while the main experiments were KA-1 and KA-2 with design temperatures of 650° and 825°C. KA-1 and -2 are heat pipes with quite precise temperature control, while KA-3 was a vacuum gap capsule with temperature control estimated to be 739 $\pm$ 42°C for reactor power fluctuations of $\pm$ 25%.

Samples for this irradiation capsule were essentially the same as those included in the capsules KA-1 and -2. Their identities are given in Table I. Details of the preparation and purpose of the composite samples are given by J. G. Hoffman in this proceedings, and choice of the monolithic samples is described by J. M. Bunch. These samples for the most part were 1 cm^2 x 0.05 cm wafers. In addition 8-mm-dia x 8-mm-long samples of both sialon and Si_2ON_2 were included in KA-3 for subsequent diametral compression testing.

A six week irradiation of this capsule was completed in EBR-II with an estimated fluence of 3 x 10^{21} neutrons/cm^2. The capsule was received back here and has been opened. The capsule vacuum gap was sampled to show that a vacuum remained and that the thermal analysis was therefore valid. We presently await further data on the run in order to fix the temperature uncertainty. A set of dummy samples representing all those irradiated were annealed at the same temperature and are available for comparison.

A new irradiation, in space made available to us in an ORNL experiment, has been initiated. In this case we will irradiate samples of a new form of hot pressed Si_3N_4 at 625°C and at 700°C to a fluence of approximately

TABLE 1. MATERIALS IRRADIATED IN KA-3

MATERIAL	FORMS
Al_2O_3	SINGLE CRYSTALS, POLYCRYSTALS
$Y_3Al_5O_{12}$	SINGLE CRYSTALS, POLYCRYSTALS
$MgAl_2O_4$	SINGLE CRYSTALS, POLYCRYSTALS
BeO	2 TYPES OF DISPERSION STRENGTHENED
Y_2O_3	POLYCRYSTALLINE, PURE & WITH 1% Zr
Si_3N_4	2 SUPPLIERS, POLYCRYSTALLINE
Si_2ON_2	POLYCRYSTALLINE
SIALON	(50 m/o Si_3N_4 -25 Al_2O_3 -25 AlN)-5 w/o Y_2O_3
Al_2O_3/Nb	VARIOUS
Al_2O_3/Mo	VARIOUS
Si_3N_4/Si	VARIOUS
Si_3N_4/Mo	VARIOUS
GLASS/HASTELLOY-X	BARIUM ALUMINUM SILICATE GLASS
GLASS/Nb	

4×10^{22} neutrons/cm^2. Samples for this experiment have been fabricated and sealed into stainless steel capsules. These samples are at ORNL awaiting their assembly of the capsules.

ANALYSIS OF SAMPLES FROM KA-3

Samples have been removed from this capsule and given a cursory inspection. Six of the samples including two Si_3N_4 wafers from Norton and 4 glass-metal composites from AI had activity levels too high for handling outside the hot cell. The latter 4 samples were stuck together, apparently by softening of the glass at the irradiation temperature. All of the other samples showed no evidence of physical degradation other than color changes in particular cases.

All of the monolithic ceramic pieces have been measured before and after irradiation to determine their dimensional stability. Results presented as volume increase in percent are listed in Table 2. In the case of the flatplate samples which were approximately 10 x 10 x 0.25-0.5 mm, volume swelling was calculated from changes in the larger dimensions. Thus,

$$\frac{\Delta V}{V_o} \simeq 1.5 \left(\frac{\Delta x}{x_o} + \frac{\Delta y}{y_o} \right) .$$

One exception was the National Beryllia samples for which

$$\frac{\Delta V}{V_o} \simeq 3 \frac{\Delta x}{x_o} .$$

The disc samples were approximately 8-mm-dia and 8-mm-long. Here volume swelling is

$$\frac{\Delta V}{V_o} = \frac{LD^2}{L_o D_o^2} - 1.$$

Three types of aluminum oxide samples are listed. The Tyco sapphire samples were cut from single crystal ribbons which were grown with their surface parallel to the crystallographic ($\bar{1}02$) plane. These samples have the direction of maximum swelling 32.5° away from the plane of measurement; it is therefore assumed that the volume swelling was less than that reported. Similarly, the Linde sapphire samples, which are slices from a Czochralski single crystal boule, are oriented such that maximum swelling would be 90° from the plane of the samples. These samples were irradiated to provide samples for other phases of the investigation.

BeO is also noted for its large and anisotropic expansion under neutron irradiation. The two types of BeO here seem to have behaved differently, perhaps a result of structural differences. Little is known of the structure or properties of either of these types of samples, at present. Further characterization will be required in order to compare these results with each other and with other results from pure BeO.

TABLE 2. AVERAGE VALUES OF SWELLING

MATERIAL	TYPE*	SUPPLIER	% VOL. CHANGE	STRUCTURE	DENSITY** (STARTING)
Al_2O_3	S,R	TYCO	2.41	HEXAGONAL	100%
	S,C	LINDE	0.21		99%
	P	COORS	1.94		96%
Si_3N_4	P	NORTON	0.39	HEXAGONAL	(3.18)
	P	CEREDYNE	0.28		(3.08)
Si_2ON_2	P	NORTON	0.05	ORTHORHOMBIC	(75%)
SIALON	P	AFML-WIMMER	0.47	Si_3N_4	2.82
BeO + SiC	P	CERADYNE	3.3	HEXAGONAL	ND.
BeO + (DISP)	P	NAT'L BERYLLIA	1.2		2.98
$Y_3Al_5O_{12}$	S	LINDE	- .02	CUBIC	99%
	P	LASL	.20		94%
Y_2O_3	P	CERADYNE	.08	CUBIC	98%
Y_2O_3-1 ZrO_2	P	CERADYNE	.29	CUBIC	(97%)
$MgAl_2O_4$	S	LINDE	.08	CUBIC	99%
$MgAl_2O_4$	P	LASL	.26	CUBIC	94%

* S = SINGLE CRYSTAL
P = POLYCRYSTAL
R = R- PLANE
C = C- PLANE

** DENSITY IS GIVEN AS % OF THEORETICAL WHERE POSSIBLE AND AS G/CM^3 IN OTHER CASES

Two cubic oxides, Yag and Spinel, were irradiated in both the single and polycrystalline forms. Both showed low swelling, but more in the polycrystalline form compared to the single crystals.

The yttria ceramics, pure and with 1% ZrO_2, showed low swelling, but slightly more for the alloyed sample. Past work with Y_2O_3 and with yttralox (10% ZrO_2) has shown conflicting results, but, in one case, a somewhat greater value of swelling for the yttralox. Again much characterization is required to begin to understand these results.

The structural ceramics included here, Si_2ON_2, Si_3N_3, and Sialon gave swelling values which ranged from a low of 0.05% for Si_2ON_2, to a high value of 0.47% for Sialon with intermediate values for the silicon nitrides. It is noted here that the Si_2ON_2 which gave the least swelling in agreement with previous results, was also visibly porous, and that the least dense of the two types of Si_3N_4 also showed the least swelling.

COMPARATIVE THERMAL AND STRENGTH PARAMETERS FOR CERAMICS

Table 3 is a collection of property and calculated property data for several technological ceramics. The quantity κ is the thermal diffusivity given by the ratio of thermal conductivity, k, to the produce density times specific heat, ρc_p. The quantity γ is a measure of thermal shock resistance and is given by the ratio of strength, σ_B, to the product of Young's modulus and thermal expansion coefficient, $E \cdot \alpha$. Other ways of estimating thermal shock resistance are available but this quantity provides a useful comparison.

The table presents these quantities over the temperature interval 300 to 1500 K (R.T. to 1227°C), which extends into the temperature range expected for very high temperature systems such as bumpers. At the highest temperatures, many ceramics including Al_2O_3 begin to display some limited plastic flow which would tend to reduce the severity of thermal shock. Thus, for such materials, the thermal shock parameter represents a worst case analysis at the highest temperatures. Of major significance in this table is the fact that the high performance materials, Si_3N_4, Sialon, and SiC show several times better heat transport and thermal shock resistance properties than the more typical ceramics Al_2O_3 and Y_2O_3. This results from quite high values of thermal conductivity along with relatively temperature insensitive strength and low values of thermal expansion.

EFFECT OF IRRADIATION OF THERMAL CONDUCTIVITY

It is known that irradiation of ceramics will result in decreased thermal conductivity. Such changes are of critical importance in applications such as the first wall application since decreased thermal conductivity affects wall temperature, thermal stresses, and thermal shock. We are considering this problem in three ways. First, with a consultant, Prof. Paul Klemens from the University of Connecticut, we are conducting a theoretical analysis of the effect of defects on the thermal conductivity. Second, we are preparing to measure thermal diffusivity changes in samples irradiated at EBR-II. Finally, in cooperation with Prof. Harold Weinstock of Illinois Institute of Technology, we shortly will prepare two sets of samples for irradiation of the 14.1 MeV source at Livermore and in the fission reactor at Argonne. Thermal conductivity and structural changes in these samples will be compared.

TABLE 3. THERMAL AND MECHANICAL DATA FOR CERAMICS OF INTEREST

	°K	CAL/CM°K SEC	GM/CM³	CAL/GM°K	CM²/SEC	KSI	MPSI	PPM/°K	°K
	T	K	ρ	C_P	κ	σ_B	E	α	γ
Al_2O_3	300	.086	3.96	2.15	.101	67	59.3	5.5	205
	500	.047	3.94	2.49	.0478	59	58.5	7.4	136
	700	.028	3.92	2.74	.0260	51	57.6	8.4	105
	900	.020	3.90	2.88	.0178	50	56.7	8.9	99.1
	1100	.016	3.88	2.96	.0139	50	55.8	9.0	99.6
	1300	.014	3.86	2.78	.0130	48	54.8	9.42	94.8
	1500	.014	3.84	2.36	.0108	43	53.6	9.24	86.8
Y_2O_3	300	.037	4.64	.108	.0738	42	25.3	8.1	205
	700	.014	4.60	.130	.0234			8.1	
	1100	.0078	4.54	.138	.0124			9.36	
	1500	.0066	4.49	.143	.0102			9.36	
Si_3N_4	300	.069	3.19	.16	.14	120	47.4	1.37	1844
	700	.059	3.18	.23	.07	117	45.4	2.37	1087
	1100	.045	3.17	.29	.05	111	43.5	3.92	651
	1500	.035	3.15	.34	.037	85	39.2	4.7	461
SiALON	300	.053	3.20		.0935	120	43.6	3.2	860
	700	.050	3.18		.0430	107	41	3.2	820
	1100					94	38	3.8	650
	1500					82	35	3.8	620
SiC	300	1.169	3.20	.18	2.03	52	58	4.3	209
	700	0.231	3.18	.240	0.303	54.1	54.5	4.3	231
	1100	0.095	3.17	.230	0.107	55.6	51.0	4.3	253
	1500	0.04	3.14	.324	0.039	56.0	46	5.4	225

Neutron irradiation of ceramics such as Al_2O_3 produces defects including (1) point defects (e.g. cation and anion interstitials and vacancies); (2) large aggregates which are opaque to lattice waves (e.g. voids, cation colloids, anion gas bubbles; and, (3) large aggregates which are partially transparent (e.g., platelet precipitates, stacking faults). In the study with Prof. Klemens we have estimated the effect on thermal conductivity of Al_2O_3 of each of these types of defects. Comparison is made for a temperature of 1000°C, and defect concentrations typical of alumina irradiated at the same temperature. Results of these calculations show that point defect scattering is most important. Conductivity in this case is predicted to be 60% of the intrinsic conductivity.

In the work with Prof. Weinstock, we are planning to irradiate samples of MgO, YAG, Al_2O_3, and spinel in the Livermore source and also at Argonne. Thermal conductivity measurements will be by a comparative technique and will be carried out by Prof. Weinstock at Illinois.

Thermal conductivity measurements will be carried out here on the samples irradiated in EBR-II. These measurements will be carried out by means of the flash diffusivity method using a Xenon flash lamp. Conductivity will be investigated between room temperature and approximately 1100°K.

SYNTHESIS AND CHARACTERIZATION OF SILICON-NITRIDE HOT PRESSED WITH ADDITIONS OF Y_2O_3

Silicon nitride is a strong ceramic which has excellent elevated temperature strength retention and is also an insulator. Two important methods of fabricating silicon nitride are hot pressing and reaction sintering. The latter usually results in somewhat porous bodies. In the hot pressing method, a second phase is added as a sintering aid, usually MgO. The final product prepared in this way, usually contains crystalline Si_3N_4 grains with a glassy grain boundary phase. Dislocation mechanisms of deformation are not expected to contribute to elevated temperature flow or failure of Si_3N_4 below 1700°C. Instead it is this grain boundary glassy phase which has been identified as the failure controlling feature. Recent work in the literature has shown that the elevated temperature strength of the hot pressed material can be improved by using Y_2O_3 additions to promote formation of a crystalline grain boundary phase.

Since material hot pressed with Y_2O_3 additions is not available commercially, we have undertaken a project, jointly with W. E. Hauth of Group CMB-6, to prepare samples of this material for evaluation. Samples containing Y_2O_3 in increments of 5 wt.% from 0 to 20% Y_2O_3 were prepared by hot pressing at 1775°C and 6500 psi. The silicon nitride powder was obtained as a mostly amorphous powder from GTE. This powder is a high purity powder which was found to be approximately 90% amorphous, the remainder probably α-phase. Approximately half of the particles were less than 0.2 μ dia. Hot pressing was carried out in carbon molds under N_2 atmosphere.

Samples have been cut from the hot pressed billets and have been encapsulated in stainless steel tubes under vacuum for irradiation at 625° and 700°C in EBR-II. These samples will receive approximately 4×10^{22} n/cm^2 (E > 0.1 MeV). Evaluation will include swelling and microhardness determination as well as electron microscopy.

Additional work is planned to produce more samples for characterization in the non-irradiated state. Specifically we plan to optimize pressing conditions and composition by determination of their effect on hot and cold MOR.

MECHANICAL PROPERTIES

The mechanical properties of irradiated materials change as the result of defects induced in the substructure and changes in the microstructure. Candidate first wall materials must withstand significant stresses during cyclic operation so determination of radiation effects on their strength is an important part of the investigation.

In the present stage of our work, only comparatively small numbers of small samples are available for investigation. Accordingly, microhardness and micro-indentation fracture testing has been chosen as a method for characterizing the effect of irradiation on mechanical properties. We are presently constructing a machine to carry out tests between room temperature and approximately 700°C. We expect to begin testing by late in the summer.

FUTURE STUDIES: IMMEDIATE PLANS

During the next year, efforts will be concentrated in three areas:

1. Characterization of the KA-3 samples including chemical analysis, microstructure, thermal conductivity and microhardness testing.

2. Preparation and analysis of hot-pressed Si_3N_4-Y_2O_3 samples.

3. Preparation of additional irradiations.

Of these, the latter, in particular will proceed very slowly at the present level of effort.

FUTURE STUDIES: GENERAL RECOMMENDATIONS

I feel that two major areas which require much more effort are in the areas of materials devlopment and mechanical properties determination. Each type of effort must be expanded in conjunction with increased opportunities for irradiation of samples under suitable conditions.

Indications at present are that the nitride and oxynitride ceramics Si_3N_4, Sialon, and Si_2ON_2 show low swelling characteristics and may therefore be promising candidates for CTR applications. If further results, especially in the areas of mechanical and electrical properties, show promise, then these materials would probably form the focal point for future study of structural ceramics. However, it is known that radiation damage is structure and composition dependent. Thus a successful effort would require synthesis of materials, work to produce special structures, and intensive characterization. Irradiation experiments to irradiate samples designed for mechanical properties evaluation would be required, and should include in situ mechanical properties determination during irradiation. It is estimated that one or two additional Staff Members with adequate technician support ($\geq$ 3) would be required in order to make progress in these areas on a reasonable timetable.