ELASTIC STABILITY OF HIGH DOSE NEUTRON IRRADIATED SPINEL - Z. Li and S.-K. Chan (Argonne National Laboratory), F. A. Garner (Pacific Northwest Laboratory)[c], and R.C. Bradt (University of Nevada-Reno)

OBJECTIVE

The objective of this effort is to identify ceramic materials that are suitable for fusion reactor applications.

SUMMARY

Elastic constants (C_{11}, C_{12} and C_{44}) of spinel ($MgAl_2O_4$) single crystals irradiated to very high neutron fluences have been measured by an ultrasonic technique. Although results of a neutron diffraction study show that cation occupation sites are significantly changed in the irradiated samples, no measurable differences occurred in their elastic properties. In order to understand such behavior, the elastic properties of a variety of materials with either normal or inverse spinel structures were studied. The cation valence and cation distribution appear to have little influence on the elastic properties of spinel materials.

PROGRESS AND STATUS

Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) has been considered as a potential fusion reactor candidate material for service as dielectric windows in radio frequency heating systems or as insulators for magnetic coils[1]. This spinel has demonstrated a remarkable insensitivity to neutron irradiation to levels as high as $2x10^{26}n/m^2$ (E>0.1 MeV)[2,3]. An extensive irradiation program using high purity $MgAl_2O_4$ spinel was conducted in the Fast Flux Test Facility (FFTF) reaching exposure levels an order of magnitude or more larger than those of all previous studies[4]. A series of non-destructive and destructive tests was performed on these highly irradiated samples. In particular the results of a neutron scattering study show that significant levels of cation disorder occurred in these samples during irradiation to high dose levels[5]. These specimens were therefore changed from normal spinel to a rather randomized spinel. In this paper the elastic properties of the irradiated spinel are reported and the effects of the cation distribution on its elastic properties are then discussed.

Experimental Procedures

The preparation and irradiation history of irradiated samples have been reported previously[4]. Both [100] and [111] oriented single crystals were used for elastic property measurements. The single crystal specimens were in the form of ~4.8mm diameter cylindrical pellets with a height of ~4.3mm for [111] and of ~2.8mm for [100] oriented specimens. The flat surfaces of the cylindrical pellets were parallel to the (100) and (111) planes for the [100] and [111] oriented specimens, respectively. The orientation error was much less than 2°, as determined from x-ray Laue patterns.

Sound velocities through the specimens were measured by the phase comparison method[6,7] in the 20-60 MHz carrier frequency range. Four sets of measurements were made for the longitudinal and transverse acoustic modes (V_L and V_T) in the directions normal to the (100) and (111) faces of the specimens.

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The three independent elastic constants of cubic spinel, C_{11}, C_{12}, and C_{44}, were derived from those sound velocities as:

$$\rho V^2_L = C_{11} \quad (1a)$$

and

$$\rho V^2_T = C_{44} \quad (1b)$$

for the [100] oriented samples and

$$\rho V^2_L = (C_{11} + 2C_{12} + 4C_{44})/3 \quad (2a)$$

and

$$\rho V^2_T = (C_{11} - C_{12} + C_{44})/3 \quad (2b)$$

for the [111] oriented samples, where L and T denote the longitudinal and transverse vibration modes, respectively, and ρ is the sample density, which was measured at 3.55 g/cm^3. The measurements were carried out at room temperatures varying from 21 to 23°C. "Nonaq" stopcock grease was used to achieve the longitudinal acoustic coupling between the sample crystal and the fused silica buffer rod, whereas solid salol was used for the coupling during the transverse acoustic wave measurements.

Results and Discussion

Tables 1 and 2 summarize the measured sound velocities and the elastic stiffness moduli of the spinel specimens at each irradiation level. The compressive modulus C_{11} and shear modulus C_{44} were directly determined from [100] oriented samples using Equations 1a and 1b. The values of C_{12} were obtained from [111] oriented samples by using either Equation 2a or 2b. The C_{12} listed in Table 2 are the average values determined from these equations. The errors in the velocity and elastic moduli are estimated to be less than 1% and 3%, respectively. The largest uncertainties arise from the measurement of the sample

Table 1. Measured sound velocities of the irradiated Mg

	[100]		[111]	
	V_L(Km/sec.)	V_T(Km/sec.)	V_L(Km/sec.)	V_T(Km/sec.)
Unirradiated	8.875	6.625	10.674	5.125
24.9*/385°C	9.007	6.510	10.602	5.106
5.3/404°C	8.967	6.559	10.628	5.075
5.6/750°C	8.930	6.647	10.672	5.125
13.7/750°C	8.932	6.540	10.616	5.161
21.7/750°C	8.842	6.553	10.554	5.118

*Neutron Fluence in units of 10^{26} n/m^2 (E>0.1 MeV)

Table 2. Elastic properties of the irradiated $MgAl_2O_4$

	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	E (GPa)	G (GPa)	ν
Unirradiated	280	155	156	274	108	0.27
24.9/385°C	288	157	150	274	108	0.27
5.3/404°C	285	158	153	273	108	0.27
5.6/750°C	283	156	156	276	109	0.27
13.7/750°C	283	154	152	273	108	0.27
21.7/750°C	278	151	152	271	107	0.27

thickness and sample density. The error range was confirmed by the cross-check of the C_{12} values calculated from Equations 2a and 2b. For example, the values of C_{12} were 150 and 151 calculated from equations 2a and 2b, respectively, for samples treated at 750°C to $21.7x10^{26}n/m^2$ (E>0.1MeV). These values are in good agreement with each other. Table 2 also lists the calculated polycrystalline elastic moduli, Young's modulus, shear modulus, and Possion's ratio from the single crystal elastic constants based on the Voigt-Reuss-Hill averaging scheme.

The primary structural effect of neutron irradiation is to produce atomic displacement by direct momentum transfer. Such displacements depend on the binding energies of the atoms relative to the maximum energy transfer. In the unit cell of $MgAl_2O_4$, there are 32 oxygen ions with 32 corresponding octahedral interstitial sites and 64 tetrahedral interstitial sites. Of these interstitial sites, 8 of the tetrahedral ones (A sites) are filled by Mg^{2+} and 16 of the octahedral ones (B sites) are filled by Al^{3+}. In general, the binding energies of the divalent and trivalent ions in spinels are relatively small, as indicated by their tendency at high temperature towards random distribution on the A and B sites, respectively, and also between the A and B sites.

The crystal structures of the irradiated spinel specimens were examined by neutron scattering at Los Alamos National Laboratory[5]. The results show that at least 35% of the cation sites had experienced Mg^{2+} for Al^{3+} or Al^{3+} for Mg^{2+} ion exchange. It is therefore reasonable to assume that the effects of the neutron irradiation are, in the order of decreasing probability of occurrence, (1) disordering in the occupancy of A and B interstitial sites by Mg^{2+} and Al^{3+}, (2) creation of oxygen vacancies (and corresponding interstitials) and (3) nucleation and growth of dislocation loops and voids. Each of these changes can affect the elastic properties.

For example, on disordering the A and B cation sites, the contraction or expansion of the tetrahedral and octahedral oxygen cages creates corresponding structural elastic dipole fields. The incoherent components of these random fields interfere destructively in the short range. Over a longer range (much larger than the dimensions of a unit cell), the coherent components of the random fields collectively produce about the same total effect as before disordering had taken place, when the A and B sites were occupied as in a normal spinel. Therefore the expected outcome is no change in the elastic properties associated with long wavelength acoustic phonons.

The creation of oxygen vacancies, particularly if a sufficient number of them occur locally to allow precipitation to take place, can produce a much more dramatic effect on elastic properties. Although there exists some evidence for the formation of dislocation loops and voids, they occur at such small densities[8] that it is not surprising that their effect on microhardness is relatively small[9]. It has been suggested[10] that most of the oxygen vacancies generated by irradiation are annihilated by vacancy-interstitial recombination so that dislocation loops account for no more than 0.01% of the total displacements per atom in the irradiated spinel. The results of our ultrasonic study are consistent with the concept of redistribution of Mg^{2+} and Al^{3+} ions on both the A and B sites. The elastic constants remained unchanged for different levels of neutron irradiation as shown in Table 2. The polycrystalline elastic properties were also found to be independent of irradiation level.

The elastic properties of unirradiated single crystals with both the normal and inverse spinel structures have previously been studied[7,11,12]. Table 3 lists the elastic constants of three normal aluminate spinel single crystals, $MgAl_2O_4$, $CoAl_2O_4$ and $FeAl_2O_4$, three inverse spinel ferrites, $NiFe_2O_4$, $CoFe_2O_4$ and Fe_3O_4, one normal spinel ferrite, $ZnFe_2O_4$ and one mixed spinel ferrite, $MnFe_2O_4$, listed in their order of increasing lattice parameter, a_o. The C_{11} values decrease gradually with increasing of a_o, whereas the C_{44} values of the ferrites are 30% to 40% smaller than those of the aluminate spinels. It is of particular interest to note that, although the $ZnFe_2O_4$ has the normal spinel structure, its C_{44} value is nearly the same as those of the inverse spinel ferrites. For $MnFe_2O_4$, it is known that 80% of the tetrahedral sites are occupied by Mn^{2+}, leaving only 20% of the Mn ions to occupy octahedral sites[13]. The C_{44} value of the $MnFe_2O_4$ is also within the same range as those of the inverse spinel ferrites. It therefore appears from Table 3, that the elastic constants, especially C_{44}, of the different spinel structures are not significantly affected by the details of cation occupation of the various sites. This is in agreement with the recent results for the irradiated spinel specimens.

Table 3. Elastic properties of single crystals with different spinel structures [7]

Formula	Type	a_o (nm)	ρ (g/cm³)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
$MgAL_2O_4$	normal	0.8083	3.578	282.5	154.9	154.7
$CoAl_2O_4$	normal	0.8103	4.416	290.5	170.3	138.6
$FeAl_2O_4$	normal	0.8119	4.280	266.0	182.5	133.5
$NiFe_2O_4$	inverse	0.8339	5.368	273.1	160.7	82.3
$CoFe_2O_4$	inverse	0.8392	5.304	257.1	150.0	85.3
Fe_3O_4	inverse	0.8396	5.163	267.6	105.6	95.3
$ZnFe_2O_4$	normal	0.8441	5.324	250.5	148.4	96.2
$MnFe_2O_4$	mix	0.8499	5.0	213.0	135.0	86.0

CONCLUSIONS

The elastic properties of high purity stoichiometric $MgAl_2O_4$ spinel appear to be remarkably resistant to neutron irradiation at temperatures in the range 385 - 750°C. The large level of cation disordering associated with high displacement levels appears to have little influence on the elastic properties of spinel materials. Comparison of these results with results of other non-irradiation studies on various spinels leads to the conclusion that such an insensitivity is not unexpected.

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