Preparation of Magnesium Aluminate Spinel Containing Controlled Amounts of $^{17}$O Isotope

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MgAl$_2$O$_4$ spinel with an $^{17}$O enrichment of about 23 at. % was prepared by reacting fine mixtures of aluminum hydroxide (enriched with $^{17}$O) and magnesium oxide of normal isotopic content. The material was prepared by milling a mixture of aluminum hydroxide (enriched with $^{17}$O) and magnesium oxide powders. The mixture was converted into pure spinel by a series of heat treatments and grindings. Essentially fully dense bodies, which contained about 45% of the $^{17}$O isotope initially present in the water, were successfully fabricated provided that all thermal treatments were conducted in argon or vacuum atmospheres. [Key words: magnesium, aluminate, nuclear reaction, spinels, processing.]

I. Introduction

Ceramic materials will be required in several locations within proposed fusion reactors, where they may be subjected to appreciable doses of 14-MeV neutron sources available that have sufficient intensity to perform high-dose tests on candidate fusion reactor materials. Nuclear fission reactors have been used to expose various ceramic materials to high-dose irradiation. However, these exposures are inadequate for estimating the degree of degradation to be expected in fusion reactors because the amount of transmutation products formed during fission neutron irradiation is generally much lower than that generated during deuteron–tritium (d–T) fusion neutron irradiation. For example, the amount of He generated in a ceramic such as Al$_2$O$_3$ is, for irradiation to the same displacement damage level, more than an order of magnitude higher for d–T fusion neutron irradiation than for fission neutron irradiation.

One technique that can be utilized to investigate He effects in fission neutron-irradiated oxide ceramics is to take advantage of the high He production rate associated with the $^{17}$O (n, $\alpha$) $^{14}$C thermal neutron reaction. Oxygen of natural abundance contains only 0.04% $^{17}$O, so this reaction does not produce significant amounts of He during fission neutron irradiation of standard oxide ceramics. The (n, $\alpha$) thermal neutron-reaction cross section is very small for the other two stable oxygen isotopes, $^{16}$O and $^{18}$O. A technique has been recently developed for producing $^{17}$O-enriched Al$_2$O$_3$ from aluminum isopropanoxide (Al(OC$_3$H$_7$)$_3$) and water containing enriched concentrations of the $^{17}$O isotope.

Studies on magnesium aluminate spinel (MgAl$_2$O$_4$) have indicated that this material has superior swelling resistance compared to most metals and ceramics during fission neutron irradiation. Because of this behavior spinel is considered a prime candidate insulator for fusion reactor applications. However, a recent ion irradiation study found that coimplantation of fusion-relevant amounts of He during the irradiation of spinel resulted in the formation of large cavities on the grain boundaries. Cavity formation did not occur in ion-irradiated spinel in the absence of He coimplantation. Because of these mixed results on such a promising material, experiments are being conducted to evaluate the behavior of this ceramic material under conditions that will simulate the damage induced by fusion neutron irradiation. The technique developed for producing $^{17}$O-enriched Al$_2$O$_3$ was modified to produce $^{17}$O-enriched MgAl$_2$O$_4$ from MgO powder, Al(OC$_3$H$_7$)$_3$, and water containing enriched concentrations of the $^{17}$O isotope. The material was evaluated for isotope enrichment using a nuclear reaction analysis technique and was characterized by transmission electron microscopy (TEM).

II. Experimental Procedures

Samples of isotopically tailored spinel were prepared by hydrolyzing a mixture of submicrometer MgO powder* and Al(OC$_3$H$_7$)$_3$ dissolved in isopropanol with $^{17}$O-isotope-enriched water. The Al(OC$_3$H$_7$)$_3$ was ground to produce a fine-grained powder that dissolved more readily in the isopropanol alcohol. The measured levels of the various oxygen isotopes in the enriched water were: 12.95%, $^{16}$O; 51.48%, $^{18}$O; and 35.57%, $^{17}$O (it is difficult to completely separate $^{17}$O from the $^{18}$O and $^{16}$O isotopes using present-day enrichment techniques). The hydrolysis reaction was conducted at 60°C in a flowing Ar atmosphere while the solution was vigorously stirred. The apparatus used for this operation has been shown previously. A fine mixture of MgO and aluminum hydroxide (γ-AlOOH, boehmite) enriched in $^{17}$O and $^{18}$O was obtained by the following reaction:

$$2\text{Al(OC}_3\text{H}_7\text{)}_3 + \text{MgO} + 4\text{H}_2\text{O} \rightarrow 2\text{AlOOH} + \text{MgO} + 6\text{C}_3\text{H}_7\text{OH(g)}$$

After the hydrolysis, the isopropanol alcohol was removed from the slurry by vacuum evaporation. The dried mixture was heat-treated to induce the calcination of AlOOH into Al$_2$O$_3$ and the subsequent reaction to form spinel. The heat treatments were performed in flowing Ar to prevent the exchange of $^{17}$O and $^{18}$O with oxygen of normal abundance. The calcination was performed at a temperature higher than 1300°C to produce complete transformation of Al$_2$O$_3$ polytypes into α-Al$_2$O$_3$. Formation of spinel was confirmed by X-ray diffraction (XRD). After the presence of pure MgAl$_2$O$_4$ was confirmed, 0.5 wt% CaO was added to the powder as a sintering aid.
aid. The powder mixture was milled with alumina balls as milling media for 3 h in isopropyl alcohol for mixing and particle-size reduction. The size of the milled powder was measured with a particle-size analyzer. Compacts were fabricated by uniaxially pressing the powders in a steel die at a pressure of 140 MPa. Sintering was performed by heating the compacts for 3 h in a vacuum at 1800°C. Control specimens were fabricated using the identical synthesis and densification procedures but using nonenriched water.

After sintering, the densities of the samples were measured by the immersion technique. A specimen for examination by TEM was cut from the sintered 3-mm-diameter cylinders of the enriched spinel. These specimens were mechanically ground and ion-milled to perforation. The enrichment levels of $^{17}$O and $^{18}$O were determined from nuclear reaction analysis and Rutherford-backscattering measurements. For the former technique, targets from the spinel specimens were bombarded with 750-keV protons ($^1$H) to promote nuclear reactions with the $^{17}$O and $^{18}$O isotopes. Details of the measurement technique have been previously reported. A recently published excitation curve for the $^{18}$O ($p, \alpha$) $^{15}$N reaction was used to calculate the $^{18}$O concentration profile.

### III. Results and Discussion

Formation of MgAl$_2$O$_4$ by the reaction between MgO and $^{17}$O-enriched AlOOH was verified by XRD with the results shown in Figs. 1(A) to (C). As expected, before heat treatment only MgO peaks were detected (Fig. 1(A)). After heat treatment for 20 h in Ar at 1300°C, strong MgAl$_2$O$_4$ peaks were detected. However, as shown in Fig. 1(B), there were still appreciable amounts of unreacted Al$_2$O$_3$ and MgO. Upon repeated regrinding and heat treatments for longer periods of time at 1300°C, the intensities of the Al$_2$O$_3$ and MgO peaks were weaker, but they still persisted. Pure MgAl$_2$O$_4$ phase was obtained only when a powder that had been heat-treated at 1300°C and reground was pelletized and heat-treated at 1400°C for ~20 h. The XRD pattern of the powder prepared with the latter procedure (Fig. 1(C)) shows that the powder has pure MgAl$_2$O$_4$ phase. After heat treatment, the pellets were again crushed, and milled in isopropyl alcohol with alumina balls as the grinding media. Small amounts (~0.5 wt%) of CaO were added during milling as a sintering aid. The average particle size of the powder after milling was 2.4 ± 0.7 µm. Sintering of the samples was performed by heating for 3 h in a vacuum at 1800°C. The densities of the sintered bodies were consistently higher than 99% of theoretical.

The $^{18}$O isotope concentration as a function of depth in the sintered MgAl$_2$O$_4$ specimens was measured for regions within 1.5 µm of the surface by collecting and analyzing the energies of $\alpha$ particles created by the 750-keV proton reaction $^{18}$O ($p, \alpha$) $^{14}$N. The $^{18}$O enrichment level was deduced from the $^{18}$O concentration measurements by assuming that the probability of replacement of the oxygen isotopes in the enriched material with levels of normal abundance was independent of isotope mass. The validity of this assumption was proved in our previous experiments with isotopically tailored Al$_2$O$_3$. The measured ratio of $^{18}$O to total oxygen atoms in the enriched MgAl$_2$O$_4$ is shown in Fig. 2, with measurements made on spinel prepared using nonenriched water ("control MgAl$_2$O$_4"),Si and single-crystal Al$_2$O$_3$. This graph shows a slight depletion of $^{18}$O in the enriched spinel within 0.5 µm of the surface. The depth-averaged ratio of $^{18}$O to total atoms was 9.24 ± 1.7 at.%, which corresponds to an oxygen ratio ($^{18}$O/$^{16}$O)$_{atm}$ of 36.2 ± 3.2 at.% in the enriched MgAl$_2$O$_4$. The hydrolysis reaction used to prepare the spinel (Eq. (1)) shows that the enriched oxygen isotopes present in the water will be diluted with natural-enrichment oxygen present in the MgO and Al(OC$_3$H$_7$)$_3$ powders. A previous measurement on AlOOH powder prepared from the hydrolysis of Al(OC$_3$H$_7$)$_3$ (Ref. 6) indicated that the (OC$_3$H$_7$) radical is efficiently replaced by the enriched H$_2$O; i.e., about 62% of the enriched oxygen isotopes in the water were transferred to the $\gamma$-AlOOH powder for hydrolysis performed in an Ar environment. (The data presented in Ref. 6 have been reduced by 20% to allow for the revised cross sections for the $^{18}$O ($p, \alpha$) $^{14}$N reaction in Ref. 7.) Assuming that the MgO powder does not react with the H$_2$O during hydrolysis, and that a similar fraction of enriched oxygen isotopes are transferred from the H$_2$O to the $\gamma$-AlOOH powder in the present case, then the maximum fraction of enriched-oxygen isotopes retained in spinel would be 50%. The measured $^{18}$O ratio in the sintered

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Fig. 1. XRD patterns of the mixture of AlOOH and MgO: (A) before heat treatment showing only MgO peaks, (B) after heat treatment in Ar at 1300°C for 20 h, showing the peaks of MgAl$_2$O$_4$ as well as those of unreacted Al$_2$O$_3$ and MgO, and (C) after heat treatment at 1400°C for 20 h after regrounding, showing only MgAl$_2$O$_4$ peaks (△) MgO, (●) Al$_2$O$_3$, and (●) MgAl$_2$O$_4$.

Fig. 2. Depth profile of the ratio of $^{18}$O to total atoms for enriched and control MgAl$_2$O$_4$ and single-crystal Al$_2$O$_3$ measured with the $^{18}$O ($p, \alpha$) $^{14}$N nuclear reaction using 750-keV protons. $^{18}$O enrichment level was deduced from the $^{18}$O concentration measurements.
spinel was 16.2 ± 3.2 at.\% ($^{18}\text{O}/^{16}\text{O}_{\text{m}}$), which corresponds to 45% ± 9% of the $^{18}\text{O}$ initially present in the enriched water. This indicates that only minimal replacement of the enriched isotopes by natural oxygen occurred during calcination and sintering of the spinel. Assuming the same retention ratio for $^{17}\text{O}$, then 23 at.\% ($^{17}\text{O}/^{16}\text{O}_{\text{m}}$) was present in the MgAl$_2$O$_4$. An enrichment ratio of 17 at.\% ($^{17}\text{O}/^{16}\text{O}_{\text{m}}$) was desired for the study on the simulation of damage in nuclear fusion reactor environments. This ratio could be achieved by simply diluting the enriched H$_2$O with normal H$_2$O. A slightly higher than expected ratio of $^{18}\text{O}/^{16}\text{O}_{\text{m}}$ was observed in the control MgAl$_2$O$_4$ specimens, as shown in Fig. 2, apparently due to the contamination of containers from prior fabrication of the enriched Al$_2$O$_3$ or spinel specimens. The amount of $^{17}\text{O}$ present in the control spinel deduced from the $^{18}\text{O}$ measurement is still too low to produce significant amounts of additional He during fission neutron irradiation.

TEM revealed that the microstructure of the sintered spinel consisted of single-phase grains with a typical diameter of 15 to 20 μm. A moderate density ($=5 \times 10^{19}/m^3$) of sintering pores with a mean size of $=0.7$ μm were observed in the interior of the grains. There was no evidence of pore formation at the grain boundaries. The volume fraction of the intragranular pores was $=1\%$, which agrees with the measured bulk density of $=99\%$ theoretical. An amorphous (glassy) intergranular phase was observed at many of the grain-boundary triple-point junctions in the spinel. Energy-dispersive X-ray spectroscopy measurements indicated that the intergranular phase was enriched in Ca and Al.

**IV. Summary**

Polycrystalline magnesium aluminate spinel enriched in $^{17}\text{O}$, necessary for the simulation of the nuclear-fusion helium-generation rate in a fission reactor, was successfully prepared. About 45% of the $^{17}\text{O}$ and $^{18}\text{O}$ isotopes initially present in the water used to prepare the spinel were retained in the sintered material, with most of the oxygen replacement likely occurring during hydrolysis of aluminum isopropoxide.

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**References**