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Neutron-induced damage in near-stoichiometric spinel ceramics irradiated below 200°C and its recovery due to annealing

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Abstract

Mg–Al spinel ceramics with different stoichiometry ($Al_2O_3/MgO = n$; $n = 1.00$, 1.01, 1.10 and 1.48) were irradiated with fast neutrons up to 3.8×10^{23} n/m^2 ($E > 0.1$ MeV) at 170°C, and 5.7×10^{23} n/m^2 at 190°C in the Japan Materials Testing Reactor. There was no obvious difference in property change between the two irradiation conditions. The amount of macroscopic length change due to these irradiations increased almost linearly with increasing Al_2O_3 content. These specimens were isochronally annealed up to 1000°C. During the annealing, macroscopic length of the specimens started to decrease at around 200°C and reduced monotonically up to 550°C. After that, the length increased slightly up to 650°C and then decreased again up to 800°C, showing a small peak. These final values corresponded to the length of the specimens before the irradiation. The shrinkage in length between 200–550°C and 650–800°C may be attributed to the recombination of Frenkel pairs of anions, and the expansion in length between 550–650°C to the order–disorder transition of cation distribution.

1. Introduction

Magnesium aluminate spinel has been proposed as a potential electrically insulating material for use in nuclear fusion reactors, since it shows superior resistance to neutron irradiation. A number of studies on neutron irradiation effect of spinel had been performed by Clinard, Hurley and Hobbs et al. [1–7], Kinoshita et al. [8,9], Tucker et al. [10], Garner et al. [11,12], Sickafus et al. [13,14], and Yano et al. [15–19], and exceptionally high performance of this ceramic has been established up to high neutron fluences (~250 dpa). The mechanism of insensitivity of spinel for neutron-irradiation was attributed to the difficulty of clustering of point defects or loop formation basing on crystal chemical considerations [1,4,8], to the presence of structural vacancy [8,9] or to possibility of cation disorder [13]. Whereas most of the studies were conducted on stoichiometric spinel, it is well known that spinel shows a wide range of non-stoichiometry between alumina and magnesia. According to the change in composition, atomic arrangement in the unit cell should be altered, and the number and distribution of vacant tetrahedral and octahedral sites should be changed to satisfy the local electrical neutrality.

Although differences in loop formation have been reported [7,9], there is little systematic study on physical property change of neutron-irradiated spinel with different stoichiometry. Our previous study [16] clarified that all changes in macroscopic length, lattice parameter, Vickers hardness and thermal diffusivity were very small from $n = 1.00$ to $n = 1.48$ polycrystalline spinel irradiated concurrently at around 500°C. The average macroscopic length change by the irradiation was slightly increased with increasing Al_2O_3 content, but the standard deviation was large especially near stoichiometric composition, i.e., some specimens even contracted. After isochronal annealing of these specimens, it is shown that the length of contracted specimens increased suddenly at around 650°C to almost the original

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length before irradiation. The presence of irradiation-induced cation disorder was suggested to explain this behavior [19]. Furthermore, investigation of the irradiation response of spinel at relatively low temperature is limited [15,20].

In this report, to confirm the above mentioned behavior of spinel with different stoichiometry due to neutron irradiation and to clarify low-temperature irradiation response, the same sets of specimens used in the previous studies [16,19] were irradiated at relatively low temperatures, i.e., less than 200°C, and changes in physical properties by the irradiation and post-irradiation isochronal annealing were investigated.

2. Experimental procedures

Spinel ceramics with different composition were synthesized from pure $Mg(OH)_2$ and $Al(OH)_3$ powders. These powders were calcined, mixed with molar ratios of $n = Al_2O_3/MgO$ as, 1.00, 1.01, 1.10, 1.50, and calcined again at 1700°C in air. Hot-pressing technique was applied to obtain dense ceramics. The detail of the specimen preparation process was described elsewhere [16]. All specimens were dense near the theoretical density and white in color. The sintered specimens were analyzed before irradiation and exact compositions were obtained as $n = 1.00$, 1.01, 1.10 and 1.48, respectively.

The rectangular specimens (about $2 \times 4 \times 26$ mm^3), polished to mirror finish, were neutron-irradiated in the Japan Materials Testing Reactor to fast neutron fluences of 5.7×10^{23} n/m^2 ($E > 0.1$ MeV) at 190°C (180–200°C), and 3.8×10^{23} n/m^2 at 170°C (160–180°C), respectively. After irradiation, these specimens were isochronally annealed at 100–1000°C for 1 h under vacuum. The specimens were cut into two parts. One was used for measurement of length, and the other part of the specimen was pulverized and mixed with Si powder for lattice parameter measurement. Both bar and powder were annealed at the same time. Macroscopic length change was measured using a point-type micrometer at 25°C. Lattice parameter was determined by XRD with Si as an internal standard ($87° < \mathrm{CuK}\alpha(2\theta) < 140°$) at 25°C.

Vickers hardness of the specimens was measured according to JIS R1610. The weight of indenter was 49 N and the holding time was 15 s. The number of indent per specimen was 10–15. Vickers hardness number was calculated using the standard formula.

3. Results and discussion

3.1. Effect of irradiation

The radiation-induced macroscopic length change and the lattice parameter change of specimens irradiated to a fluence of 5.7×10^{23} n/m^2 at 190°C are shown in Fig. 1, and those of the specimens irradiated to a fluence of 3.8×10^{23} n/m^2 at 170°C were shown in Fig. 2, respectively. The macroscopic length change data were averages of five specimens. As shown in both figures, correspondence of the change in the macroscopic length and in the lattice parameter was good in every specimen with different stoichiometry in both irradiation conditions. The length and the lattice parameter of every specimen increased by these irradiations, and average changes increased almost linearly with an increase in Al_2O_3 content. Comparing with the results of the specimens irradiated at 500°C [16], the amount of swelling is larger in the specimens irradiated at 170°C or 190°C.

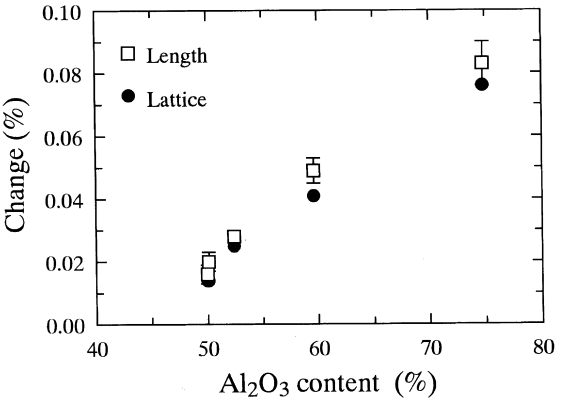

Fig. 1. Radiation-induced macroscopic length change and lattice parameter change of specimens irradiated to a fluence of 5.7×10^{23} n/m^2 at 190°C. The data points of $n = 3.0$ single crystal irradiated to 1.8×10^{23} n/m^2 at 100°C [15] are also plotted.

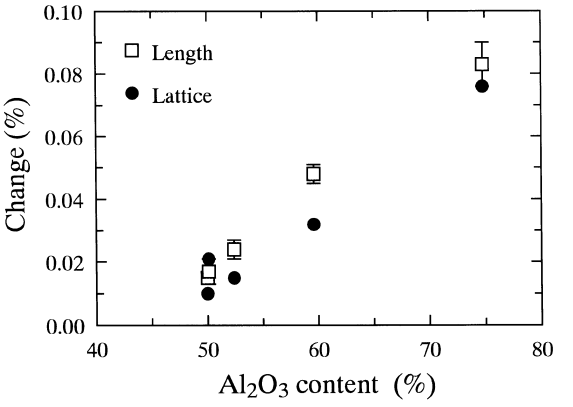

Fig. 2. Radiation-induced macroscopic length change and lattice parameter change of specimens irradiated to a fluence of 3.8×10^{23} n/m^2 at 170°C. The data points of $n = 3.0$ single crystal irradiated to 1.8×10^{23} n/m^2 at 100°C [15] are also plotted.

The standard deviations of each stoichiometry were relatively small and no specimen contracted during irradiation.

Fig. 3 indicates the change in Vickers hardness of the specimens irradiated to a fluence of 3.8×10^{23} n/m^2 at 170°C. The data of the $n = 3.0$ single crystal is also plotted [17]. The Vickers hardness shows the tendency to increase with an increase in Al_2O_3 content. Considering of the tendency of the length change shown in Fig. 1, it is concluded that Vickers hardness increases with increasing length/lattice parameter change.

Limited number of data on swelling of polycrystalline spinel have been reported to date, particularly when irradiated at temperatures lower than 600°C. Clinard et al. [5] mentioned that two types of stoichiometric polycrystalline spinel irradiated at 410°C and 540°C up to 2.2×10^{26} n/m^2 showed small contraction (0.2–0.4 vol%). Tucker et al. [10] also showed small contraction of the specimens (0.3 vol%) irradiated at 390°C to 2×10^{26} n/m^2. Our data indicated that the changes in macroscopic length were very small for $n = 1.00$–1.48 polycrystalline spinel irradiated at around 500°C [16]. The average macroscopic length change by the irradiation was slightly increased with increasing Al_2O_3 content (−0.04–0.03%), but some specimens contracted, especially near stoichiometric compositions. On the other hand, Hurley et al. [3] showed 0.8 vol% expansion for the specimen irradiated at 160°C to 2.1×10^{26} n/m^2. Precise measurement of 50°C-irradiated single crystal spinel revealed expansion of 0.02–0.04 vol% (8×10^{22} n/m^2) [20]. These data are comparable to the present results of $n = 1.00$ specimens. Our previous report [15] on $n = 3.0$ single crystal irradiated at 100°C up to 1.8×10^{23} n/m^2 also showed expansion of 0.08% in length, and on the extrapolated line for change in composition, as shown in Figs. 1 and 2. Thus, it is concluded from these data that spinel swells slightly if the irradiation temperature is relatively low, below 200°C or probably around 400°C, whether polycrystal or single crystal.

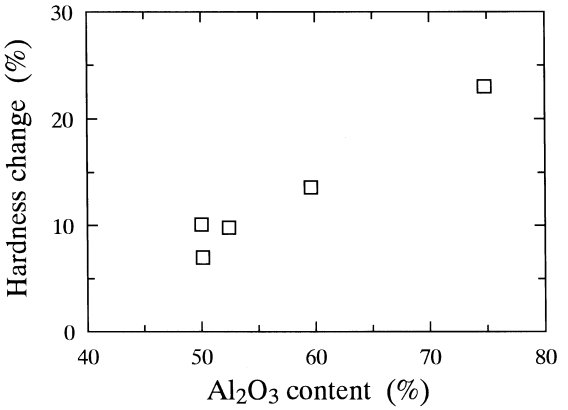

Fig. 3. Change in Vickers hardness of the specimens irradiated to a fluence of 3.8×10^{23} n/m^2 at 170°C. The data of $n = 3.0$ single crystal irradiated to 1.8×10^{23} n/m^2 at 100°C is also plotted [17].

Furthermore, based on the results shown in Figs. 1 and 2, it is clear that the amount of swelling increases almost linearly with increasing Al_2O_3 content. The correspondence between the macroscopic length change and the lattice parameter change was good in the two irradiation conditions. In such case, defects induced by neutron irradiation are most probable point defects, such as vacancies and interstitials [20]. The presence of anion vacancies such as F centers in neutron-irradiated spinel was confirmed by spectroscopic measurements [21] and positron annihilation studies [22]. With an increase in Al_2O_3 content (increase in n), the number of structural vacancies increase and the lattice parameter reduces. The distribution of divalent A cations (namely Mg) and trivalent B cations (namely Al) in tetrahedral and octahedral sites in AB_2O_4 spinel is changed by changing n. From simple exchange, redistribution of cations happens as $(A_{1-i}B_i)^{tet}[A_iB_{2-i}]^{oct}O_4$. But actually, Al ions preferentially occupy tetrahedral sites, and vacant sites are left at octahedral sites. Then, the inversion parameter of tetrahedral site (A-site) is defined as i_A, the fraction of A-sites occupied by B ions. A part of cation inversion is kept at room temperature in synthetic spinel. An inversion parameter of $n = 1.0$ synthetic spinel was reported as about 0.2 and that of $n = 3.5$ spinel as 0.6 [23]. Inversion parameters of $i_A = 0.43$ for $n = 3.0$ spinel [24] and $i_A = 0.35$ for $n = 3.1$ spinel [25] were obtained by X-ray structural determination. Thus, the inversion parameter increases with increasing Al_2O_3 content (increase in n). With an increase in inversion parameter, the lattice parameter reduces [26–28]. Neutron irradiation also increases the inversion parameter due to displacement of atoms. Sickafus et al. confirmed cation disorder of heavily neutron-irradiated spinel by X-ray diffractometry [13] and by NMR [14]. Thus, an inversion of cation distribution would be progressed in the specimens of the present study, as in the case of the previous specimens irradiated at around 500°C [19]. It is reasonable that the cation disorder is introduced by irradiation, but the degree of increase in inversion parameter is reduced with an increase in n, since inversion of cations originally existing in nonstoichiometric spinel is larger with an increase in n. In other words, redistribution induced by displacements is partly ineffective in these specimens with larger n. As a result, the lattice contraction due to the effect of increase in cation disorder reduces with an increase in n. On the other hand, neutron irradiation displaces oxygen atoms, and induces anion vacancies and interstitials, which could expand the lattice to some extent. If we assume that the effect of lattice expansion by the formation of Frenkel pairs of anions is almost the same in every composition, since the anion sublattice is common in these crystals,

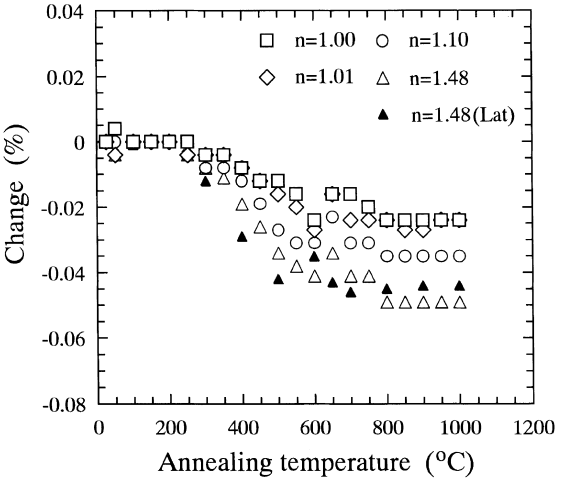

Fig. 4. Change in macroscopic length of the specimens irradiated to 3.8×10^{23} n/m^2 at 170°C due to post-irradiation isochronal annealing up to 1000°C. Change in lattice parameter of the $n = 1.48$ specimen (closed mark) is also plotted.

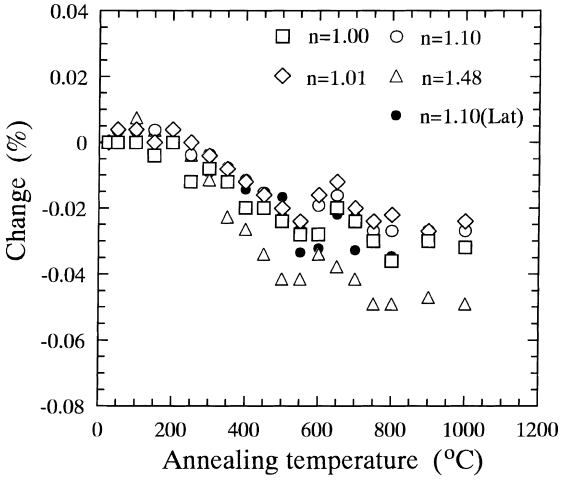

Fig. 5. Change in macroscopic length of the specimens irradiated to 5.7×10^{23} n/m^2 at 190°C due to post-irradiation isochronal annealing up to 1000°C. Change in lattice parameter of the $n = 1.10$ specimen (closed mark) is also plotted.

the expansion due to irradiation increases with an increase in n. Thus, the apparent expansion is related to the balance of anion Frenkel defects and that of an increase in inversion parameter. The increase in hardness shown in Fig. 3 also suggests the presence of point defects, which blocks dislocation movement under an indenter [17].

3.2. Recovery by post-irradiation annealing

The change in macroscopic length of the specimens irradiated to 3.8×10^{23} n/m^2 at 170°C due to post-irradiation isochronal annealing up to 1000°C is shown in Fig. 4. The results for the specimens irradiated to 5.7×10^{23} n/m^2 at 190°C are also shown in Fig. 5. Both figures indicate the same recovery tendency. Macroscopic length of the specimens started to decrease at around 200°C and reduced monotonically up to 550°C. After that, the length increased slightly up to 650°C and then decreased again up to 800°C, showing a small peak in every specimen, independent on stoichiometry. The length did not show significant change above 800°C. These final values correspond to the length of the specimens before the neutron irradiation. The change in lattice parameter due to annealing was also observed for the same specimens used for length measurement. It was clarified that lattice parameter also showed the same change as length. Some results are also included in Figs. 4 and 5.

The continuous decrease in length above an irradiation temperature is fairly common behavior for neutron-irradiated inorganic materials such as SiC [29], AlN [30], α-Al_2O_3 [31] and BeO [31]. For spinel to date, only a few recovery data are available since the swelling has been reported to be negligibly small. The first data for $n = 3.0$ single crystal irradiated at 100°C showed a continuous decrease in length above the irradiation temperature [17]. After isochronal annealing of the same sets of specimens irradiated at 500°C [19], it has been shown that the length of contracted specimens did not change up to 600°C, and then increased suddenly at around 650°C to almost the original length. No further length change was observed up to 1000°C. The specimens which were swelled less than 0.01% in length by the irradiation showed almost no change up to 1000°C. Comparing those results with the present study, it is obvious that the recovery behavior of the specimens in the present study is not similar to the case of 500°C irradiation [19], and is almost equal to the case of 100°C irradiation [17] and to those of typical ceramics such as SiC, AlN, α-Al_2O_3, and BeO. Thus, it is supposed that the gradual shrinkage of spinel above the irradiation temperature up to 550°C can be attributed to annihilation of point defects via recombination of vacancies and interstitials.

The reason for the increase in length around 650°C could be attributed to the recovery of cation disorder, since the order–disorder transition of cations has been reported to happen at around 650°C [26,32]. Our previous study on the annealing behavior of 500°C-irradiated specimens showed step wise increase in length between 600 and 700°C [19]. Comparing the present results to the previous one, the temperature of length increase, i.e., between 600°C and 700°C is common in both cases, whereas the changes above 700°C are different. In the previous report, above 700°C the length

did not change further. On the contrary, the present specimens show a decrease in length between 650°C and 800°C. This contradiction can be explained as follows. The present specimens irradiated at lower temperatures contain point defects, and recovery by recombination of interstitials and vacancies continues up to 800°C. This idea is supported by the report that the recovery of hardness induced by neutron irradiation continued up to 800°C [17]. During this recovery, the order–disorder transition of cations occurs and some amount of expansion at 600–650°C is superimposed to the continuous decreasing. Up to this temperature, the cations seems to be stable and the distribution does not change significantly during annealing. Then the continuous line of decreasing in length is interrupted and a shift toward the counter direction, thus making a peak. The slopes between 200–550°C and 650–800°C in all specimens look almost the same, supporting the idea. The other contradiction is why the previous specimens did not show any decrease in length between irradiation temperature and 800°C. It is supposed that the previous specimens did not contain an effective amount of anion interstitials and vacancies, because the prolonged exposure during irradiation at 500°C promotes thermally activated recombination of these point defects during irradiation. These phenomena has also been observed in BeO and Al_2O_3 reviewed by Wilks [31] and in SiC [29].

4. Conclusion

Mg–Al spinel ceramics with different stoichiometry were neutron-irradiated up to 3.8×10^{23} n/m^2 and 5.7×10^{23} n/m^2 below 200°C, and then isochronally annealed up to 1000°C. There was no obvious difference in property change within the two irradiation conditions. The amount of macroscopic length change due to these irradiations increased almost linearly with increasing Al_2O_3 content. During the annealing, macroscopic length of the specimens started to decrease at around 200°C and reduced monotonically up to 550°C. After that, the length increased slightly up to 650°C and then decreased again until 800°C. These final values corresponded to the length of the specimens before the irradiation.

It is supposed that neutron irradiation induced both anion Frenkel defects (vacancies and interstitials) and cation disorder into spinel at temperature below or around 200°C. Anion Frenkel defects induces lattice expansion and inversion of cation distribution induces lattice contraction. In the case of 1 h annealing, cation disorder is preserved up to 600°C and recovers above that temperature, whereas Frenkel defects of anions gradually annihilate from irradiation temperature up to 800°C.

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