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Neutron irradiation effect on site distribution of cations in non-stoichiometric magnesium aluminate spinel

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Abstract

Neutron irradiation effects on cation distribution in non-stoichiometric Mg–Al spinel were examined by ALCHEMI (Atom Location by Channeling Enhanced Microanalysis) method. Parameter n, or non-stoichiometry of $MgO \cdot nAl_2O_3$ of the specimens, were $n = 1.00$, 1.01, 1.10, 1.48. These specimens were neutron-irradiated up to a fluence of 2.3×10^{24} n/m^2 ($E > 0.1$ MeV) at 500–530 °C in JMTR. Some specimens contracted by the irradiation and the arrangement of cations became more disorder. The other specimens showed very small swelling by the irradiation and the cation distribution became slightly ordered. The cation distribution of the contracted specimen returned stepwise to the pre-irradiated condition after the annealing at 700 °C. The cation distribution of the slightly swollen specimens did not change after the annealing up to 700 °C. Cation distribution in the T-site was more sensitively influenced by the irradiation.

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1. Introduction

Magnesium aluminate spinel crystallizes in the isometric system with an octahedral habit. The general chemical formula is as $A^{2+}B_2^{3+}O_4^{2-}$, with A representing a divalent cation (Mg^{2+}) and B a trivalent cation (Al^{3+}). The oxygen anions are arranged in the cubic closest-packed structure. There are 32 octahedral interstices, 16 of which are occupied by trivalent cations (O-site). The divalent cations are located at eight of the 64 tetrahedral interstices (T-site). The remaining interstices, which are called as structural vacancies, are unoccupied in natural spinel but have the capability to accommodate cation species within a stable structure at high temperature and pressure [1]. The physical and structural properties of magnesium aluminate spinel vary according to the following factors: lattice parameter (a), anion parameter (u, which is a measure of the oxygen dilation) and cation inversion parameter (x) [2]. The general chemical formula is shown as $(A_{1-x}B_x)[A_xB_{2-x}]O_4$ with the parameter x. For normal spinel, $x = 0$; for random spinel, $x = 2/3$; and for inverse spinel, $x = 1$. Natural, or mineral, $MgAl_2O_4$ spinel exhibits approximately the normal spinel-structure, so that $x \approx 0$; but synthetic Mg–Al spinels exhibit cation distribution between tetrahedral and octahedral sites [3].

The degree of cation distribution in spinel has been determined by various methods such as IR (infrared spectroscopy) [4] and Raman spectroscopy [5–7], NMR (nuclear magnetic resonance) [3,8–10], calorimetric measurements [11,12], neutron diffraction [13,14], and ALCHEMI (atom location by channeling enhanced microanalysis) [15].

On the other hand, spinel exhibits a wide range of non-stoichiometry, and it is denoted as $MgO \cdot nAl_2O_3$. The value of n in $MgO \cdot nAl_2O_3$ ranges from <0.6 to >7 at $\sim$1990 °C [16]. As n increases, the lattice parameter decreases from $a = 0.8078$ nm for $n = 1.0$ to 0.7964 nm for $n = 3.5$ composition [17]. In non-stoichiometric spinel, Al cations are substituted for Mg cations accompany with formation of cation vacancies (unoccupied sites) to

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maintain charge neutrality. Chemical formula of non-stoichiometric spinel can be shown as $Vc_{(n-1)/(3n+1)}Mg_{4/(3n+1)}Al_{8n/(3n+1)}O_4$, where Vc represents cation vacancy.

It is well-known that spinel shows superior radiation resistance against a very severe fast neutron irradiation. Spinel exhibits very small swelling by neutron irradiation [18–24], and the strength and toughness of spinel are increased [19,25–29]. The reason for radiation resistance has been attributed to difficulty of loop nucleation and unfaulting dislocation loops [30–34]. Most of the point defects generated during irradiation probably annihilate by interstitial-vacancy recombination [30–32,35]. The interstitial-vacancy recombination in irradiated spinel was confirmed as inducement of cation relocation which was measured by neutron diffraction [35], NMR [36] and ALCHEMI technique [15].

There are a limited number of systematic studies of irradiation effect for non-stoichiometric spinel, particularly the effect of thermal annealing on recovery of defects. Parker et al. reported that faulted loops appeared with $\mathbf{b} = a/4\langle 1\,1\,0\rangle$ on $\{1\,1\,0\}$ planes in the $n = 1$ and 1.1 spinels, and with $\mathbf{b} = a/6\langle 1\,1\,1\rangle$ on $\{1\,1\,1\}$ planes in the $n = 1.1$ and 2 spinels [32]. Soeda et al. measured the site distribution of cations in spinels with different n, and the non-stoichiometric spinel showed more resistance to radiation damage than the stoichiometric one [15]. One of the present authors reported changes in macroscopic length, lattice parameter, Vickers hardness and thermal diffusivity of spinel ceramics with different compositions [22–24]. Macroscopic length of some of the near-stoichiometric spinels reduced by the neutron irradiation (2.3×10^{24} n/m at 500–530 °C) and they returned to the pre-irradiation value by the annealing at around 650 °C [23]. These studies clarified that the irradiation effects of near-stoichiometric spinels were different from ones of non-stoichiometric spinels. Since reasons for these differences are not clear, then the extended studies in irradiated $MgO \cdot nAl_2O_3$ spinels are necessary to understand the role of non-stoichiometry. In this study, spinel specimens with four compositions ($n =$ 1.00, 1.01, 1.10, 1.48) whose irradiation condition was the same as our previous study [23] were concurrently irradiated by fast neutrons. Cation distribution of the specimens was examined by ALCHEMI to clarify the neutron irradiation effect and subsequent annealing effect in these specimens. Then the mechanism of those irradiation effects was elucidated from the viewpoint of the cation distribution.

2. Theory

The technique of ALCHEMI, which was proposed by Spence and Taftø [37–39], enables the fraction of impurity atoms on a given host-site in the crystal. It is determined from ratios of characteristic X-ray count rates at various crystal orientations. Spinel-structure compounds can be separated into alternating (4 0 0) planes of tetrahedral site (T-site) and octahedral site (O-site) in the [0 0 1] projection. In the 'ideal' stoichiometric spinel, Mg cations occupy only T-site and Al cations occupy only O-site. Cation occupancy in natural spinel is nearly equivalent to the ideal case, but in synthetic spinel, part of Mg and Al cations occupy O-site and T-site, respectively [7,35,40].

Let $N_i^{(\zeta)}$ be the characteristic X-ray intensity from the element i for the two incident beam orientation (ζ). X-ray intensity is shown as Eq. (1). $I_T^{(\zeta)}$ and $I_O^{(\zeta)}$ are the thickness averaged electron intensities on the T-site and O-site, respectively. P_i is the ratio of the element i in the T-site to the whole element i, and K_i is a factor that accounts for fluorescence yield and other scaling factors

$$N_i^{(\zeta)} = K_i\left\{I_T^{(\zeta)}P_i + I_O^{(1\zeta)}(1-P_i)\right\}. \tag{1}$$

Channeling orientation is $\zeta = 1$. The X-ray intensities from the element Mg and Al in spinel are shown as

$$\begin{aligned} N_{Al}^{(1)} &= K_{Al}\{I_T^{(1)}P_{Al} + I_O^{(1)}(1-P_{Al})\},\\ N_{Mg}^{(1)} &= K_{Mg}\{I_T^{(1)}P_{Mg} + I_O^{(1)}(1-P_{Mg})\}. \end{aligned} \tag{2}$$

Non-channeling orientation is $\zeta = 2$, which makes $I_T^{(2)} = I_O^{(2)} = I$. The X-ray intensities on the non-channeling condition are shown as

$$\begin{aligned} N_{Mg}^{(2)} &= K_{Mg}I,\\ N_{Al}^{(2)} &= K_{Al}I. \end{aligned} \tag{3}$$

Then, we obtain the relation Eq. (4) using Eqs. (2) and (3)

$$\begin{aligned} \frac{N_{Mg}^{(1)}}{N_{Mg}^{(2)}} &= \frac{I_T^{(1)}}{I}P_{Mg} + \frac{I_O^{(1)}}{I}(1-P_{Mg}),\\ \frac{N_{Al}^{(1)}}{N_{Al}^{(2)}} &= \frac{I_T^{(1)}}{I}P_{Al} + \frac{I_O^{(1)}}{I}(1-P_{Al}). \end{aligned} \tag{4}$$

Thus, the parameter P_{Mg} and P_{Al} can be found if $I_T^{(1)}/I$ and $I_O^{(1)}/I$ can be found. The cation distribution of stoichiometric spinel was expressed as $Mg_{1-x}Al_x(Mg_xAl_{2-x})O_4$. The relations of P_{Mg}, P_{Al} and x are $P_{Mg} = 1 - x$ and $P_{Al} = x/2$ in the case of stoichiometric spinel. The measured x values in natural spinel ranged within 0–0.06 at room-temperature [14,35,40,41]. In the case of $x = 0$, no cation substitution occurs and corresponds to the ideal cation distribution. The value of $x = 0.06$ indicates slight disordering.

P_{Mg} and P_{Al} were calculated on the three assumptions (a), (b) and (c). (a) Cations are not in structural vacancies in natural spinel but they are allowed staying in structural vacancies in synthetic spinels and irradiated spinels. (b) Al cation had 97.3% ideal cation distribution ($1 - P_{Al} =$ 0.973) in natural spinel, which is based on the previous report ($x = 0.054$) by Kashii et al. [1]. (c) One Mg cation in T-site displaces one Al cation in O-site in natural spinel because of (a). Then, $P_{Mg} = 0.946$ and $P_{Al} = 0.027$ were calculated by (a) and (b). $I_T^{(1)}/I$, $I_O^{(1)}/I$ can be found from Eq. (4). And unknown P_i of the other samples can be found by the analysis data, $I_T^{(1)}/I$, $I_O^{(1)}/I$ and Eq. (4). Shortage of cation occupancies from the ideal occupancies in the