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Neutron irradiation effects on isotope tailored aluminum nitride ceramics by a fast reactor up to 2×10^{26} n/m^2

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Abstract

Physical property changes of AlN ceramics prepared with ^{14}N and ^{15}N by fast neutron irradiation were investigated. Sintered specimens were concurrently fast-neutron irradiated in JOYO fast reactor up to a fluence of 1.94×10^{26} n/m^2 at 530 °C. After irradiation and post-irradiation annealing up to 1500 °C, changes in macroscopic length, thermal diffusivity and microstructure were observed to examine the isotope effects. Swelling of Al^{15}N was slightly larger than that of Al^{14}N. Degree of recovery in length of Al^{15}N after annealing was less than that of Al^{14}N. Degradation of thermal diffusivity in both specimens was almost the same, but recovery in Al^{15}N was more restricted. He release profiles up to 1500 °C was qualitatively similar, although the evolution amount was larger in Al^{14}N. No clear isotope effect on microstructure change was observed. One of the possible reasons for the difference in property change due to the irradiation and recovery behaviour in Al^{14}N and Al^{15}N ceramics is the difference in diffusion rate of ^{14}N and ^{15}N, but further confirmation should be necessary.

1. Introduction

In fusion reactors, many ceramics will be applied as structural and functional components to sustain fusion plasma under very severe environment such as intense radiation, high temperature, high heat load. In present experimental fusion facilities, radio-frequency heating of plasma is a necessary support heating system. In that system, ceramic window with very low tan δ and very high heat-transfer properties is required to separate vacuum chamber and radio-frequency wave generator. Aluminum nitride (AlN) has very high heat transfer property within existing ceramics, and then it is one of the candidate materials [1,2]. Aluminum nitride is recently also considered as one of the coating materials for use in liquid-cooled blanket type fusion reactors to reduce MHD force and as a permeation barrier of hydrogen isotopes. Major reasons to select this material to these applications are chemical compatibility with liquid coolant media such as Li or Flibe, high electrical resistively and high thermal conductivity [3].

Up to now, only limited information about physical property changes of AlN ceramics due to neutron irradiation was reported. The present authors observed that AlN ceramics suffered from anisotropic lattice expansion due to the formation of tiny interstitial loops on the basal plane, (0 0 0 1) of AlN, with neutron fluences on the order of ~10^{25} n/m^2 [4–7]. The crystalline form of AlN is wurtzite-type (hexagonal crystal system). Anisotropic lattice expansion caused severe reduction of mechanical strength. Thermal diffusivity of AlN reduced relatively quickly due to the irradiation of neutrons, and finally it lost almost 95% of the original value after irradiation up to 10^{26} n/m^2 at irradiation temperature of ~500 °C, but absolute value was still higher than that of concurrently irradiated Al$_2$O$_3$ ceramics [7,8]. The change in macroscopic length and thermal diffusivity due to

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post-irradiation annealing revealed that the recovery of macroscopic length roughly corresponded with that of thermal diffusivity [9].

Whereas AlN has promising material properties, there is a possibility to generate long-lived isotope, ^{14}C, due to the nuclear transmutation of ^{14}N in a fusion neutron environment [10]. This is a common problem when nitride ceramics will be applied for fusion reactors. This demerit can be cancelled by use of isotope tailored material. Therefore, in this study, we investigated physical property changes of AlN ceramics prepared with ^{14}N and ^{15}N by high-fluence fast neutron irradiation to clarify the effects of different transmutation gas production rates between ^{14}N and ^{15}N, and to confirm performance of Al^{15}N ceramics.

2. Experimental procedures

2.1. Preparation of isotope tailored AlN ceramics

Aluminum nitride powders were prepared by a direct nitridation method using high purity metallic aluminum powder (99.98%, Toyo Aluminum Co., Ltd. Japan) and $^{15}N_2$ gas ($^{15}N_2$:$^{14}N_2$ = 99.7 at.%:0.3 at.%, Nippon Sanso Co., Japan). Details of powder preparation and sintering dense ceramics were described elsewhere [11]. The density of Al^{14}N and Al^{15}N sintered bodies was 93.5% and 97.3%, respectively. Enrichment of ^{15}N in Al^{15}N ceramics was 99.2%. Other impurities in the sintered bodies were oxygen (~1.1%), carbon (~0.2%) and silicon (~0.05%) in both specimens. The difference in density of Al^{14}N and Al^{15}N could be attributed to the difference in amount of additives in sintered bodies, 0.62 and 1.2 wt%Y, respectively. From the sintered plate, specimens for swelling measurement (rectangular bars: $1.6\times2.0\times20$ mm in size), thermal diffusivity measurement (disc: 10 mm in diameter and 1.6 mm in thickness) and microstructure observation by transmission electron microscopy (disc: 3 mm in diameter and 1 mm in thickness) were machined.

2.2. Neutron irradiation

The Al^{14}N and Al^{15}N specimens were concurrently neutron irradiated in a core region of the JOYO fast experimental reactor in Japan up to a fast neutron fluence of 1.94×10^{26} n/m^2 ($E > 0.1$ MeV) and total neutron fluence of 2.81×10^{26} n/m^2 at 530 °C in a helium filled SVIR-1 irradiation rig. Based on the neutron spectrum, dpa, helium and hydrogen generation amounts of Al^{14}N were calculated to be 17 dpa, 194 and 209 appm, respectively, using the SPECTER code and JENDL-Gas Production Library [12,13]. Both helium and hydrogen cannot be generated from a pure Al^{15}N based on the nuclear data in this experiment [13,14], but generated from ^{14}N (content: 0.8%) in the Al^{15}N specimen, where both amounts were about one-hundredth of the case of Al^{14}N specimen.

2.3. Measurement of properties

Post-irradiation isochronal annealing was conducted using a vacuum furnace for 1 h at each annealing temperature. Heating rate of temperature was ~50 °C/min up to 1000 °C and ~30 °C/min between 1100–1500 °C. After cooling the specimen to room temperature, following properties were evaluated. The same specimens were used to successively measure the properties with increasing annealing temperature. The length of the rectangular bars was measured using a point-type micrometer on a fixture zig.

Thermal diffusivity was measured at room temperature using disc specimens by laser-flash method in vacuum. The surface of the specimen was coated by carbon spray. Before next annealing, coated carbon was removed.

Helium release from the irradiated specimens was measured using a mass-spectrometer during increasing temperature with heating rate of 15 °C/min up to 1500 °C and kept for 1 h at 1500 °C. The irradiated bulk specimen was crushed into powder using a B_4C mortar. He evolved amount was calibrated with a standard leak.

3. Results

Macroscopic length increase due to the neutron irradiation was 1.04% and 1.15% for Al^{14}N and Al^{15}N specimens in average of five bars, respectively. Thermal diffusivities of unirradiated Al^{14}N and Al^{15}N were 0.294 and 0.293 cm^2/s, respectively. These values were reduced significantly by the irradiation, 0.034 and 0.037 cm^2/s for Al^{14}N and Al^{15}N, respectively.

Fig. 1 represents changes in macroscopic length of Al^{14}N and Al^{15}N as a function of isochronal annealing temperature up to 1440 °C. Both the length of Al^{14}N and Al^{15}N specimens did not show obvious change up to around 1200 °C, and then quickly shrunk above that temperature. The changes of length of the two specimens were mostly parallel in manner, and difference at each annealing temperature corresponded with the difference of swelling due to the irradiation. Recovery rate at 1440 °C of the Al^{14}N specimen was slightly higher than that of the Al^{15}N specimen.

Changes in thermal diffusivity of the Al^{14}N and Al^{15}N specimens due to the post irradiation isochronal annealing are shown in Fig. 2. Except for the beginning of the annealing, the values were mostly constant up to 1000 °C, and then they increased rapidly with increasing annealing temperature in both the Al^{14}N and Al^{15}N specimens. The recovery (increase) rate was seen more

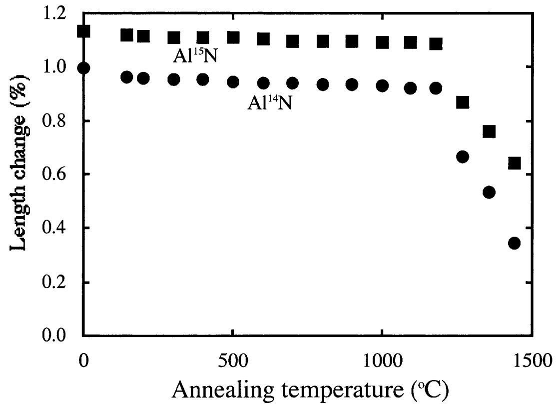

Fig. 1. Macroscopic length change of $Al^{14}N$ and $Al^{15}N$ due to post-irradiation isochronal annealing.

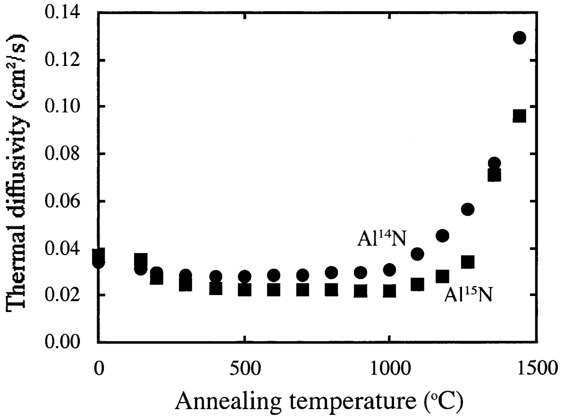

Fig. 2. Thermal diffusivity of $Al^{14}N$ and $Al^{15}N$ due to post-irradiation isochronal annealing.

rapidly above 1300 °C. Recovery rate was higher for the $Al^{14}N$ specimen than the $Al^{15}N$ specimen.

Fig. 3 is low magnification TEM photograph of the as-irradiated ceramics, indicating microcrack formation along grain boundaries as reported earlier [7,8]. Furthermore, inside grains there were high density dislocation loops as shown in Fig. 4. These dislocation loops were interstitial type formed on the basal plane of AlN. Comparing size distribution of dislocation loops before and after the post-irradiation annealing at 1350 °C, the distribution range expanded to larger size direction (average loop diameters: 11.1 → 13.3 nm in the case of $Al^{14}N$ and 11.6 → 12.4 nm in the case of $Al^{15}N$), indicating growth of dislocation loops both for $Al^{14}N$ and $Al^{15}N$ specimens. Difference in average size of dislocation loops in $Al^{14}N$ and $Al^{15}N$, both before and after post-irradiation annealing was not identified. No void/bubble formation was observed in the as-irradiated and annealed specimens, independent of N isotope.

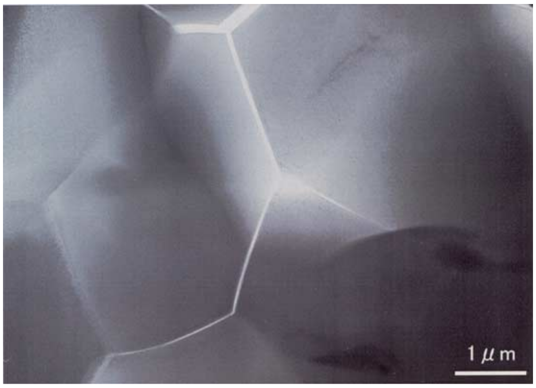

Fig. 3. Transmission electron micrograph of the as-irradiated $Al^{15}N$ specimen.

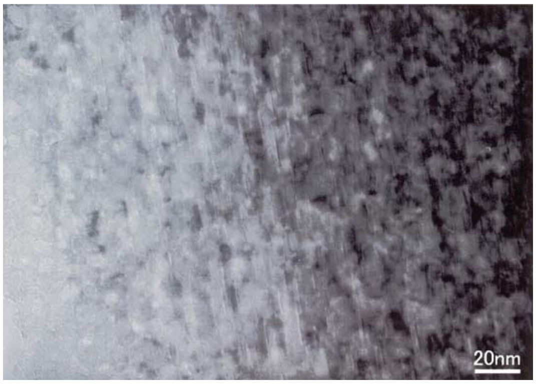

Fig. 4. High-magnification electron micrograph of the as-irradiated $Al^{14}N$ specimen showing dislocation loops.

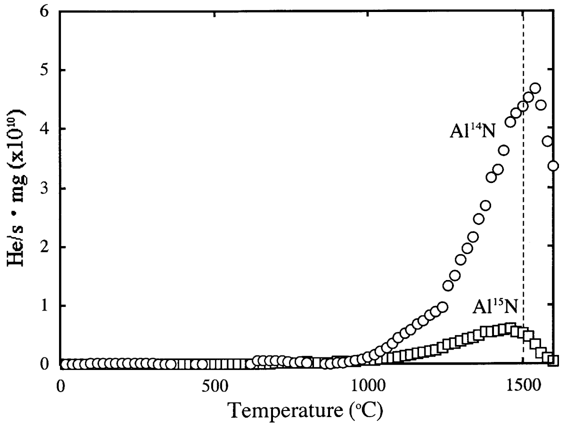

Fig. 5. Helium evolution rate from $Al^{14}N$ and $Al^{15}N$ powders during continuous heating. Note that after reaching 1500 °C, temperature was kept at 1500 °C for 1 h.

Helium release rate during continuous heating is shown in Fig. 5. It was clear that helium was started to release from the powder around 1000 °C, and gradually increased with increasing temperature up to around 1500 °C from both specimens. From the $Al^{14}N$ powder, release rate increased rapidly above 1200 °C. During holding at 1500 °C, release rates from both powders were reduced quickly. The amount of helium evolved from the $Al^{14}N$ specimen was significantly larger than that from $Al^{15}N$ specimen, as expected.

4. Discussion

Macroscopic length was started to recover after annealing at ~1200 °C as shown in Fig. 1, whereas the thermal diffusivity gradually recovered after annealing at around 1000 °C and then rapidly above ~1200 °C, as shown in Fig. 2. There is a slight difference in starting temperature of recovery. In the case of AlN ceramics, it is reported that the recovery in macroscopic length or lattice parameter was started at around irradiation temperature for conditions where the damage was predominantly Frenkel defects (fast neutron fluence on the order of 10^{22} n/m^2), whereas it was shifted to ~800 °C in the case of interstitial loop formation region (fast neutron fluence in the order of 10^{24} n/m^2) [6]. Recovery of thermal diffusivity was mostly consistent with that of length change under Frenkel defect formation conditions whereas it was shifted to ~1000 °C for the specimen consisting of interstitial loops [9]. This was also confirmed for specimens irradiated in the JOYO reactor up to very high fluences on the order of 10^{26} n/m^2: length recovery was started at around 1100 °C, whereas recovery of thermal diffusivity was started ~1000 °C [15]. It is known that vacancy concentration is strongly related to thermal diffusivity. No void/bubble formation was observed otherwise formation of high-density interstitial loops was confirmed in the present AlN. Therefore, it is reasonable to speculate that vacancies should be distributed throughout the matrix, whereas most of interstitials were migrated into loops and only a slight number of free interstitials remained after present neutron irradiation. During post-irradiation annealing up to 1000 °C, the defects produced by high dose neutron irradiation (loops, vacancies) were immobile and thermally stable, thus no recovery both in macroscopic length and thermal diffusivity was observed. Beyond ~1000 °C, vacancies can migrate and recombine with interstitials from interstitial loops or migrate to grain surface where it is open to atmosphere due to microcrack formation, and thermal diffusivity recovered gradually. The number of free vacancies is reduced but macroscopic length does not fully recover since a large part of the macroscopic length change can be attributed to the effects of microcrack formation, and it is not influenced by heat treatment up to 1200 °C. Above 1200 °C, vacancies migrate more rapidly to recombine with interstitials from interstitial loops or disappear at grain surfaces, and at the same time so called 'sintering/densification' may proceed gradually, resulting recovery of both macroscopic length and thermal diffusivity. After annealing at 1440 °C, macroscopic length did not completely recovered as indicated in Fig. 1, as well as thermal diffusivity as shown in Fig. 2.

Difference in physical property changes induced by the irradiation and these recoveries due to post-irradiation annealing in $Al^{14}N$ and $Al^{15}N$ can be attributed mainly to the difference in diffusion rate of ^{14}N and ^{15}N in AlN lattice. According to the diffusion theory [16], the mass difference causes their vibrational frequencies to differ. The jump frequencies should be inversely proportional to square root of masses. For two isotopes σ and ρ of the same element, the ratio of jump frequencies are written as

$$\frac{\omega_\rho}{\omega_\sigma} = \left(\frac{m_\sigma}{m_\rho}\right)^{1/2}. \tag{1}$$

This difference in jump frequency causes the correlation factors, f_ρ and f_σ, and diffusion coefficients, D_ρ and D_σ to differ also. For both isotopes, $D_i = k\omega_i f_i$ where k depends on geometric factors and defect concentrations. Since k is the same for any two isotopes,

$$\frac{D_\sigma - D_\rho}{D_\rho} = \frac{\omega_\sigma f_\sigma - \omega_\rho f_\rho}{\omega_\rho f_\rho}. \tag{2}$$

If one can define $\Delta D = D_\sigma - D_\rho$, $\Delta\omega = \omega_\sigma - \omega_\rho$ and $\Delta f = f_\sigma - f_\rho$, (2) can be written as

$$\frac{\Delta D}{D_\rho} = \frac{\Delta\omega}{\omega_\rho}\left(1 + \frac{\omega_\rho}{f_\rho}\frac{\Delta f}{\Delta\omega} + \frac{\Delta f}{f_\rho}\right) = \Omega\frac{\Delta\omega}{\omega_\rho}. \tag{3}$$

Ω represents the part in parenthesis. If we introduce reduced mass instead of actual mass, Eq. (1) is,

$$\frac{\Delta\omega}{\omega_\rho} = \Delta K\left[\left(\frac{m_\rho}{m_\sigma}\right)^{1/2} - 1\right]. \tag{4}$$

ΔK is smaller than unity. Then,

$$\frac{\Delta D}{D_\rho} = \Delta K\Omega\left[\left(\frac{m_\rho}{m_\sigma}\right)^{1/2} - 1\right]. \tag{5}$$

Eq. (5) indicates difference in mass can affect the diffusion coefficient. In the present case, $m_\sigma = 14$ and $m_\rho = 15$ gives 3.5% smaller diffusion coefficient for ^{15}N than ^{14}N. After neutron irradiation, increase in macroscopic length of $Al^{15}N$ is larger than that of $Al^{14}N$. Recovery rates of length change and thermal diffusivity of $Al^{15}N$ were smaller that those of $Al^{14}N$. This suggests that the ratio of independent point defects remaining in the lattice after irradiation in $Al^{15}N$ should be slightly larger due to slower diffusivity of interstitials, if the number of defects is the same in $Al^{14}N$ and $Al^{15}N$. Furthermore, recombination of vacancies with interstitials is also less in $Al^{15}N$ due to slower diffusivity during annealing.

The other possibilities of difference in the two AlN are different amount of H and He in these specimens. The $Al^{14}N$ specimen contained larger amount of He as shown in Fig. 5. From TEM observation, no void/helium bubble formation was observed for the as-irradiated and annealed specimens. It indicates the effect of transmutation helium is not so significant, since changes in length and thermal diffusivity of $Al^{14}N$ due to the irradiation was smaller than those of $Al^{15}N$. There is a possibility of formation of submicroscopic bubbles, which could increase the sink strength for annihilating interstitials, thereby slightly reduce the number and size of interstitial loops. Such a secondary sink effects could be a one of the possible mechanisms. Furthermore, it is not clear at present whether or not the density of the specimen or amount of sintering aids/impurities can affect the change in properties.

5. Conclusions

Physical property changes of AlN ceramics prepared with ^{14}N and ^{15}N were evaluated after fast neutron irradiation to examine the isotope effects. Swelling of $Al^{15}N$ was slightly larger than that of $Al^{14}N$ after irradiation up to a fluence of 1.94×10^{26} n/m^2 at 530 °C. Degree of recovery in length of $Al^{15}N$ after annealing was less than that of $Al^{14}N$. Degradation of thermal diffusivity in both specimens was almost the same, but recovery of thermal diffusivity of $Al^{15}N$ was restricted. He release profiles from $Al^{14}N$ and $Al^{15}N$ up to 1500 °C is qualitatively similar, although the amount of He evolution was much larger in $Al^{14}N$. No isotope effect on microstructure change such as loop, grain-boundary microcrack and void/bubble formation was observed by TEM. One of the possible reasons for the difference in property change due to the irradiation and recovery behavior in $Al^{14}N$ and $Al^{15}N$ ceramics is the difference in diffusion rate of ^{14}N and ^{15}N, but further confirmation should be necessary.

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