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Thermal stability and kinetics of defects in magnesium aluminate spinel irradiated with fast neutrons

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Abstract

Thermal stability of interstitial-type dislocation loops and cavities in single crystals of $MgAl_2O_4$ was examined during isochronal and isothermal annealing. The specimens were irradiated with fast-neutrons in FFTF/MOTA at 658 and 1023 K up to 249 dpa. During the isochronal annealing, dislocation loops started to shrink around 1000 K and completely disappeared at 1470 K without changing their character. Cavities grew slightly around 1570 K, and above this temperature, cavities shrunk with increasing annealing temperature. The recovery stage of point defects in $MgAl_2O_4$ was discussed in terms of the thermal stability of defect clusters; vacancy migration starts around 1000 K (corresponding to stage III), whereas vacancy clusters start to dissociate around 1570 K (corresponding to stage V). The vacancy migration energy for rate controlling species was estimated from the shrinkage process of interstitial-type dislocation loops to be 2.0 ± 0.7 eV. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Numerous investigations have shown that stoichiometric magnesium aluminate spinel, $MgAl_2O_4$, is highly resistant to radiation damage with energetic electrons, ions and neutrons [1–9]. High recombination rates of interstitials with structural vacancies, site exchanges of different cations, high stability of faulted dislocation loops, large nuclei of dislocation loops and high sensitivity to irradiation spectrum are the reported possible physical mechanisms responsible cited for the superior radiation resistance of $MgAl_2O_4$.

Recent neutron-irradiation studies up to a high dose of 249 dpa have revealed the excellent resistance of $MgAl_2O_4$ to dimensional instability [10], degradation of elastic properties [11] and void swelling [10,12,13]. Microstructural observations [12,13] have shown interstitial-type dislocation loops whose Burgers vector and habit planes are 1/4[1 1 0] and (1 1 0) or (1 1 1), respectively. No cavities were seen in $MgAl_2O_4$ irradiated at 658 K up to 229 dpa. At a temperature of 1023 K, stacking faults (SFs) were formed on (1 1 0) planes to more than 1 μm in width, but few dislocation loops were observed. Tiny cavities were seen at doses higher than 137 dpa and 1023 K, preferentially on SFs, but were also seen in the matrix. The void swelling at this temperature was estimated to be only 0.07% at 217 dpa. These results confirmed again the high resistance of $MgAl_2O_4$ to void swelling, and provide support for some physical mechanisms responsible to the radiation resistance, as described above. Furthermore, the formation of large SFs implies a high mobility of point defects in $MgAl_2O_4$ crystals, though very limited information is available on the migration energies of both vacancies and interstitials in this material [14–16].

In the present study, we have investigated the thermal stability of dislocation loops and cavities in heavily neutron-irradiated $MgAl_2O_4$ specimens [12,13] during isochronal and isothermal annealing. The recovery stage of point defect kinetics and vacancy migration energy is examined through analysis of the growth and shrinkage process of both dislocation loops and cavities, which is useful for further understanding of the mechanisms of radiation resistance in $MgAl_2O_4$.

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2. Experimental details

Man-made single crystals of stoichiometric spinel, $MgAl_2O_4$ (Union Carbide Corporation), whose surface orientations are $\langle 1\,1\,1\rangle$ and $\langle 1\,0\,0\rangle$ were used in this study. Chemical analysis of impurities of the spinel crystals was presented in a previous paper [10]. Cylindrical pellets with 4.8 mm diameter and 2.5–5.8 mm height, and square plates of 12.7×12.7×(2.8–5.8) mm were irradiated in the Materials Open Test Assembly in the Fast Flux Test Facility (FFTF/MOTA) at 658 K to fluences of 2.2, 4.6, 22.9, 24.9×10^{26} n m^{-2} ($E>0.1$ MeV) and at 1023 K to 5.6, 13.7, 21.7×10^{26} n m^{-2} ($E>$ 0.1 MeV). The highest displacement damage was estimated to be 249 dpa, using an equivalence of 1.0 dpa per 1×10^{25} n m^{-2} ($E>0.1$ MeV).

The microstructure evolution was investigated by transmission electron microscopy (TEM) on electron-transparent $MgAl_2O_4$ powder specimens. The powder specimens were prepared by grinding the neutron-irradiated specimens on a diamond film followed by suspension of the powder on a carbon grid with *n*-propyl alcohol. This approach was used to avoid alterations of defect clusters formed by neutron irradiation, which usually occurs during an ion-milling process for TEM specimen preparation. Also, this technique was highly effective to reduce the radioactivity of TEM specimens. The specimens irradiated at 658 K to 2.2×10^{26} n m^{-2} and at 1023 K to 21.7×10^{26} n m^{-2} were cut into 1×1×3 mm^3 pieces and subjected to isochronal and isothermal annealing. In the isochronal annealing, the specimens were kept for 1.8 ks at a specific temperature before rapid cooling to room temperature in air. TEM transparent specimens were prepared from the annealed specimens by using the powder technique mentioned above. The isochronal annealing was repeated at temperatures of every 50 K from 573 to 1573 K, so that the rate of temperature increase was estimated to be 2.78×10^{-2} K s^{-1}. Some of the specimens were subjected to isothermal annealing at temperatures of 1273, 1373 and 1473 K. For both the isochronal and isothermal annealing, a special electronic furnace with a size of 3 mm $\varnothing\times20$ mm was developed, employing the hot-thermocouple technique [17]. The small heat capacity of the furnace enables us to raise the temperature rapidly to 1773 K. TEM observations were carried out in a JEOL 2000 EX operated at 200 kV in the Radioisotope Center of Kyushu University.

3. Results and discussion

3.1. Thermal stability of dislocation loops and cavities in $MgAl_2O_4$

Fig. 1(a) shows a weak-beam dark-field (WBDF) image of $MgAl_2O_4$ irradiated at 658 K to a dose of 22 dpa, illustrating well-defined dislocation loop structure. The dislocation loops have been found to be interstitial type with $1/4\langle 1\,1\,0\rangle\{1\,1\,0\}$ or $\{1\,1\,1\}$ [13]. The average diameter of dislocation loops was determined to be 31 nm. Figs. 1(b) and (c) show a sequential change of microstructure in $MgAl_2O_4$ during isochronal annealing at (b) 1373 and (c) 1473 K. Dislocation loops are seen to shrink with increasing annealing temperature, and disappear at temperatures above 1473 K. The change in the dislocation structure is interpreted to show that dislocation loops absorb irradiation-induced vacancies which migrate via a thermally activated process. No cavities were observed even at 1573 K with under- and over-focused kinematical diffraction conditions. The Burgers vector of dislocation loops annealed at 1373 K was de-

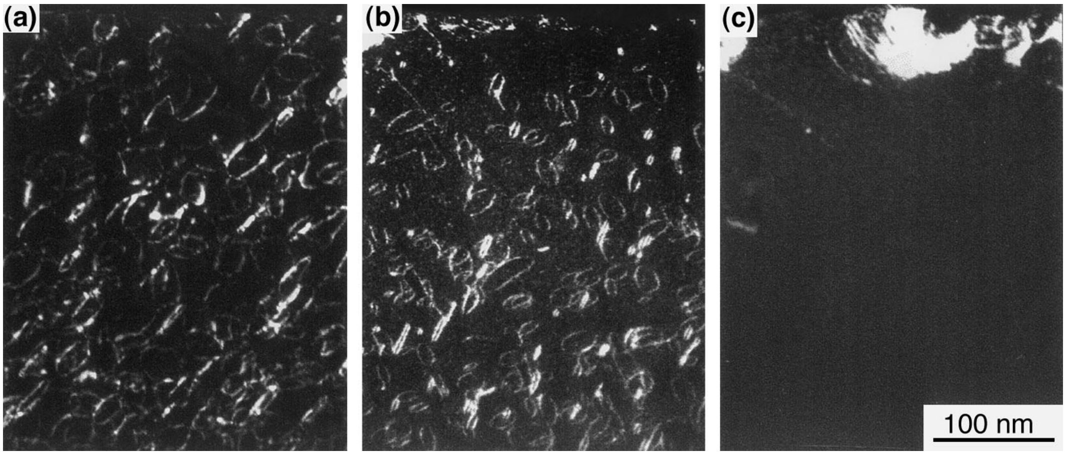

Fig. 1. WBDF images of $MgAl_2O_4$ irradiated at 658 K to 2.2×10^{26} n m^{-2} ($E>0.1$ MeV; 22 dpa) (a); those subjected to isochronal annealing at 1373 K (b); 1473 K (c).

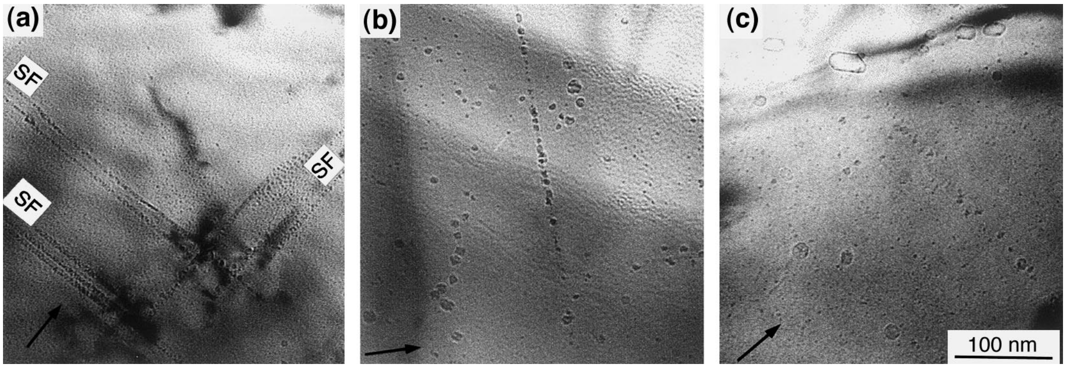

Fig. 2. Bright-field images taken from a [1 0 0] direction in the over-focused condition, showing cavity structure in $MgAl_2O_4$ irradiated at 1023 K to 2.17×10^{27} n m^{-2} ($E > 0.1$ MeV; 217 dpa) (a); those subjected to isochronal annealing at 1573 K (b); 1773 K (c). The arrows and SF in the micrographs represents one of $\langle 1\,0\,0\rangle$ directions and stacking faults, respectively.

termined to be $b = 1/4\langle 110\rangle$, which is consistent with that observed in as-irradiated specimens (Fig. 1(a)).

Fig. 2 shows bright-field (BF) images of $MgAl_2O_4$ irradiated at 1023 K to a dose of 217 dpa showing cavity structure, taken under a kinematical condition with the incident electron-beam along the [1 0 0] direction. SFs lie on (1 1 0) planes in Fig. 2(a) seen in the edge-on condition (they are not visible under the diffraction condition in Fig. 1(a)). Larger cavities are seen on SFs, and a high density of tiny cavities (4×10^{21} cavities m^{-2}) is also seen in the matrix with an average size of 7 nm. With increasing annealing temperature, cavities in the matrix are seen to grow but to decrease their density. Some of the SF contrasts are found to shrink and disappear during isochronal annealing, and change to partial dislocations with $b = 1/4\langle 110\rangle$. At higher temperatures (Figs. 2(b) and (c)), cavities at positions where SFs exist have grown up to 30 nm with facets consisting of (1 0 0) and (1 1 0) planes.

Results of the isochronal annealing are summarized in Fig. 3, in which the normalized diameter of dislocation loops and cavities (r/r_0) are plotted as a function of annealing temperature. It is seen that dislocation loops start to shrink around a temperature of 1000 K, and that values of r/r_0 approach zero at temperatures higher than 1470 K. On the other hand, cavities grow slightly around 1570 K and then start to shrink with increasing annealing temperature. These results provide information on the recovery stage of point defect kinetics in $MgAl_2O_4$. The irradiation temperature of 658 K is considered to belong to stage II, where only dislocation loops were formed (Fig. 1(a)) and no significant shrinkage of dislocation loops was seen (Fig. 3). Vacancy migration is considered to start around 1000 K (corresponding to the stage III) at which temperature the shrinkage of dislocation loops started. Temperatures higher than 1570 K are considered to belong to the stage V, where the density of cavities decreased in the matrix via coalescence to form larger cavities.

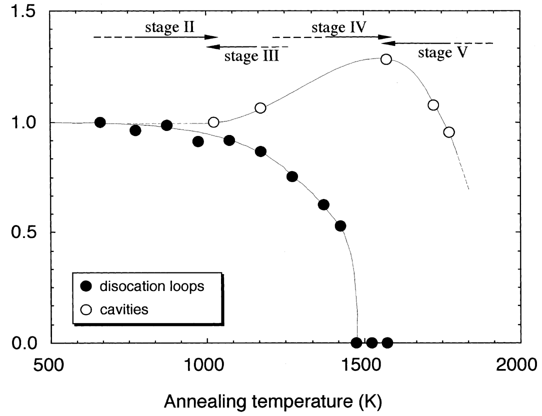

Fig. 3. Variations of normalized size of dislocation loops in $MgAl_2O_4$ irradiated at 658 K to 22 dpa and cavities irradiated at 1023 K to 217 dpa (r/r_0) vs temperature during isochronal annealing. r and r_0 are the radii of defect clusters neutron-irradiated at 658 or 1023 K, and those annealed at a specific temperature for 1.8 ks, respectively. The sizes of cavities were measured only for those formed during isochronal annealing in the matrix but not on the stacking faults.

3.2. Determination of vacancy migration energy from isothermal annealing

As mentioned in Section 3.1, interstitial-type dislocation loops are thought to shrink by absorbing thermally activated vacancies. An estimation of the rate controlling (or highest) vacancy migration energy is shown in this section from an analysis of the shrinkage process of dislocation loops during isothermal annealing. Fig. 4 shows the variation of normalized diameter of dislocation loops in $MgAl_2O_4$ irradiated at 658 K to 22 dpa against annealing time for temperatures of 1273, 1373 and 1473 K. Dislocation loops are seen to shrink rapidly at the beginning of the annealing, and the size of

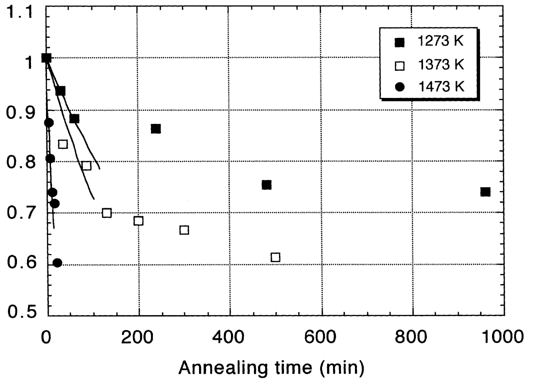

Fig. 4. Variations of normalized size of dislocation loops in $MgAl_2O_4$ irradiated at 658 K to 22 dpa vs time during isothermal annealing at temperatures of 1273, 1373 and 1473 K. Solid curves in the figure were obtained by fitting data at the early stage of the shrinkage process of dislocation loops using an equation of $r/r_0 = \exp(-Bt)$, where B is constant.

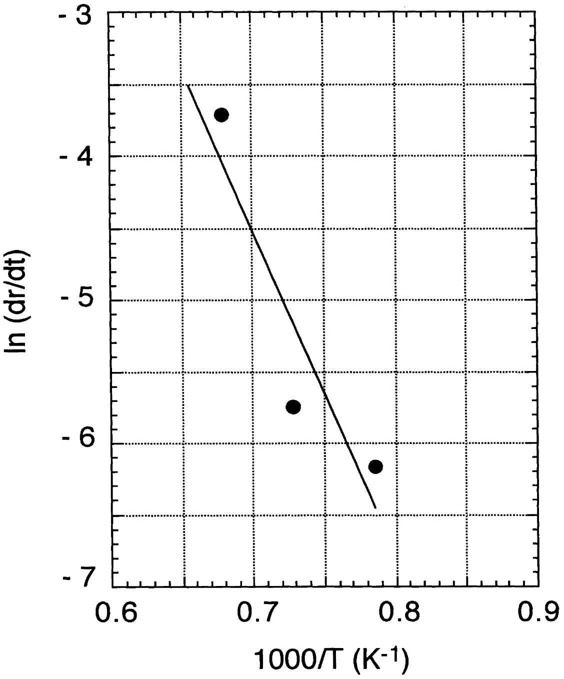

Fig. 5. Relationship between ln (dr/dt) and the reciprocal temperature. The solid line in the figure was obtained by the least-squares method, which leads to a migration energy of vacancy diffusion for the rate controlling step to be 2.0 ± 0.7 eV.

loops decreases gradually with increasing time. The shrinkage speed of dislocation loops during isothermal annealing, $-dr/dt$, can be written as follows, if one assumes a thermal equilibrium condition [18]

$$-\left(\frac{dr}{dt}\right) \cong 2\pi \frac{D_0}{b\ln(R/a)} \exp\left(\frac{-Q}{kT}\right), \qquad (1)$$

where Q is the activation energy for vacancy diffusion, D_0 the diffusion constant, k the Boltzmann constant, R the radius of dislocation core, a the atomic distance, b the Burgers vector and T is the annealing temperature. The term of $b\ln(R/a)$ in Eq. (1) represents the change in diameter of a dislocation loop by absorbing one vacancy. The vacancy migration energy can be obtained from a slope of ln (dr/dt) vs $1/T$ plot. The value of dr/dt was evaluated by fitting the data with an equation of $r/r_0 = \exp(-Bt)$; B is a constant, although no particular physical meaning is implied in this equation. Here, as already mentioned above, Eq. (1) is suitable under thermal equilibrium conditions where the vacancy concentration is constant at a specific annealing temperature. The vacancy concentration in the specimen is, however, considered to decrease with increasing annealing time, because loops absorb primarily those vacancies induced by neutron irradiation. The decrease in the shrinkage speed with time (Fig. 4) is, therefore, understood to be due to the decrease in the vacancy concentration in the specimens. For this reason, data only in the early stage of shrinkage process were used to evaluate the shrinkage speed of dislocation loops, or $-dr/dt$, and the evaluated values are plotted in Fig. 5 against reciprocal of temperature. A rough estimation of 2.0 ± 0.7 eV was obtained using the least-squares method, and the obtained value is considered to be the migration energy for the rate controlling or slowest vacancy species in $MgAl_2O_4$. There have been no known measurements for the migration energy of radiation-induced vacancies in $MgAl_2O_4$, comparable to the estimated value in the present study [14,15]. Although vacancy activation energies for self-diffusion of oxygen have been reported as 4.3–4.6 eV [19–21], those values include contributions of the formation enthalpy of the Schottky defect. A simple calculation of the jump frequency of vacancies yield $\sim 10^3$ jumps s^{-1} around 1000 K with the evaluated vacancy migration energy of 2.0 eV where $\sim 10^3$ jumps/s is a typical value of jump frequency with which vacancies have enough mobility to cause shrinkage of dislocation loops. A value of 10^{13} s^{-1} was assumed for the lattice vibration frequency in the calculation. The estimated temperature shows good agreement with that of stage III determined by isochronal annealing (Fig. 3), suggesting that the evaluated value for rate controlling vacancy migration energy is reasonable. Further investigations are necessary to establish the migration energies of both vacancies and interstitials in $MgAl_2O_4$, including those subjected to ionizing radiation [20], which have been shown to strongly affect the production and stability of defect clusters in $MgAl_2O_4$ [7–9].

4. Summary and conclusions

Thermal stability of defect clusters in neutron irradiated $MgAl_2O_4$ was investigated during isochronal and isothermal annealing to evaluate the recovery stage of point defects and the vacancy migration energy. The following conclusions are derived from this study:

1. During the isochronal annealing, interstitial-type dislocation loops started to shrink around 1000 K, and disappeared at temperatures higher than 1470 K. Burgers vector did not change during the shrinkage process. Cavities grew slightly at 1573 K and then started to shrink with increasing temperature.
2. The recovery stage of point defects was evaluated. Vacancies were considered to migrate at temperatures higher than ~1000 K (corresponding to stage III), and stage V to exist above 1570 K. A rough estimation using isothermal annealing showed the rate controlling vacancy migration energy to be 2.0 ± 0.7 eV.

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