中性子重照射環境での利用を目的とした耐照射セラミック材料の照射に伴う機械的特性変化と微細構造との相関に関する研究

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論文内容要約

Ceramic materials are important constituents in nuclear systems, including the nuclear power plants. In general, ceramic materials are mechanically fragile and vulnerable to radiation effects, namely, their mechanical properties as well as other physical properties are deteriorated by the radiation effects substantially.

Radiation will introduce a variety of structural and electronic defects in the ceramic materials and will modify their microstructures, resulting in the property changes. Due to the intrinsic properties of ceramic materials, such as strong electronic interactions among defects including vacancies, interstitials, and their complexes, complicated structures of dislocation loops, and relatively large concentration of transmutation gases of hydrogen isotopes and helium, the radiation effects are much more complicated in the ceramic materials compared with those in metallic materials. Thus, the efforts have been very limited in the ceramic materials to understand correlation between the radiation induced nano-to-micro structures and the changes of mechanical properties.

For the application of the ceramic materials as the inert matrices of nuclear fuels, the ceramic materials have to endure the displacement damage level above 100dpa, keeping their good mechanical properties. The candidate ceramics will be refractory oxides, carbides, and nitrides, having small neutron capture cross sections, and isotropic crystal structures in general. Preliminary studies suggested that the ceramics having isotropic crystal structure are more resistant to the structural degradation by the heavy radiation damages.

In the present study, several candidate ceramics as the inert matrices were irradiated in the sodium cooled fast reactor of Joyo up to 55dpa at about 700°C. The radiation induced defects were examined by transmission electron microscopy (TEM) and the mechanical properties were evaluated by the Vickers Indentation technique. And, the correlation between the radiation induced nanostructures and the changes of fracture toughness, which will be the most important mechanical property for the inert matrix application, was studied. Detailed studies were already carried out on the magnesia-alumina spinel and yttria stabilized

zirconia by Watanabe, especially on the radiation induced evolution of nanostructures. The present study mainly focuses on the silicon nitride, in comparison with other two ceramics.

In this series of studies, three ceramics, the silicon nitride (Si_3N_4), the magnesia-alumina spinel ($MgAl_2O_4$, hereafter denoted as the spinel) and the yttria stabilized zirconia (ZrO_2 with 8mol%Y_2O_3, hereafter denoted as the YSZ) were examined. They were irradiated in the sodium cooled fast reactor of the Joyo in the Oarai Research and Development Engineering Center of the Japan Atomic Energy Agency. The irradiation rig was the so-called CMIR(the Core Materials Irradiation Rig)-6 inserted into the core center of the Joyo. The irradiation parameters are shown in following, where the dpa is estimated from the relationship of the model proposed by Sickafus et al..

The neutron energy spectrum is typical for the medium-size sodium cooled fast reactor. As discussed in the later section, the neutron having energy higher than 0.1MeV might have had an important role in nuclear gas transmutation. In the irradiation position, the maximum neutron flux and the averaged energy are $4.9\text{x}10^{21}$ n/m^{2}sec, and 250eV, respectively. Si_3N_4, $MgAl_2O_4$ and YSZ irradiated up to $3.9 \text{ x } 10^{25}$n/m^2(3.9dpa) and $5.5 \text{ x } 10^{26}$n/m^2(55dpa), 680 °C and 710 °C for irradiation temperature, respectively.

After the irradiation, the specimens were kept in the storage for more than several years at room temperature and then post-irradiation-examined. For the nanostructural examination, the conventional TEM method was applied with the JEOL2000-FX. For the evaluation of the mechanical fracture toughness, the Vickers Indentation Fracture (VIF) method was applied. The sizes of the indented dimple and the generated cracks from corner of Vickers dimple were examined by a scanning electron microscope (SEM). The fracture toughness was evaluated from the following relationship, originally proposed by Evans et al. and improved by Liang et al..

$$\left(\frac{K_{IC}\phi}{Ha^{1/2}}\right)\left(\frac{H}{E\phi}\right)^{0.4} 14\left[1-8\left(\frac{4\nu-0.5}{1+\nu}\right)^4\right]=\left(\frac{c}{a}\right)^{(c/18a)-1.51} \tag{1}$$

Here, H is the Vickers micrhardness, E is the Young's modulus, c is the length of the crack, a is the diagonal length of the Vickers-indentation dimple, ϕ is the constraint($\approx$ 3), and ν is the Poisson's ratio. Lawn and Niihara categorized the cracks into two modes, the median crack and the palmqvist crack, depending on c/a. If the value of c/a is larger than 2.5, the crack is categorized into the median crack, and otherwise, the crack will be the palmqvist crack. They proposed the two different relationships for these different crack types. However, Watanabe observed the exact configuration of the generated cracks by TEM and found that the value of c/a for categorizing two cracks depends on the irradiation dose. Thus, the unique relationship independent of the value of c/a proposed by Liang et al. was adopted by the present analysis.

The transmutation gas atoms may play a role in modifying the fracture toughness. In general, the effects of transmutation gas were thought marginal except for some cases, such as high nuclear transmutation effects of nitrogen-14 and boron-10, in the case of the fast reactor irradiation. With the instrument of High Resolution Thermal Desorption Spectroscopy (HR-TDS), which can measure the small amount of light gas atoms, the amounts of deuterium, tritium and helium were evaluated by measuring desorption spectra from room temperature up to 1000°C, with the temperature raising speed of 0.2°C/s. Neutron irradiation effects on fracture toughness, Vickers micro hardness and microstructures for Si_3N_4, $MgAl_2O_4$ and YSZ are measured.

The Fracture toughness is evaluated by the relationship (1) on Si_3N_4, $MgAl_2O_4$, and YSZ. In general, the crack was introduced by the indentation test with the loads larger than 250mN and the estimated fracture toughness showed a small dependence on the indentation load, having a little larger fracture toughness with the higher load. It reflected the results that the hardness measured showed the dependence on the indentation load, namely the less hardness with the larger indentation load Si_3N_4.

$MgAl_2O_4$ showed increase of the fracture toughness with the increase of irradiation to 55dpa as shown. The fracture toughness of YSZ looked unaffected by the irradiation up to 3.9dpa, then some increase was observed for the high dose irradiation of $5.5x10^{26}n/m^2$. In the meantime, the YSZ showed high density void formation which might contribute to hindering the crack propagation and the resultant improvement of the fracture toughness. Spinel showed the radiation induced hardening, but YSZ didn't describe hardening.

In the meantime, Si_3N_4 also showed the radiation induced hardening, however, its fracture toughness was decreased by the irradiation, namely, extended propagation of cracks in the irradiated specimens, in contrast to spinel and YSZ. The result of TEM observation on Si_3N_4 irradiated up to $3.9 \times 10^{25}n/m^2$ and $5.5 \times 10^{26}n/m^2$ shows following. In general, the observed radiation induced defects are small in their size and low in their density. The measured densities were 1.10×10^{22} (m^{-3}) and 5.40×10^{21}(m^{-3}), and their averaged sizes were 6.1(nm) and 21(nm) for the 3.9 and 55dpa irradiation, respectively. In the meantime, the densities and the sizes of the Frank type interstitial loops in the spinel were 2.9×10^{20}(m^{-3}) and 42(nm) at 3.9dpa, and the void density in YSZ is difficult to observe due to black and white contrast, but could measure the size of voids, 5.6(nm) at 55dpa.

The black dots observed in Si_3N_4 of the lower neutron fluence were too small of less than a few nano meters to analyze its structure, however, the larger defects observed in the higher neutron fluence were analyzed to be the interstitial type dislocation loop of 1/6<023>{10-10}, which agreed with the results of Akiyoshi et al.. The results suggest that this type of dislocation loop would not hinder the propagation of the cracks or its density and size were too low and small to contribute to hindering the propagation of cracks.

Some transmutation gases may contribute to the high density and the small size of radiation induced defects in Si_3N_4. The TDS show profile of helium from Si_3N_4, $MgAl_2O_4$ and YSZ. In the present analysis, a large amount of desorption of hydrogen isotopes was not observed in Si_3N_4. Probably, the generated hydrogen was ad-hoc released from the specimens due to high mobility of the hydrogen isotopes at the irradiated temperature of around 700°C. However, a very clear desorption peak of helium was observed at about 950°C and small peak at about 750°C. The peak at 950°C is high and sharp, indicating that the substantial amount of helium is trapped at the well-defined trap sites. The estimated amount of helium of high dose Si_3N_4 was $3.5 \times 10^{24}(m^{-3})$, $1.73 \times 10^{26}(m^{-3})$ in the $2 \times 2 \times 1(mm^3)$ specimen size for the 3.9, 55dpa irradiation, respectively. In the meantime, the amounts of released helium from spinel and YSZ were marginal of about 1.47×10^{24}, $2.73 \times 10^{24}(m^{-3})$ and 0, $1.45 \times 10^{23}(m^{-3})$ at the same specimen size for the 3.9, 55dpa irradiation, respectively, indicating that the concentration of the transmutation helium was low in these two ceramics. For a moment, the results were interpreted that the helium trapped at the small interstitial clusters, probably the identified 1/6<023>{10-10} interstitial loop, was released at 750°C and the helium trapped by the vacancy was released at 950°C. Akiyoshi and Hurley reported void swelling of silicon nitride in a variety of neutron irradiation conditions. Thus, it is likely that in the neutron irradiated Si_3N_4, vacancies or voids that are too small to observe by TEM exist.

The transmutation of the large amount of helium was unexpected, but the TDS analysis clearly showed existence of helium at the well-defined trap sites. The large amount of helium transmutation and their strong interaction with radiation induced defects would result in the observed high density and small size of radiation induced defect clusters, namely the observed high density and small size of dislocation loops and no observable voids. And, the high density of the defect clusters, which could contribute to extending the propagation of the cracks, will cause the decrease of the fracture toughness.