

# Dose Rate Dependence of Radiation Induced Conductivity for Hydrogen-Doped Perovskite-type Ceramics

Dose rate dependence of radiation induced conductivity (RIC) of hydrogen doped yttrium-doped perovskite-type barium-cerium oxide ceramics ( $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ ) was investigated under 1.8 MeV electron irradiation within dose rate of 10 - 1000 Gy/s at temperature of 473 K. For the dose rates below 200 Gy/s, the RIC of the H-doped  $BaCe_{0.9}Y_{0.1}O_{3-\delta}$  was higher by one order of magnitude than that of the H-undoped one. The results may show that the RIC takes place due to hydrogen diffusion as well as electronic excitation, enhanced by ionizing effects. For the dose rate range 300 to 1000 Gy/s, the RIC of H-doped  $BaCe_{0.9}Y_{0.1}O_{3-\delta}$  is similar to that of H-undoped one. The radiation enhanced diffusion of constitutive oxygen dominates for the RIC.

So far, it has been reported that the electrical properties of insulating materials such as oxide ceramics are dynamically changed by several radiation induced phenomena [1, 2]. It will be predicted that the radiation induced phenomena are further enhanced by behavior of hydrogen isotopes trapped in the insulating materials during long term D - T discharge.

In the present study, to clarify the changes in proton and ionic conduction by electronic excitation effects, electrical, proton and ion conductivities of  $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ , heated at temperature of 473 K, were in-situ measured with changing dose rates of 10 - 1000 Gy/s using 1.8 MeV electron beams from Van de Graaff at Euratom/CIEMAT.

Fig. 1 shows radiation induced conductivity,  $\sigma_{RIC}$ , for H-doped  $BaCe_{0.9}Y_{0.1}O_{3-\delta}$  as a function of ionizing dose rate for 200, 500 and 1000 Gy/s, respectively, during electron irradiation. The RIC at 200 Gy/s increases about 23 times higher, as compared base conductivity,  $\sigma_{BC}$ , without radiation. The RIC in the initial dose is similar to that in the final one which means that the irradiation time is 60 min. On the other hand, the RIC in the initial at 500 and 1000 Gy/s is respectively about 293 and 3485 times as much as those before irradiation, whereas the RIC in the final one changes to be respectively about 130 and 5484 times as much as those after irradiation. The degradation of  $\sigma_{RIC}$  and  $\sigma_{BC}$  is possibly called Radiation Induced Electrical Degradation (RIED) which is generally considered to occur with an electric field during irradiation. The RIED phenomenon has been associated with displacement damage and radiation induced impurity diffusion. In the present study the mobilities of dopant Y

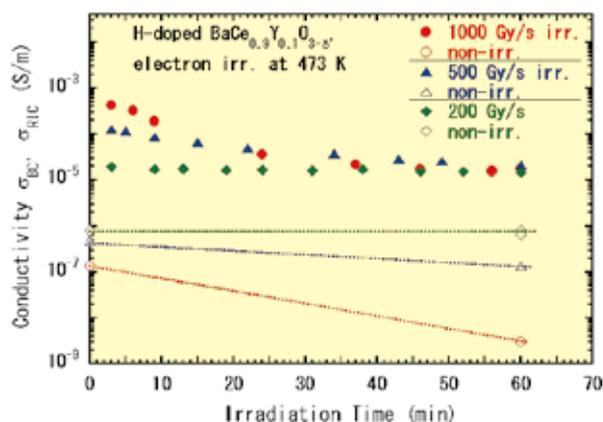


Fig. 1 Radiation induced conductivity (RIC) against irradiation time at 200, 500, and 1000 Gy/s.

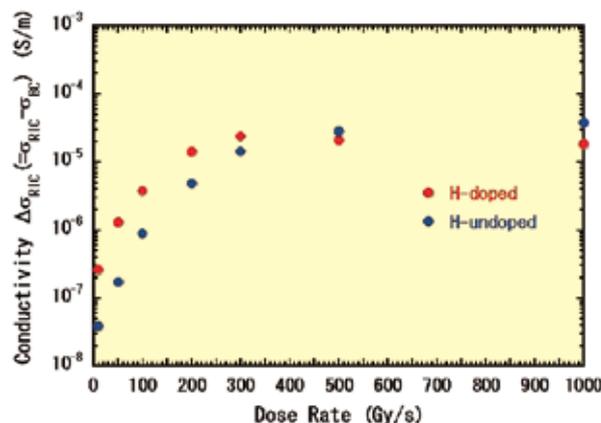


Fig. 2 Dose rate dependence of  $\Delta RIC$  ( $\Delta RIC = \sigma_{RIC} - \sigma_{BC}$ ).

atoms, constitutive oxygen, barium and cerium ions and impurities, and in particular hydrogen atoms, may be enhanced under the present irradiation conditions at elevated temperature of 473 K. The dose rate dependences of  $\sigma_{RIC}$  and  $\sigma_{BC}$  for H-undoped  $BaCe_{0.9}Y_{0.1}O_{3-\delta}$  show the same results with that for H-doped one, although the absolute values are different.

Fig. 2 shows dose rate dependence of  $\Delta RIC$  ( $\Delta RIC = \sigma_{RIC} - \sigma_{BC}$ ), which means the increment of the RIC, obtained by subtracting the base conductivity from the RIC, for H-doped and -undoped  $BaCe_{0.9}Y_{0.1}O_{3-\delta}$  respectively in the final doses during electron irradiation at 473 K. For dose rates under 200 Gy/s, the  $\Delta RIC$  of H-doped  $BaCe_{0.9}Y_{0.1}O_{3-\delta}$  is about one order magnitude higher than that of H-undoped one. The difference of the  $\Delta RIC$  between H-doped and -undoped  $BaCe_{0.9}Y_{0.1}O_{3-\delta}$  may be caused by enhancement of diffusion of H due to ionizing irradiation. On the other hand, for the dose rates above 300 Gy/s, the  $\Delta RIC$  of H-doped  $BaCe_{0.9}Y_{0.1}O_{3-\delta}$  was close to that of H-undoped one. The coincident of the  $\Delta RIC$  indicate that the charge carrier for the conductivity is not hydrogen but constitutive atoms in the matrix, mainly oxygen. The mobility of oxygen ions in  $BaCe_{0.9}Y_{0.1}O_{3-\delta}$  generally starts at elevated temperature above 973 K. The diffusion of oxygen ions may be enhanced by ionizing effects with high dose rates above 300 Gy/s even if the temperature is 473 K.

## References

- [1] B. Tsuchiya, A. Moróño, S. M. González, E. R. Hodgson, S. Nagata, K. Toh and T. Shikama, *J. Nucl. Mater.* **386-388**, 342-344, (2009).
- [2] B. Tsuchiya, T. Shikama, S. Nagata, K. Toh, M. Narui and M. Yamazaki, *J. Nucl. Mater.* **367-370**, 1073-1078 (2007).

## Key Words

Radiation Induced Conductivity, Proton Conducting Perovskite-type Oxide Ceramics, Radiation Enhanced Diffusion

## Contact to

Tatsuo Shikama (Nuclear Science Materials Division)  
e-mail: shikama@imr.tohoku.ac.jp

# Observation of One-dimensional Motion of Self-interstitial Atom Clusters in A533B Steel for Nuclear Reactors

*Self-interstitial atom (SIA) clusters in practical steel A533B used for nuclear power plants were shown to cause one-dimensional (1D) motion under electron irradiation. Frequency of 1D motion was greatly reduced at elevated temperatures. Interstitial atoms, namely, carbon, nitrogen and oxygen were thought to segregate on SIA clusters and to pin them down.*

Recent molecular dynamics simulations and experimental observation with TEM revealed that SIA clusters in pure metals cause 1D motion with low activation energy. It has been pointed out that 1D motion of SIA clusters plays a vital role in microstructural evolution of materials under irradiation, such as swelling of materials due to void growth (Fig. 1). Therefore, it is important to elucidate how actively SIA clusters cause 1D motion in materials used for nuclear reactors under the service conditions. It is also important to understand to what extent 1D motion affects the microstructural evolution.

The 1D motion of SIA clusters is observed frequently with a high voltage electron microscope (HVEM): electron irradiation promotes 1D motion. Experimental observations have also shown that impurities and alloying elements reduce the frequency and distance of 1D motion [1]: solute/impurity atoms are considered to pin down SIA clusters. Moreover, it has been revealed that the effects of impurities and solutes appear even with very small concentrations [1]. Judging from these findings, one may simply infer that 1D motion hardly occurs in commercial materials containing larger amounts of alloying elements.

By means of in-situ observations using an HVEM, we studied 1D motion of SIA clusters in A533B steel used for reactor pressure vessels (RPV) in nuclear power plants. Electron irradiation and in-situ observations were carried out by using JEMARM-1250 (JEOL Ltd.) operated at an acceleration voltage of 1250kV. The irradiation was done at room temperature or 563K; 563K is close to the temperature at which A533B steels are used at nuclear reactors. The electron flux was  $3 \times 10^{24} \text{e/m}^2\text{s}$ ; this corresponds to a damage

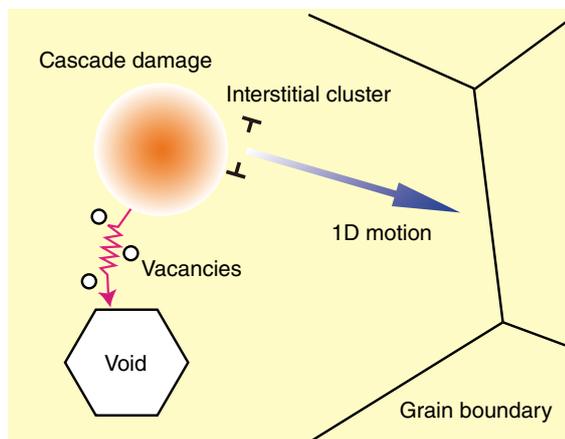


Fig. 1 'Production bias mechanism' for void swelling under cascade damage condition.

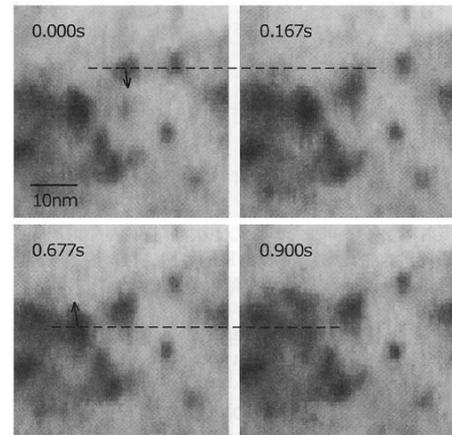


Fig. 2 In-situ observation of 1D motion of SIA clusters in A533B under electron irradiation at room temperature.

rate of  $2 \times 10^{-2} \text{dpa/s}$ .

Fig. 2 shows that 1D motion certainly occurred in the A533B steel under electron irradiation at room temperature [2]. The direction of 1D motion was along  $\langle 111 \rangle$ , and the distance of most 1D motion was less than 10 nm. On the other hand, 1D motion was greatly suppressed under electron irradiation at 563K. We defined the motion frequency as the average number of 1D motion observed per single SIA cluster during unit time. The motion frequencies were  $1.7 \times 10^{-2}$  and  $0.1 \times 10^{-2} \text{ s}^{-1}$  at room temperature and 563 K, respectively.

The effect of annealing on 1D motion at room temperature was investigated to understand why the frequency is low at 563K. SIA clusters became less mobile after annealing at 473K and above. Although the annealing reduced the mobility of clusters which had been formed before the annealing, the annealing effect was not detected on clusters which were formed after the annealing. SIA clusters which had become less mobile due to annealing recovered their mobility by prolonged irradiation at room temperature. Accordingly, the atoms of interstitial elements, namely carbon, nitrogen and oxygen were considered to segregate on SIA clusters considerably and to pin them down at 563K. These results suggest that 1D motion is possible to occur in A533B under irradiation with neutrons depending on the irradiation condition.

## Reference

- [1] Y. Satoh, H. Matsui, T. Hamaoka, Phys. Rev., B77, 94135 (2008).
- [2] T. Hamaoka, Y. Satoh, H. Matsui, submitted to J. Nucl. Mater.

## Key Words

Radiation Damage, Defect Clusters, Void Swelling

## Contact to

Yuhki Satoh (Nuclear Materials Engineering Division)  
e-mail: ysatoh@imr.tohoku.ac.jp

## Development of Hydride Neutron Absorber

Hydride neutron absorbers have been proposed to be used in Fast Breeder Reactor. Demonstration of pellet fabrication have been successfully done. Irradiation behavior of hydride materials were tested in the fast experimental reactor, JOYO.

A metal-hydride has very high hydrogen atom density, which is equivalent to that of liquid water. Fast neutrons in nuclear reactors are efficiently moderated and are absorbed in the metal-hydride. The Hf hydride and Zr-Gd hydride are considered as neutron absorber in FBR (Fast Breeder Reactor).

The development program of hydride neutron absorber was started in Jun 2006. It was accepted as an innovative nuclear research and development program of Ministry of Education, Culture, Sports, Science and Technology of Japan. The program was accomplished in March 2009.

In this study the core design is performed to examine its characteristics and to evaluate cost reduction effect. One of the major R&D items of the present the program is development of hydride pellet, which is used in the reactor core[1]. Figure 1 shows the Hf hydride pellet and Zr-Gd hydride pellet. The slight barrel-shaped transformations were observed, since the pellets were expanded by hydrogen absorption. The transformations can be removed by grinding their sides [2,3].

Irradiation test of hydride neutron absorber was conducted in the fast experimental reactor, JOYO, at Japan Atomic Energy Association (JAEA), where Hf hydride disks and Zr-Gd hydride disks were irradiated with neutron fluence of  $2.92 \times 10^{21}$  (n/cm<sup>2</sup>) ( $E > 0.1$  MeV) and  $3.25 \times 10^{21}$  (n/cm<sup>2</sup>) ( $E > 0.1$  MeV) for Hf hydride ones and Zr-Gd hydride disks respectively. Irradiation temperatures are 590°C and 580°C for Hf hydride disks and Zr-Gd hydride disks, respectively. After irradiation, the capsule containing of the hydride disks was tested by X-ray CT Inspection method (Fig.2). The result show that the capsule was irradiated with keeping it's integrity. The chipping and the cracking of the disks were not found in the hydrides.

After the non-destructive examinations, the capsule was cut for sampling of the irradiated hydride disks for destructive examinations; measurement of weight, metallographic test, X-ray diffraction test, measurement of thermal diffusivity. No swelling was found in the disks. Figure 3 shows the results of thermal diffusivity test. Thermal diffusivity data of un-irradiated sample (blue diamond symbols) are also plotted in Fig.3 for comparison with irradiated data (red rectangular symbols). Figure 3 shows that no effect of neutron irradiation on thermal

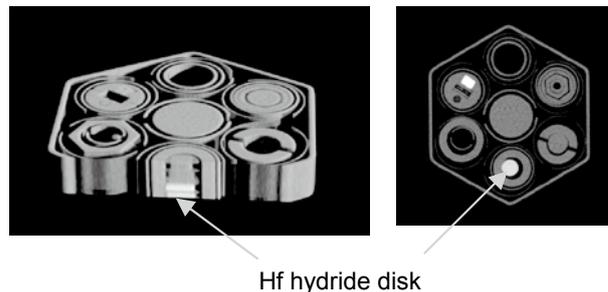


Hf hydride pellet



Zr-Gd hydride pellet

Fig. 1 Hydride neutron absorber pellets



Hf hydride disk

Fig. 2 X-ray CT image of irradiated capsule

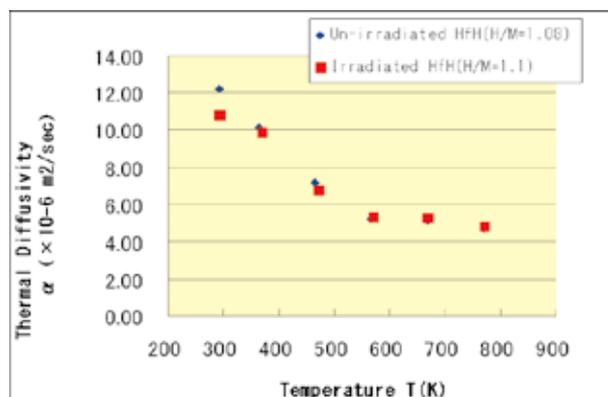


Fig. 3 comparison of thermal diffusivity data of irradiated Hf hydride disk with un-irradiated one

diffusivity of Hf hydride. This is the first experimental result of thermal diffusivity of irradiated Hf hydride. In the case of oxide (e.g. UO<sub>2</sub>), it is well known that the thermal diffusivity decreases with the increase of the accumulated neutron irradiation dose because of radiation damage. The present results of thermal diffusivity of irradiated Hf hydride are noteworthy.

### References

- [1] T. Iwasaki and K. Konashi, 'Development of Hydride Absorber for Fast Reactor - Application of hafnium hydride to control rod of large fast reactor -', to be published in J. Nucl. Sci. Technol..
- [2] K. Konashi et al., 'Study on an innovative Fast Reactor utilizing Hydride Neutron Absorber', Proc. of International Congress on Advances in Nuclear Power Plants (ICAPP2008), June.8-12, 2008, Anaheim, USA.
- [3] Y. Kitano et al., 'Fabrication and mechanical characterization of zirconium and gadolinium hydrides', J. Nucl. Mater. 389 (2009) 170-172.

### Key Words

Hydride, Nuclear Material, Irradiation Test

### Contact to

Kenji Konashi (International Research Center for Nuclear Materials Science)  
e-mail: konashi@imr.tohoku.ac.jp