

# Solubility of hydrogen isotopes in zirconia ceramics

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The hydrogen solubility in zirconia (yttria stabilized zirconia, YSZ) using a tritium imaging plate (IP) technique has been measured in a temperature region ranging from 673K to 973K. The tritium distribution in the zirconia specimens was nearly uniform suggesting an equilibrated dissolution. The hydrogen solubility in specimens were rather low (around ppm or below) and showed Arrhenius type temperature dependence, while it seemed to be independent of Y contents.

Keywords: Zirconia, YSZ, Tritium Gas Exposure, Imaging Plate Technique, Hydrogen Solubility

## 1. Introduction

Oxide materials are used in fusion reactors as plasma diagnosis windows, electric insulators and tritium permeation barriers [1-7]. Tritium dissolution and permeation in the oxide materials are a significant issue from a stand point of tritium retention and leakage. However, compared with metals and alloys, tritium (hydrogen) solubilities in oxides have not been studied well, because very low hydrogen solubility in oxides made difficult to detect hydrogen in them [8].

In this study, we have tried to examine the hydrogen solubility in  $Y_2O_3$  stabilized  $ZrO_2$  (YSZ) using a rather high concentration tritium gas and an imaging plate (IP) technique. The single- and poly-crystalline YSZ specimens were used in order to clarify the influences of grain boundary and Y content on hydrogen solubility.

## 2. Experimental

Mirror polished single crystal plates ( $10 \times 5 \times 0.5$  mm<sup>3</sup>) of cubic zirconia (13% $Y_2O_3$ - $ZrO_2$ (100)) from Dalian Keri Optoelectronic Technology Co. Ltd. were used as specimens. Polycrystalline specimens were prepared with conventional sintering process using PSZ powders manufactured by Toso Co. Ltd (grades: TZ-3Y, TZ-4Y, TZ-6Y, TZ-8Y and TZ-10Y, Y contents of which ranged from 6 % (TZ-3Y) to 20 % (TZ-10Y)). The each grade powder was die-pressed into disks and then isostatically pressed at 200 MPa. The disks were sintered at 1773 K for 20 h. The size of the disk specimens was about 8 mm in diameter and 1 mm in thickness. The densities of

the disks exceeded 95 % of theoretical ones for all grades. The crystal structure of the disk specimens characterized by X-ray diffraction was tetragonal for TZ-3Y, the mixture of tetragonal and cubic for TZ-4Y, and cubic for TZ- 6Y, 8Y and 10Y as shown in Fig.1. The single- and poly-crystalline specimens were heated at 873 K for 1 h in a vacuum to remove an initially dissolved hydrogen, and then exposed to 133 Pa of tritium-deuterium gas mixture ( $T/(T+D) \sim 0.17$ ) at temperatures ranging from 673 to 973 K for 1-5 h. No apparent pressure change was observed during the tritium gas exposure. After that, the specimens

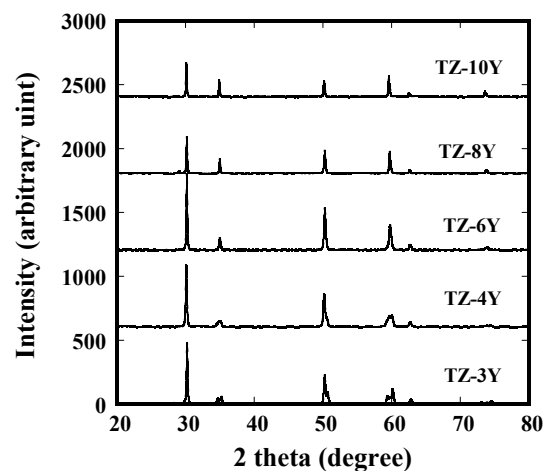


Fig.1 XRD spectra of polycrystalline specimens

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were quenched down to fix tritium distribution. After the specimen surfaces were exposed to IP (TR2025, GE Health Care Co.) for 15 min in order to measure surface tritium densities, the specimens were cut in halves with a diamond saw, and the cross sections of the specimens were exposed to IP for 15 h. The details of this procedure were described in elsewhere [7]. Photo-stimulated luminescence (PSL) intensities were obtained from IP Reader (FLS7000, Fujifilm). The PLS values were converted to tritium activities by calibration with a tritium standard sample (ART 123A, American Radiolabeled Chemicals, Inc.). Hydrogen surface density and solubility were evaluated from the tritium activity and isotope abundance ratio.

### 3. Results and Discussion

Figure 2 shows the examples of the PSL images of specimen surface and cross section. The PSL intensities

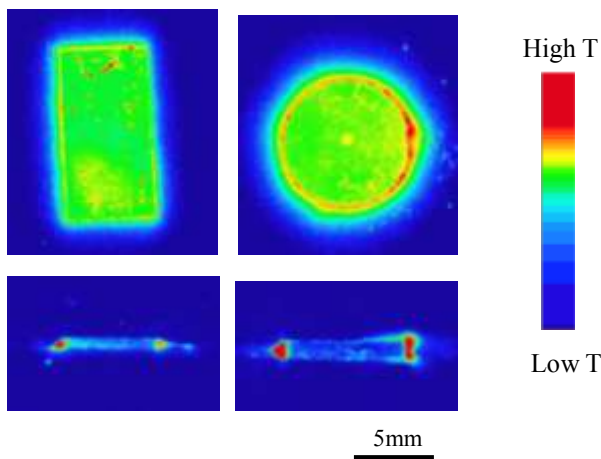


Fig. 2 PSL images of surface and cross section. Single crystal plate (left) and polycrystalline disk (right) exposed to D-T gas at 873 K for 1 h.

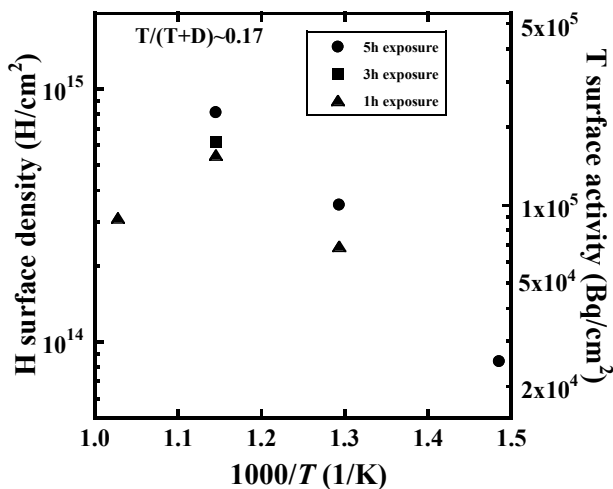


Fig. 3 Hydrogen isotope surface density (T surface activity) on single crystal specimen.

(tritium activities) seemed to be rather uniform except for much intense parts which should be surface contaminations, particularly in specimen edges where were not polished. Since the high PSL intensity area was limited around the edges, these PSD data were omitted. The errors without the contaminations were estimated to be  $\pm 30\%$  for all specimens. The PSL images of the cross sections suggested an equilibrated dissolution of tritium.

Figure 3 shows the tritium activities (hydrogen surface densities) on the specimens exposed to the tritium gas. The amount of tritium uptaken on the specimen surface increased with increasing temperature up to  $2 \times 10^5$  Bq/cm<sup>2</sup> (equivalently  $\sim 10^{15}$  H/cm<sup>2</sup>) and almost saturated at 873 K. At 973 K the tritium density on the single crystalline surface decreased, where tritium desorption should be more dominated than its adsorption. In any case, no clear difference appeared among the specimens.

Figure 4 shows the tritium activities in the single- and poly-crystalline specimens which increase with the exposure temperature, which appear to be very similar to that of its surface density. Figure 5 also shows the tritium activities in poly-crystalline specimens against an oxygen deficiency  $x$  which was simply calculated from Y contents of YSZ. No clear difference in tritium activities appeared for the single- and poly-crystalline specimens. Several studies previously suggested that the hydrogen solubility in grain boundary was high, compared with the oxide grain inside. Unfortunately, the spatial resolution of IP technique is not high enough to detect tritium only in the grain boundary. The influence of grain boundary would be examined in the future study. In any case, it should be safely concluded that no clear influence of grain boundary and O deficiency (Y content) in the present experimental condition.

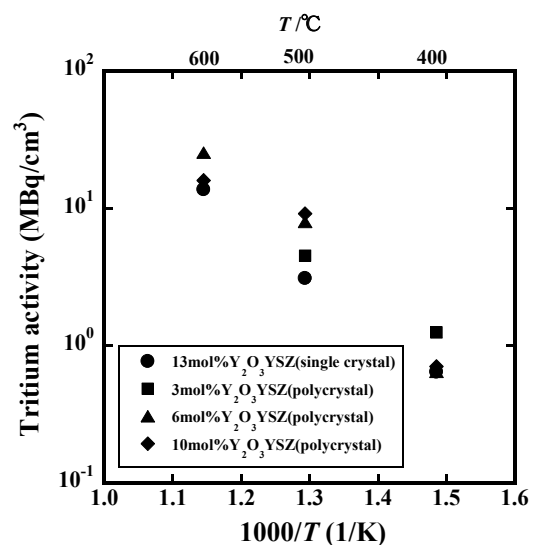


Fig. 4 Tritium activities in single- and poly-crystalline specimens (5 h exposure to D-T gas).

The color of the specimens after the tritium gas exposure slightly changed to be brownish. Not only the characteristics of surface but that of bulk might be influenced by the reductive reaction. However, the effect of this reaction is not discussed here because the adsorption reaction of hydrogen is too complicated to make a quantitative analysis.

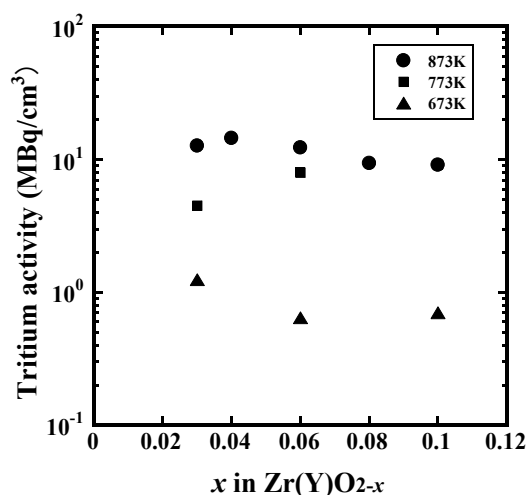


Fig. 5 Tritium activities vs O deficiency  $x$  in poly-crystalline specimens.

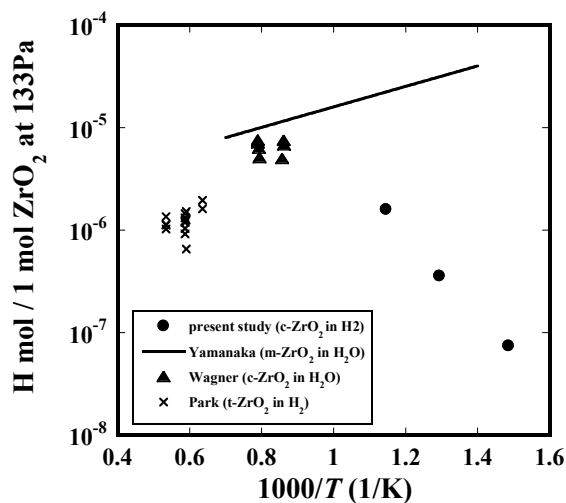


Fig. 6 Comparison of hydrogen solubility in zirconia (5h-exposed single-crystal for the present data).

The present data on hydrogen solubility are compared with literature data [9-12] in Fig. 6. The all literature data have been converted to those at a pressure of 133 Pa of hydrogen containing gases ( $H_2$  or  $H_2O$ ), based on relations  $s \propto p_{H_2}^{1/2}$  and  $s \propto p_{H_2O}^{1/2}$ . As shown in Fig. 6, the values of solubility and its temperature dependence are rather scattered. Reasons of the scattering are not clear at present stage, but might be attributed to differences in experimental conditions such as dissolution temperatures,

crystal structures of zirconia (monoclinic, tetragonal and cubic) and hydrogen containing gas species ( $H_2$  or  $H_2O$ ).

The present study focused on the solubility of hydrogen in zirconia ceramics. The dependence of hydrogen amounts uptaken on surface and bulk in the oxides becomes clear using the IP technique. This also indicates that the IP technique was a useful tool to study the kinetics of hydrogen dissolution and hydrogen solubility in various oxides.

#### 4. Summary

Using an imaging plate (IP) technique and high concentration tritium gas ( $T/(T+D) \sim 0.17$ ), tritium solubility in zirconia ceramics (YSZ) was measured in a temperature region ranging from 673 K to 973 K. The surface activity of tritium on the specimens increased with increasing temperature and almost saturated at 873 K, which reached  $2 \times 10^5$  Bq/cm<sup>2</sup> (equivalently  $\sim 10^{15}$  H/cm<sup>2</sup>).

The hydrogen solubility in the oxides also increased with increasing temperature. No clear difference in the solubility appeared between single crystal and polycrystalline specimens and among the specimens with various Y contents.

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#### 6. References

- [1] F. W. Clinard, Jr., G. F. Hurley, J. Nucl. Mater., **103&104**, 705 (1981).
- [2] W. Dienst, T. Fett, R. Heidinger, H.D. Rhörig, B. Shultz, J. Nucl. Mater., **174**, 102 (1990).
- [3] R. Heidinger, J. Nucl. Mater., 179-181 (1991) 64.
- [4] E.R. Hodgson, Nucl. Instr. Met. Phys. Res., **B191**, 744 (2002).
- [5] A. Ibarra, E.R. Hodgson, Nucl. Instr. Met. Phys. Res., **B218**, 29 (2004).
- [6] Y. Hatano, K. Zhang, K. Hashizume, Physica Scripta, **T145**, 0140144 (2011).
- [7] K. Hashizume, K. Ogata, M. Nishikawa, T. Tanabe, A. Abe, S. Akamaru, Y. Hatano, Proceeding of ICFRM-15, to be published.
- [8] T. Norby, Solid State Ionics, **40/41**, 857 (1990).
- [9] V.C. Wagner, Ber. Bunsenges. Physik Chem., **72**, 778 (1968).
- [10] K. Park, D.R. Olander, J. Am. Ceram. Soc., **74**, 72 (1991).
- [11] S. Yamanaka, T. Nishizaki, M. Uno, M. Katsura, J. Alloys Compd., **293-295**, 38 (1999).
- [12] M. Miyake, M. Uno, S. Yamanaka, J. Nucl. Mater., **270**, 233 (1999).