§90. Study on Dissolution and Diffusion Behavior of Hydrogen Isotopes in Oxide Ceramics Using Tritium

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We have clarified the tritium dissolution behavior in several oxides (including single crystals and poly-crystalline ceramics). In this year, we tried to clarify tritium adsorption behavior on oxides exposed to both DT gas and DTO vapor using the installed apparatus for exposing the oxides to tritiated water vapor.

Mirror polished oxides ($10 \times 10 \times (0.5 \text{ or } 1) \text{mm}^3$) of alpha-$Al_2O_3$(0001), $MgAl_2O_4$(100), cubic zirconia (13% Y_2O_3-ZrO_2(100)) and silica glasses with several OH contents (water free to 1000ppm OH) were used as specimens. These specimens were heated at given temperatures for 1h in a vacuum, and then exposed to 133Pa of T-D gas mixture (T/(T+D): $5 \times 10^{-4} \sim 0.17$) or to 3kPa of DTO vapor (T/(T+D): $\sim 1 \times 10^{-3}$) at temperatures ranging from RT to 1273 K for 1h. After that, the specimens were quenched down to fix adsorbed tritium. The specimens were exposed to IP (TR2025, GE Health Care Co.) for a time ranging from 15 min to 24 h, and 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 densities were also obtained from the isotope abundance ratios of exposure gas. The hydrogen isotopes are here described as H, although DT or DTO was used in the experiment. Part of specimens were used for long term exposure in ambient atmosphere or for vacuum heating to examine the desorption behavior of tritium out of the oxide surfaces.

Fig. 1 shows H surface density on oxide specimens exposed to DT gas or DTO vapor. The data are somewhat scattered, but the maximum amount of adsorbed H reached the order of 10^{15} H/cm^2 around 873K for both atmospheres. The value of 10^{15} H/cm^2 corresponded to the number density on the oxygen and metal ions, and a longer exposure at this temperature did not increase the hydrogen density appreciably. Therefore, this H density was considered to be a saturated one, in which O-H and M-H bonds on the surface formed. At temperatures below 873 K, it should take more time to reach the saturated value. Around room temperature, H density for the DTO-exposed samples was higher than that for DT, as it is well-known because of the higher adsorption energy of water vapor. At temperatures over 873 K, H density trended to decrease with temperature, but that of silica glass exposed to DTO vapor seemed to exceed the saturated value. This suggests that tritium dissolved inside the bulk. In the previous study, those of single crystals were found negligible in the experimental conditions, but that of silica glass would become high. From the temperature dependence of the H
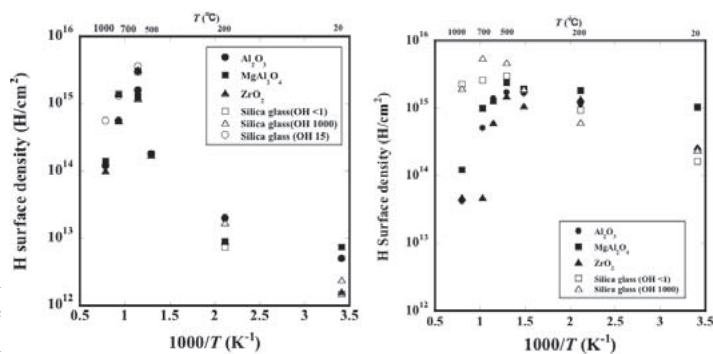

Fig.1 Hydrogen (tritium) density on oxide samples exposed to DT gas (left) and DTO vapor (right).
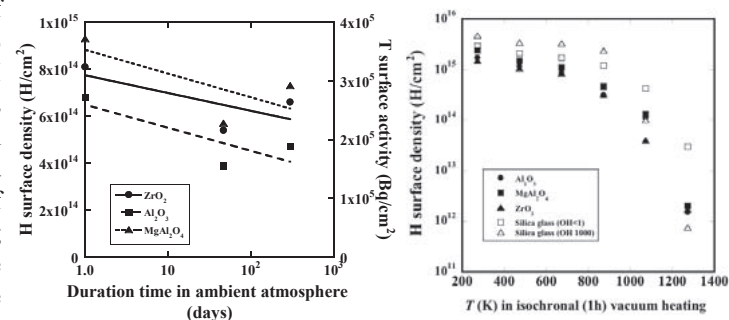

Fig. 2 (Left) Time evolution of hydrogen (tritium) density on single crystal oxides exposed to ambient atmosphere after DT gas exposure at 873 K. (Right) Hydrogen density change on oxides due to consecutive isochronal (1h) vacuum heating.

Table 1 Adsorption energies of hydrogen on oxides according to the first principle calculation.

Oxide	Al_2O_3 [1]	$MgAl_2O_4$ [2]	ZrO_2 [3]
Structure&Surface	(0001)	(100)	Tetragonal (101)
Adsorption energy O-H (kJ/mol)	-227	-265	-199

density at higher temperatures, the binding (adsorption) energy between H and single crystal oxides was estimated to be 120±50 kJ/mol. This value was rather small but comparable with the adsorption energies [1-3] listed in Table 1.

Fig.2 shows the H desorption behavior in ambient atmosphere and vacuum in elevated temperatures. Desorption of H in ambient atmosphere seemed rather slow, and for H desorption in a vacuum the oxides had to be heated above 873 K. These also suggested a strong binding between H and oxide surfaces.

In summary, adsorption and desorption behavior of H on oxide surfaces was clarified in the atmospheres of both H gas and water vapor. The binding energy of H on oxide surfaces was estimated to be 120±50 kJ/mol.

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