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Study on surface defect structures of ZrO_2 and some doped ZrO_2 by means of work function measurement

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Abstract

The work function change of the $ZrO_2 + 2\%Y_2O_3$ sintered pellet, caused by a change of the composition of the sweep gas, was measured using a high temperature Kelvin probe. The Pt reference electrode was calibrated by using $ZrO_2 + 2\%Y_2O_3$ as a standard material. Work function changes of undoped ZrO_2 and Nb-doped ZrO_2 ($2\%Nb_2O_5$) were measured as a function of equilibrium oxygen partial pressure, P_{O_2}. The thus obtained exponents of P_{O_2}, $1/n$, were $1/6.2$ and $1/33.6$ for ZrO_2 and $ZrO_2 + 2\%Nb_2O_5$, respectively. These exponent values were discussed in terms of defect chemistry of the surface layer. © 1997 Elsevier Science B.V.

1. Introduction

Recently, increased burnup of nuclear fuel and higher coolant temperature have been eagerly sought for light water reactors. Corrosion of the zircaloy, its cladding material, has been regarded as an important factor to determine the fuel life. Corrosion of zircaloy results in the formation of a ZrO_2 scale. A lot of efforts have been made to reduce the corrosion rate of the cladding material, involving a modification of the production process and an improvement of the corrosion resistance by altering the composition of the alloy [1]. Y_2O_3 stabilized ZrO_2 (YSZ) is also an important functional material because of its ionic conductivity [2,3]. The work function is a surface sensitive property which can be discussed in terms of the defect structure of near surface layers. Nowotny et al. studied work function data for YSZ ($ZrO_2 + 9\%Y_2O_3$), which were considered in terms of segregation-related effects [4]. Aim of this study was to determine the oxygen potential dependence of the work function of $ZrO_2 + 2\%Y_2O_3$, as a standard material, using a high temperature Kelvin probe, and to calibrate the work function change for the Pt electrode. In this study, we have determined the work function changes of undoped ZrO_2 and $ZrO_2 + 2\%Nb_2O_5$ as a function of oxygen potential. Thus obtained data are considered in terms of the defect structure near the surface of ZrO_2.

2. Principle of measurement

When two materials (A, B) are kept in contact with each other, the CPD (contact potential difference) is formed between the materials. The CPD is equal to the difference in the work function of both materials:

$$\mathrm{CPD} = \frac{1}{e}(\Phi_B - \Phi_A) = \frac{1}{e}(E_{F,A} - E_{F,B}), \qquad (1)$$

where Φ and E_F are the work function and the Fermi energy level, respectively, for each material.

The high temperature Kelvin probe was used for the work function measurement in this study, where the work function measurement is based on measuring CPD between the sample and the reference electrode (Pt).

The principle of measuring CPD, using the Kelvin method [5–7], is shown in Fig. 1. The circuit in Fig. 1 is composed of a dynamic condenser, a measuring resistance

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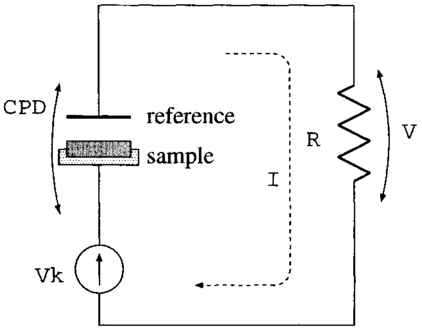

Fig. 1. The principle of the Kelvin method.e

(R), and the compensation voltage (V_k). When $V_k = 0$, the charge of the condenser, q, is depicted as follows:

$$q = C \cdot \mathrm{CPD}, \tag{2}$$

where C is the capacitance of the condenser. When C changes with time, the following equation is obtained:

$$R \frac{\delta}{\delta t}\left[C(t) + V_k + V\right] + V = 0, \tag{3}$$

where V is the ac voltage generated across the resistance. Under an assumption that the distance between the condenser plates, d, is

$$d = d_0(1 + m\sin(\omega t)), \quad 0 < m < 1, \tag{4}$$

the first approximation of $C(t)$ is expressed as follows:

$$C(t) = C_0(1 + m\sin(\omega t)). \tag{5}$$

According to MacDonald and Edmondson, the basic harmonic of the solution of Eq. (3) is expressed as follows [9]:

$$V_1 = m\omega R C_0 (C_k + \mathrm{CPD})(1 + RC_0)^{-2}. \tag{6}$$

When CPD is completely compensated, i.e., $V_k + \mathrm{CPD} = 0$, V_1 is equal to 0 as seen in Eq. (6).

3. Experimental

The configuration of the high temperature Kelvin probe system used in this study is shown in Fig. 2. An integral feedback system [8] was employed for the automatic compensation. The signal from the probe, $V(t)$, is introduced to the lock-in amplifier and the output value from it, which is proportional to the amplitude of $V(t)$, is integrated. The integrated voltage is applied to the sample as a feedback voltage. The composition of the gas phase was controlled by regulating the relative flow rates of He and O_2. The oxygen partial pressure was measured with a Y_2O_3 stabilized ZrO_2 oxygen sensor.

The powders of $ZrO_2 + 2\%Y_2O_3$, pure ZrO_2 and Nb_2O_5 were provided by Toso Manufacturing, Japan. The powder compacts of $ZrO_2 + 2\%Y_2O_3$ and pure ZrO_2 were sintered at 1623 K for 5 h, while that of $ZrO_2 + 2\%Nb_2O_5$ was sintered at 1623 K for 10 h after closely mixing of ZrO_2 and Nb_2O_5 powders.

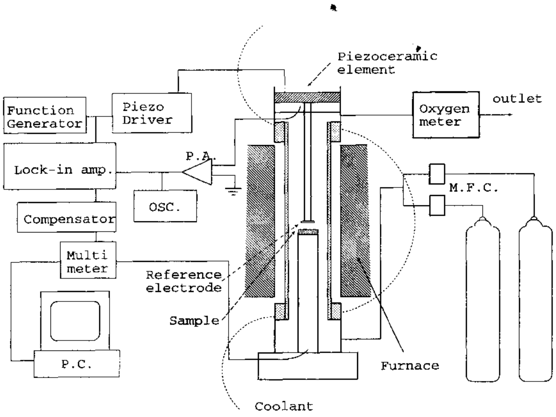

Fig. 2. The configuration of the high temperature Kelvin probe system.

4. Results and discussion

The measurements were performed at 913 K under the gas atmosphere of different P_{O_2}. Fig. 3 shows the change of CPD between $ZrO_2 + 2\%Y_2O_3$ and Pt caused by the change of oxygen partial pressure (P_{O_2}), which is shown

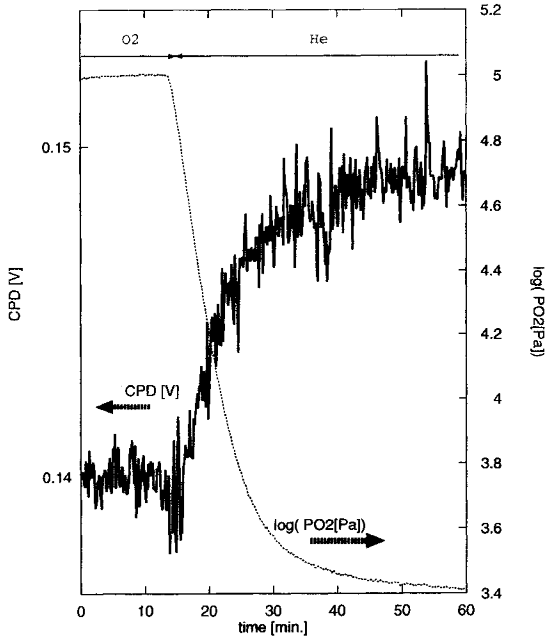

Fig. 3. The change of CPD between $ZrO_2 + 2\%Y_2O_3$ and Pt caused by the change of oxygen partial pressure.

in Fig. 3 by the dotted line. The flowing gas was changed from O_2 to He. CPD in He was ~ 10 mV higher than that in O_2. The CPD change in Fig. 3 included the work function change of Pt reference electrode and the $ZrO_2 + 2\%Y_2O_3$ sample.

Based on defect equilibria, work function change can be related to the oxygen partial pressure [11]. Reaction between ZrO_2 and O_2 can be expressed by the equilibrium,

$$O_O^{\times} \rightleftharpoons \tfrac{1}{2}O_2 + V_O^{\cdot\cdot} + 2e^-, \qquad (7)$$

where $V_O^{\cdot\cdot}$ is a doubly charged oxygen vacancy. From the mass action law, we obtain

$$K = [V_O^{\cdot\cdot}][e^-]P_{O_2}^{1/2}, \qquad (8)$$

where K is the equilibrium constant of Eq. (7).

In the case of Y_2O_3 doped ZrO_2, anion vacancies are formed as

$$Y_2O_3 \rightleftharpoons 2Y'_{Zr} + V_O^{\cdot\cdot} + 3O_O^{\times}. \qquad (9)$$

When the concentration of Y_2O_3 ($[Y'_{Zr}]$) is high enough, it can be assumed that $[V_O^{\cdot\cdot}]$ is determined by $[Y'_{Zr}]$ according to the electroneutrality condition, i.e.,

$$[V_O^{\cdot\cdot}] = \tfrac{1}{2}[Y'_{Zr}]. \qquad (10)$$

From Eqs. (8) and (10), the concentration of the electronic defect, $[e^-]$, can be expressed as

$$[e^-] = \text{const.}P_{O_2}^{-1/4}. \qquad (11)$$

Using Fermi-Dirac distribution function, the relation between $[e^-]$ and the Fermi energy (E_F) is given. When $E_F \gg kT$ (k: Boltzmann constant), the following approximate equation is obtained according to Maxwell–Boltzmann statistics:

$$[e^-] = N\exp\left(\frac{-E_F}{kT}\right), \qquad (12)$$

where N is the state density. From the Eqs. (1), (11) and (12) P_{O_2} dependence of E_F is given as follows:

$$\frac{1}{kT}\left[\frac{\partial\Phi}{\partial \ln P_{O_2}}\right] = -\frac{1}{4}. \qquad (13)$$

When $[e^-]$ in Eq. (8) is not determined by doped impurities, the electroneutrality condition, $[e^-] = 2[V_O^{\cdot\cdot}]$, can be applied to Eq. (8) and the following equation is obtained:

$$[e^-] = \text{const.}\ P_{O_2}^{-1/6} \qquad (14)$$

and it can be derived that $\Phi - P_{O_2}$ relation in the case of pure ZrO_2 is expressed as follows:

$$\frac{1}{kT}\left[\frac{\partial\Phi}{\partial \ln P_{O_2}}\right] = -\frac{1}{6}. \qquad (15)$$

In the case of Nb_2O_5 doped ZrO_2, it is considered that the Nb ion, which is assumed to be five-valent, prevents the formation of oxygen vacancies. Then $[e^-]$ can be expressed as

$$[e^-] = \text{const.}P_{O_2}^{-1/m}, \quad (1/m < 1/6). \qquad (16)$$

And the relation between ϕ and P_{O_2} in this case is expressed as follows:

$$\frac{1}{kT}\left[\frac{\partial\Phi}{\partial \ln P_{O_2}}\right] = -\frac{1}{m}, \quad \left(\frac{1}{m} < \frac{1}{6}\right). \qquad (17)$$

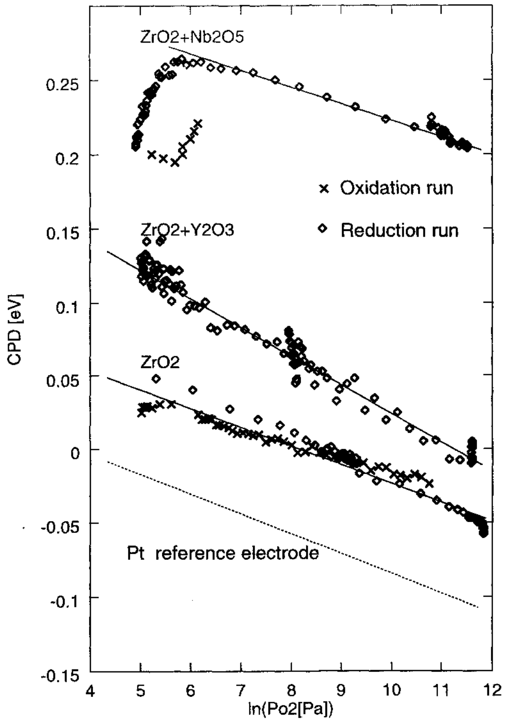

Fig. 4. Plots of the work function changes of several zirconia specimens (undoped ZrO_2, $ZrO_2 + 2\%Y_2O_3$ and $ZrO_2 + 2\%Nb_2O_5$) as a function of equilibrium oxygen partial pressure at 913 K.

Fig. 4 shows the work function change ($\Delta\Phi$) vs natural logarithm of the oxygen partial pressure (P_{O_2}). We put $\Delta\Phi$ for $ZrO_2 + Y_2O_3$ in oxygen to be zero. Values of the power of Φ dependence on $\ln P_{O_2}$ ($1/n$) obtained in this study are shown in Table 1. $ZrO_2 + Y_2O_3$ was used in this work for calibration of the Pt reference electrode [4]. The exponent, $1/n$, determined from the CPD for the Pt–$ZrO_2(2\%Y_2O_3)$ system is equal to 1/24.6 (Table 1). As-

Table 1
The power of the P_{O_2} dependence of work function

	$ZrO_2 +$ $2\%Y_2O_3$	$ZrO_2 +$ $2\%Nb_2O_5$	ZrO_2
Experimental	$-1/24.6$	$-1/5.6$	$-1/21.3$
Calibrated	$-1/4$	$-1/7.4$	$-1/6.2$
Theoretical	$-1/4$	$-1/m\,(1/m < 1/6)$	$-1/6$

suming that $1/n$ for the YSZ specimen is equal to $1/4$ we thus obtain that the exponent for the Pt electrode is equal to $1/4.8$, which is shown in Fig. 4 by the dotted line. The nature of the $1/n$ parameter for the Pt electrode could not be clarified in this study. Nowotny et al. reported that $1/n$ for Pt was $1/7.1$ [10,11]. They discussed this exponent in terms of defect chemistry of a PtO_2 layer formed on Pt and its solid solution with SiO_2 formed as a result of Si segregation. One may expect that the contamination spectrum in our Pt electrode, and related $1/n$ value, is different. Assuming that $1/n$ for Pt is $1/4.8$, the value of $1/n$ for undoped ZrO_2 is $1/6.2$. There is a good agreement between the experimental and the theoretical values, for undoped ZrO_2. This agreement indicates that the Pt electrode was calibrated correctly. On the other hand, the result for $ZrO_2 + 2\%Nb_2O_5$ in Fig. 4 can be divided into two different regions corresponding to two different P_{O_2} exponent values, $\ln P_{O_2} < 6$ and $\ln P_{O_2} > 6$. In the region of $\ln P_{O_2} > 6$, the value of $1/n$ for $ZrO_2 + 2\%Nb_2O_5$ is $1/7.4$. This result shows that the formation of oxygen vacancies was prevented by doped Nb_2O_5. In the region of $\ln P_{O_2} < 6$, the behavior of CPD is complicated. If it is assumed that the valence number of the Nb ion in the lattice was changed, the P_{O_2} dependence of $\Delta\Phi$ for $ZrO_2 + 2\%Nb_2O_5$ might change.

5. Conclusion

The high temperature Kelvin probe was used to determine work function changes of $ZrO_2 + 2\%Y_2O_3$ as a function of oxygen partial pressure at 913 K. The power of the slope of Φ against $\ln P_{O_2}$, $(1/n)$, for $ZrO_2 + 2\%Y_2O_3$ was applied to calibrate the Pt reference electrode. There is a good agreement between the power of the Φ dependence on $\ln P_{O_2}$, $(1/n)$, for ZrO_2 determined experimentally and the theoretical value. In the case of $ZrO_2 + 2\%Nb_2O_5$, the oxygen potential dependence of work function has a complicated behavior. Nb_2O_5 doping might affect the P_{O_2} dependence of work function.

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