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Effect of oxygen potential change on the surface potential of YSZ, ZrO_2–Y_2O_3

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Abstract

The change in contact potential difference (CPD) between YSZ (2% Y_2O_3 stabilized ZrO_2) and a Pt reference electrode was measured under a controlled oxygen partial pressure (Po_2) with a high temperature Kelvin probe. The work function change of the Pt reference electrode ($\phi_{ref.}$) was calculated by comparing the results of the YSZ–Pt measurement and that of the Pt-Pt measurement, and thus the work function change of YSZ (ϕ_{YSZ}) caused by the change of the flowing gas composition was determined. From the experimental results, the exponent of Po_2 dependence of ϕ_{YSZ} was estimated to be 1/4.1 in the Po_2 range of 2×10^2–3×10^3 Pa. This was in good agreement with the value of 1/4 predicted from the estimate based on defect equilibria. © 1997 Elsevier Science S.A.

Keywords: Yttria stabilized zirconia; Work function; Oxygen potential; High temperature Kelvin probe

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1. Introduction

Knowledge of the interactions between the surface and/or near surface layers of materials and the surrounding gas phase is important in various engineering problems. The work function is very sensitive to the surface composition or structure resulting from the interactions or chemical processes at and near the surface.

A high temperature Kelvin probe, which allows the measurement of the work functions of samples in flowing gas, has been developed [1,2,4,5]. Nowotny et al. [1] measured work functions for NiO and YSZ (9% Y_2O stabilized ZrO_2) [4] by using a high temperature Kelvin probe and discussed the surface defect structure and segregation related effects. The authors studied the defect structure near the surface of some doped ZrO_2 [2,3] and the surface non-stoichiometry of Li_4SiO_4 [5], which is one of the possible candidates for solid breeder materials of fusion reactors [6], by means of work function measurement. Thus, a high temperature Kelvin probe is a very useful method for the investigation of surface and near surface processes under a controlled atmosphere at high temperature.

However, it is the difference of the work function between the investigated sample and the reference electrode that is measured by the Kelvin method. Therefore, the interpretation of the obtained data is not evident since the data may include the change of both the work function of the sample and that of the reference electrode.

In this article, the work function of YSZ (2% Y_2O_3 stabilized ZrO_2) was measured by using a high temperature Kelvin probe with a platinum reference electrode. The work function change of the Pt reference electrode was partially distinguished by the blank test. From the experimental results, the relation between

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the work function of YSZ and the oxygen potential was discussed.

2. Experimental

A high temperature Kelvin probe has been developed for use at high temperatures on the basis of the conventional Kelvin method [7-11], with which the contact potential difference (CPD) between a sample and a reference material can be measured. The CPD between two materials (A and B) is equal to the difference of the Fermi levels of those materials (E_{F_A} and E_{F_B}), which can be related to the work functions of the two materials (ϕ_A and ϕ_B) as follows,

$$\mathrm{CPD} = \frac{\phi_A - \phi_B}{e} = -\frac{E_{F_A} - E_{F_B}}{e}, \tag{1}$$

where e is the charge of an electron.

The configuration of the Kelvin Probe system used in this study is shown in Fig. 1. The reference electrode and the sample support were made of platinum. The integral feedback system was employed for the automatic compensation [12]. The signal from the probe, $V(t)$, is introduced to the lock-in amplifier and the output value, which is proportional to the amplitude of $V(t)$, is integrated. The integrated voltage is applied to the sample as a feedback voltage.

The He + O_2 mixture was used as the flowing gas. The concentration of O_2 was controlled by regulating the relative flow rates of He and O_2 with mass flow controllers. The oxygen partial pressure and moisture concentration were measured with a Y_2O_3 stabilized oxygen sensor and a hygrometer, respectively.

The powders of YSZ (ZrO_2 + 2% Y_2O_3) were provided by Toso Manufacturing Co., Japan. The impurities in the powders reported by the company are shown in Table 1. The powder compact of ZrO_2 + 2% Y_2O_3 was sintered at 1623 K for 5 h. The form of the sintered sample was a disk whose diameter and thickness was 8 mm and 1.5 mm, respectively. The CPD between YSZ and the Pt reference electrode was measured at 973 K.

Since the CPD measured in this system was expressed as follows,

$$\mathrm{CPD} = \phi_{YSZ} - \phi_{ref.}, \tag{2}$$

where ϕ_{YSZ} and $\phi_{ref.}$ are the work functions of YSZ and the Pt reference electrode, respectively. The increase of measured CPD may include the increase of ϕ_{YSZ} and the decrease of $\phi_{ref.}$. Therefore it is vitally important to know the change of $\phi_{ref.}$ for the strict measurement of ϕ_{YSZ}. In most cases, the reference level has been assumed to be constant. However, reliable evidence that $\phi_{ref.}$ was kept constant during study has not been provided. In order to estimate the change of $\phi_{ref.}$, the measurement of CPD between the Pt sample support and the Pt reference electrode was made under the same conditions as those in the case of YSZ.

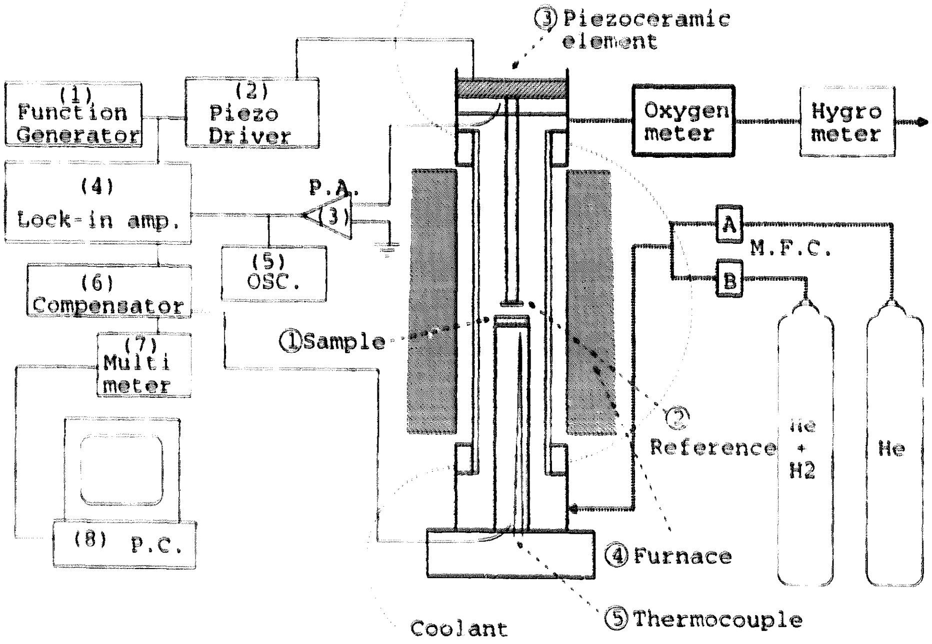

Fig. 1. The configuration of the high temperature Kelvin probe system.

Table 1
The impurities in YSZ powders reported by Toso Manufacturing Company

Impurity	Amount
SiO_2	0.009 wt%
Fe_2O_3	0.004 wt%
Na_2O	0.018 wt%

3. Results

Fig. 2 shows the change of the CPD between YSZ and the Pt reference electrode as caused by the change of the composition of the flowing gas. The flowing gas was changed from 100% He (R) to 95% He + 5% O_2 (O) as shown in Fig. 2. The total flow rate of the sweep gas was 10^{-4} m^3/min. The oxygen partial pressure (Po_2) in the flowing gas is shown by the dashed line in Fig. 2. Po_2 in (R) and (O) were approximately 2×10^2 Pa and approximately 3×10^3 Pa, respectively. When the flowing gas was changed from (R) to (O), CPD decreased sharply by approximately 30 mV as shown by change (A) in Fig. 2 and then an increase of approximately 60 mV, shown by (B) in Fig. 2, was observed subsequently.

In Fig. 3, the result of the CPD measurement between the Pt sample support and the Pt reference electrode (blank run) is shown. CPD in this figure means the difference between the work function of the sample support ($\phi_{sup.}$) and the reference electrode ($\phi_{ref.}$). The dashed line shows Po_2 in the flowing gas. As shown in Fig. 3, CPD decreased sharply when the flowing gas was changed from (R) to (O). From an earlier publication [13], it is considered that adsorption of O_2 on the Pt surface, the formation of PtO_2 layer and oxidation of the contamination adhering to the Pt surface lead to the increment of ϕ_{Pt}. The change (A′), as shown in Fig. 3, might include the increase of both $\phi_{sup.}$ and $\phi_{ref.}$ and the decrease of A′ might show that the increase of $\phi_{ref.}$ caused by the factors described above was larger than that of $\phi_{sup.}$ during change (A′).

From the comparison between Fig. 2 and Fig. 3, it is considered that the change (A) and (B) in Fig. 2 correspond to the change of $\phi_{ref.}$ and ϕ_{YSZ}, respectively. The value of the change (B) in run 1 was 60 mV as shown in Fig. 2 and it means the change of ϕ_{YSZ} ($\Delta\phi_{YSZ}$) was +60 mV when Po_2 changed from approximately 2×10^2 Pa to approximately 3×10^3 Pa. The value of ϕ_{YSZ} obtained in runs 2-9, performed in the same condition as that in run 1, are tabulated in Table 2 as well as $\Delta\phi_{YSZ}$ in run 1.

Fig. 4 shows the change in CPD between YSZ and the reference electrode when the flowing gas was changed from (O) to (R). Since the change of Po_2 in the flowing gas, which is shown by the dashed line in Fig. 4, was slow compared with those in runs 1-9, the change of ϕ_{YSZ} and that of $\phi_{ref.}$ were considered to be slow and could not be distinguished from each

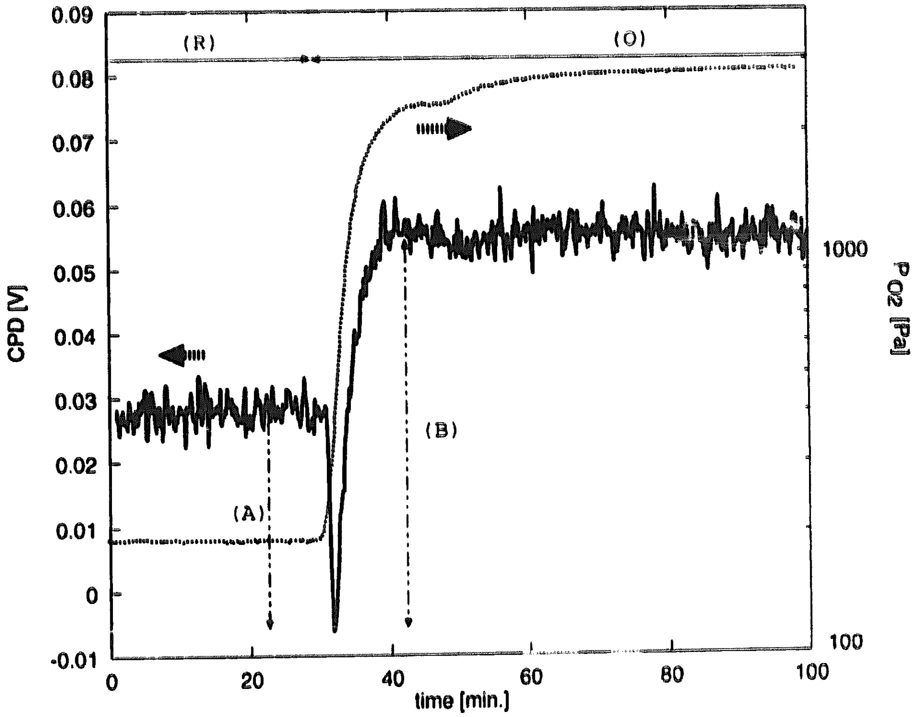

Fig. 2. The change of CPD between YSZ and Pt caused by the change of the composition of the flowing gas, from (R) to (O).

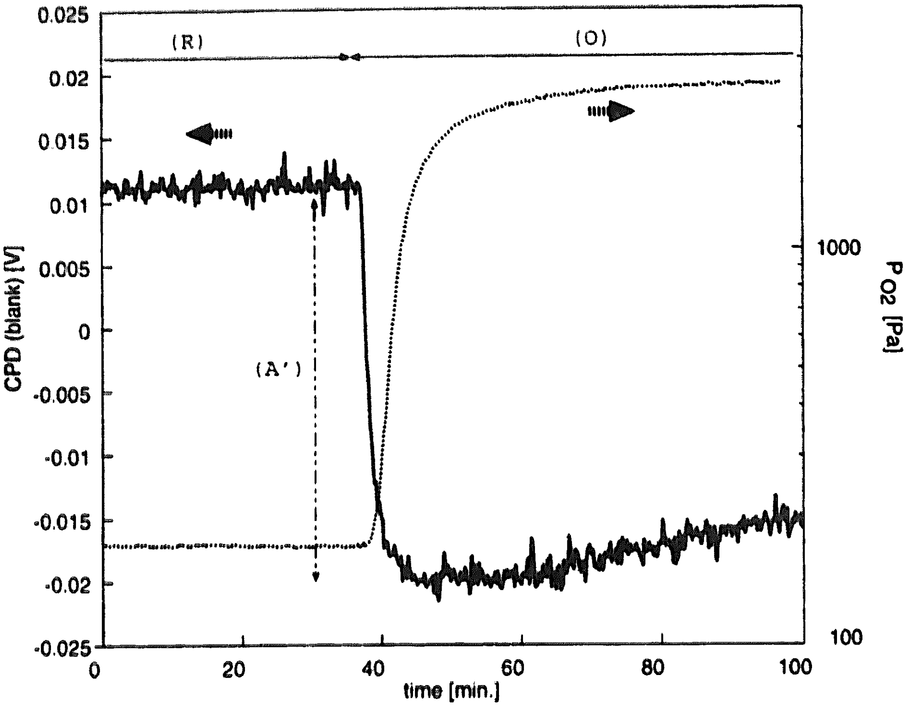

Fig. 3. The change of CPD between the Pt sample support and the Pt reference electrode caused by the change of the composition of the flowing gas, from (R) to (O) (blank test).

other. The change (C) in Fig. 4 might include the change of both ϕ_{YSZ} and ϕ_{ref}.

4. Discussion

In this article we discuss the value of change (B), $\Delta\phi_{YSZ}$, on the basis of defect equilibria near the surface. If quasi-equilibrium between the near surface layer of YSZ and O_2 in the gas phase is assumed, the reaction between ZrO_2 and O_2 can be expressed as follows [4]:

$$\tfrac{1}{2}O_2 + V_O + 2e^- \rightleftharpoons O_O^x, \tag{3}$$

Where V_O is a doubly charged oxygen vacancy. From the mass action law, we obtain:

$$K = [V_O][e^-]P_{O_2}^{1/2}, \tag{4}$$

where K is the equilibrium constant of reaction (3).

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

$$Y_2O_3 \rightleftharpoons 2Y'_{Zr} + V_O + 3O_O^x. \tag{5}$$

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

$$[V_O] = \tfrac{1}{2}[Y'_{Zr}] \tag{6}$$

From Eqs. (4) and (6), the concentration of the electronic defect, $[e^-]$, can be expressed as

$$[e^-] = \mathrm{const.}P_{O_2}^{-1/4}. \tag{7}$$

Using the Fermi–Dirac distribution function, the relation between $[e^-]$ and the Fermi energy (E_F) is given as follows,

$$\frac{[e^-]}{N} = \frac{1}{\exp\left(\frac{\epsilon - E_F}{kT}\right) + 1}, \tag{8}$$

Table 2
The value of the change (B) and the estimated value of n for runs 1 ~ 9.

Run no.	1	2	3	4	5	6	7	8	9
$\Delta\phi_{YSZ}$	60 mV	46 mV	50 mV	59 mV	58 mV	49 mV	58 mV	63 mV	63 mV
n	3.8	4.9	4.5	3.9	3.9	4.6	3.9	3.6	3.6

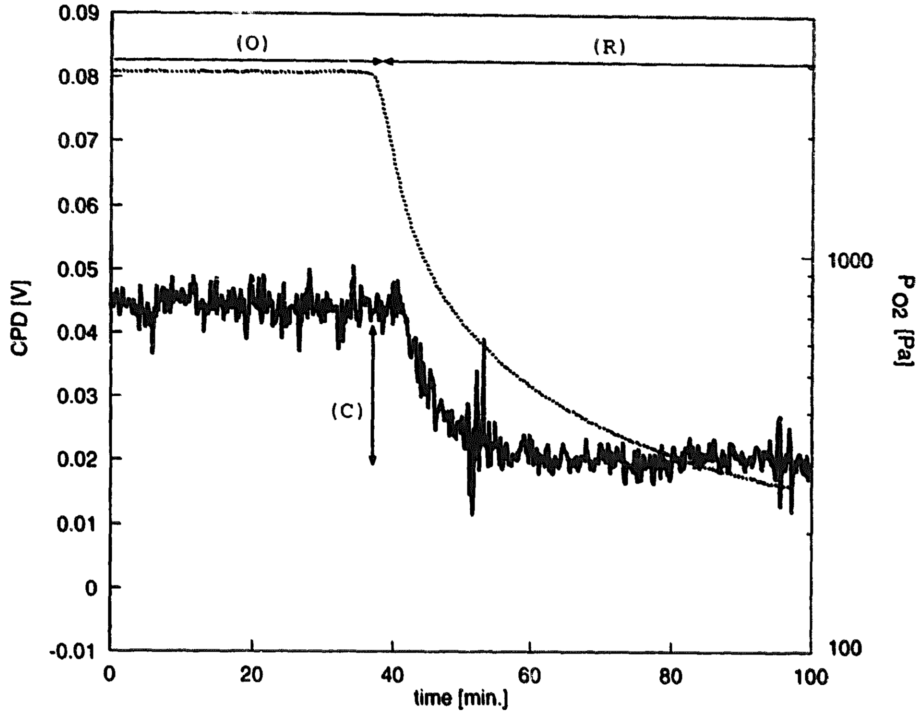

Fig. 4. The change of CPD between YSZ and Pt caused by the change of the composition of the flowing gas, from (O) to (R).

where ϵ is the energy of the electron produced by reaction (3) and N is the state density. When $\epsilon - E_F \gg kT$ (where k is the Boltzmann constant), the following equation is obtained according to Maxwell–Boltzmann statistics,

$$\frac{[e^-]}{N} = \exp\left(\frac{-(\epsilon - E_F)}{kT}\right). \tag{9}$$

From Eqs. (7) and (9), E_F can be related to Po_2 as follows,

$$\frac{E_F - \epsilon}{kT} = -\frac{1}{4} \ln P_{O_2} + \ln N + C, \tag{10}$$

where C is a constant value. Assuming that ϵ and N are independent of Po_2, we obtain Po_2 dependence of E_F as follows:

$$\frac{1}{kT}\left[\frac{\partial(-E_F)}{\partial \ln P_{O_2}}\right] = \frac{1}{4}. \tag{11}$$

Since ϕ_{YSZ} is the difference between vacuum level and E_F, Po_2 dependence of ϕ_{YSZ} is given as follows:

$$\frac{1}{kT}\left[\frac{\partial \phi_{YSZ}}{\partial \ln P_{O_2}}\right] = \frac{1}{4}. \tag{12}$$

From the experimental data in Table 2, we could estimate the value of Eq. (12) and the estimated value of the denominator, n, are shown in Table 2. The average value of n was 4.1 ± 0.4. This was in good agreement with the value of 4, which was predicted from the discussion described above.

The slow change observed after the change (B) was considered to include the slow change of ϕ_{YSZ} and ϕ_{Pt}. The formation of a thin layer of SiO_2 which forms as a result of Si segregation to the surface of Pt was reported as a factor of ϕ_{Pt} change [4]. On the other hand, a possibility of Si segregation on the surface of YSZ can be considered. These factors might be included in the slow change.

5. Conclusion

The change of CPD between YSZ (2% Y_2O_3 stabilized ZrO_2) and the Pt reference electrode was measured with a high temperature Kelvin probe. The change in oxygen partial pressure strongly affected the work function of YSZ and Pt. The work function change of Pt was calculated based on a comparison of the data of the YSZ–Pt measurement and those of the Pt-Pt measurement. From the results, the work function change of YSZ caused by the change of oxygen potential was determined and the relation between ϕ_{YSZ} and Po_2 was discussed on the basis of defect quasi-equilibria. The Po_2 dependence of ϕ_{YSZ} obtained in this study was in good agreement with that predicted from the consideration based on defect equilibria.

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