Effect of H₂ Exposure on TiO₂-based Ceramic Thick Films

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Thick-film sensors based on TiO₂ (anatase and rutile) and composites of TiO₂-Al₂O₃ and TiO₂-Y₂O₃ have been tested for their electrical response on exposure to H₂. Film d.c. resistance was measured in the temperature range 500-650°C as a function of time and gas-phase composition (air, N₂ and 10% H₂ in an N₂-based stream); the equilibrium gas-phase Po₂ was simultaneously monitored with a ZrO₂-based oxygen sensor. The detection mechanism of TiO₂ to H₂ involves the formation of fully ionised oxygen vacancies for both anatase and rutile. The addition of Al₂O₃ and Y₂O₃ did little to affect film sensitivity at the tested H₂ concentration levels.

Keywords: Electrical properties, TiO₂, sensors, H₂

Efecto de la exposición A H₂ sobre láminas gruesas cerámicas basadas en TiO₂

Los sensores de lámina gruesa basados en TiO₂ (Anatasa y rutilo) y materiales compuestos de TiO₂-Al₂O₃ y TiO₂-Y₂O₃ han sido evaluados en función de su respuesta eléctrica a la exposición de H₂. La resistencia d.c. de las láminas fue medida en el rango de temperaturas de 500-560°C en función del tiempo y la composición de la fase gaseosa (aire, N₂ y 10% H₂ en un vapor basado en N₂); el equilibrio de P_{O2} de la fase gaseosa fue simultáneamente monitorizado con un sensor de oxígeno basado en ZrO₂. El mecanismo de detección del H₂ por el TiO₂ incluye la formación de vacantes de oxígeno totalmente ionizadas por la anatasa y el rutilo. La adición de Al₂O₃ y Y₂O₃ apenas afecta la sensibilidad de la lámina en los niveles de H₂ evaluados.

Palabras clave: propiedades eléctricas TiO₂, sensores, H₂

1. INTRODUCTION

Recent studies on ceramic-oxide gas sensors have focused on the use of TiO₂ (anatase) as a CO and H₂ sensor with uses such as the detection of potentially explosive gas leaks in industrial processes and to indicate the efficiency of hydrocarbon combustion (1,2). The mechanism for detection of reducing gases in simple binary metal oxides, most commonly SnO₂, has been ascribed to a change in the concentration of chemisorbed surface oxygen at the semiconductor surface, commonly forming the species O₂⁻ and creating a potential barrier between grains (3,4). The reducing gas depletes the coverage of adsorbed oxygen ions and supplies electrons to the conduction band; in n-type semiconductors, such as TiO₂, this is accompanied by a fall in resistance. However, we have recently shown that in the case of TiO₂ (anatase), the electrical response of the sensor is a function of the oxygen partial pressure rather than direct interaction of H₂ with the titania film (5). The detection mechanism for H₂ may, thus, be interpreted as involving the formation of fully ionised oxygen vacancies. Measurements with both Pt and Au electrodes indicated that, in the measured temperature range (500-650°C) there was no catalytic surface effect and that the equilibration of the film with the surrounding Po₂ environment involved a bulk effect. It had previously been reported that the response time of anatase to H₂ exposure is much slower than to CO exposure. This can be explained as resulting from surface- and bulk-controlled sensing mechanisms for CO and H₂, respectively.

A current trend in sensor research is to attempt to improve the selectivity and sensitivity of the ceramic oxide by elimina-

ting similar responses from interfering gases (6). In the case of anatase, where we have shown that the detection mechanism of H₂ is a bulk effect, it may be possible to exploit the difference in detection mechanism with other reducing gases to achieve this aim. One way in which this may be brought about is by the addition of secondary oxide phases or elemental metals. A recent study has shown the effects of a second insulating phase on the sensing properties of anatase: it is reported that the addition of 10wt.% Y₂O₃ resulted in an increase in sensitivity to CO and decreased sensitivity to H₂, whereas the effect of 10wt.% Al₂O₃ was to cause the sensor to respond to H₂ alone (6).

In this paper, we extend our previous work of the effects of H₂ exposure on the electrical behaviour of TiO₂ (anatase) to include the rutile polymorph of TiO₂ and to determine the effects of the addition of 10wt.% Al₂O₃ and 10wt.% Y₂O₃ on both of these TiO₂ polymorphs. The resistance of thick-film samples of the above compositions is measured at series of temperatures in the range 500-650°C as a function of time, gas phase composition and oxygen partial pressure.

2. EXPERIMENTAL

Experimental details, including a detailed description of the measuring system, are given in Ref. (5); only a brief description of the experimental procedure is, therefore, given here. Thick-film sensors of the anatase and rutile polymorphs of

TiO₂ and TiO₂-10wt.% Al₂O₃, TiO₂-10wt.% Y₂O₃ composites were prepared on Al₂O₃ substrates by screen printing. In the case of the anatase and anatase-composite materials, the wet films were dried, fired at 800°C for 1 hour then cooled to room temperature. A similar routine was performed with the rutile and rutile-Al₂O₃ film, but with final firing at 1200°C. For the rutile-Y₂O₃ composite, the film was fired at 900°C since, above this temperature, significant amounts of Y₂Ti₂O₇ were formed. Electrical contacts were provided by two strips of Pt paste on the sensor surface separated by approximately 4 mm; the organic matter was removed from the paste after application by firing for a short time at 800°C. The anatase and rutile polymorphs of TiO₂ and the unreactivity of the additional oxides were confirmed after firing by X-ray diffraction (XRD).

The test system consisted of the sensor attached to a pressure mount in a sealed vertical tube furnace with a ZrO₂-based oxygen sensor placed close to the sensor surface in order to determine oxygen partial pressure. A gas-flow meter (Bronkhurst Hi-Tec) supplied a constant gas-flow rate of 50 ml/min from N₂ and 10% H₂ in N₂ gas lines; a line of compressed air could also be supplied to the furnace. The electrical response of the sensor could be measured by both a.c. impedance (H.P. 4284A a.c. impedance analyser working in the frequency range 20 Hz - 1 MHz) and d.c. methods (Fluke 45 multimeter); the oxygen sensor electromotive force (emf) was measured with a Fluke 45 multimeter. Both multimeters were computer-controlled in order that the oxygen partial pressure and film resistance could be measured simultaneously.

3. RESULTS AND DISCUSSION

Test runs involved measuring the sensor resistance and oxygen sensor emf through a series of gas changes. The furnace was flushed with air for a short period then N₂ for approximately 1 hour to ensure that the sample environment was as free of O₂ as possible; the H₂/N₂ mixture was then introduced into the furnace chamber. The same procedure was repeated for all samples, throughout the range of measured temperatures (500-650°C), to ensure conditions were as equivalent as possible for every run. However, faithful reproducibility of the sensor response between air and reducing conditions was not fully attainable due to long-term drift of the sensor resistance.

The information obtained from a.c. impedance spectra was limited: in air, the cell impedance was in the MΩ range, close to the upper limit of the machine operating range. Furthermore, the relaxation frequencies of the impedance arcs were quite low, which meant that the definition of the arcs was poor and limited to the high frequency part of the entire spectrum (Figure 1). Under highly reducing conditions (10% H₂ + 90% N₂) and at lower temperatures, however, the cell impedance approached resistance values (~10 kΩ) where the Z'-Z'' plot was characterised by a single semicircle, which was depressed to a degree depending on the film composition. However, depression angles were small in every case. Figure 1 shows typical examples of the impedance spectra of anatase-alumina and rutile films at 500°C in air and in an H₂/N₂ atmosphere. As mentioned previously there was no evidence for possible deconvolution of spectra into contributions with physical meaning. Hence, the majority of the electrical measurements were carried out using d.c. techniques.

Fig 1. Impedance spectra of rutile (A, B) and anatase-10wt% alumina (C, D) thick-films at 500-550°C in air and in an 10% H₂+90% N₂ atmosphere, respectively.

Fig 2. Log of film resistance ($\log R$) and YSZ oxygen sensor (emf) response of rutile (A), rutile-10wt% yttria (B) and anatase-10wt% yttria (C) thick-film sensors at 500-600°C, when the furnace atmosphere is flushed firstly with air, then N₂ and finally 10%H₂+90% N₂.

Fig 3. Plot of the log of a rutile sensor resistance ($\log R$) against log of the oxygen partial pressure ($\log P_{O_2}$) at 600°C.

3.1. Anatase and Rutile

The TiO₂ sensor response and corresponding YSZ sensor emf response on changing the gas atmosphere (air → N₂ → N₂+H₂) is very similar for both anatase and rutile TiO₂ polymorphs. Figure 2 shows the rutile resistance and O₂ sensor emf at 600°C for such a cycle. In air, the ZrO₂-based oxygen sensor emf is zero and the film resistance is very large (~ MW). After approximately 50 minutes, the air is cut off and N₂ is introduced; the oxygen sensor emf correspondingly increases to ~100 mV, but the film resistance remains in the MW range. When 10% H₂ is introduced into the N₂ flow, after approximately 110

mins., there is a sudden decrease in both the film resistance (to a few kW) and oxygen partial pressure (the oxygen sensor emf increases to ~1V). The emf and resistance curves change in a reciprocal fashion on introducing H₂, as previously described for the anatase sensor. The rutile and anatase polymorphs showed similar behaviour, although the time required for the rutile film resistance to stabilise in N₂ was somewhat longer than for the anatase films.

We have previously shown that, for anatase, the sensor resistance (R) and gas-phase equilibrium oxygen partial pressure (mV) display an almost linear log-log plot with a gradient of approximately +1/6 (see Ref. (5)). It can be seen in Fig. 3 that rutile has a similar $\log(R)$ vs. $\log(P_{O_2})$ plot. Deviations from the 1/6 gradient for higher values of P_{O_2} ($> 10^{-22}$ atm.) may be explained by sensor limitations, as discussed elsewhere (5,7). Only the very low P_{O_2} range is, therefore, shown in Fig. 3 in order to avoid the intermediate P_{O_2} range where the ZrO₂-based sensor is affected by these limitations. In previous work, we have shown that a gradient of +1/6 in the $\log(R)$ vs. $\log(P_{O_2})$ plot can be attributed to n-type conductivity associated with the formation of fully ionised oxygen vacancies in accordance with the following equilibrium:

(Kröger-Vink notation). A simplified electroneutrality condition

$$n = 2[V_o^{\bullet\bullet}] \quad [2]$$

involving such oxygen-defect formation can be combined with the thermodynamic equilibrium constant:

$$K = n^2 \cdot P_{O_2}^{1/2} \cdot [V_o^{\bullet\bullet}] \quad [3]$$

to give $n \propto P_{O_2}^{-1/6}$ and $R \propto P_{O_2}^{1/6}$. A gradient of +1/6 in the $\log(P_{O_2})$ vs. $\log(R)$ plot is, thus, consistent with semiconductivity associated with formation of oxygen defects, assuming bulk equilibrium between the sensor film and surrounding atmosphere.

There appears to be little difference in the behaviour of the anatase and rutile forms of TiO₂. Previous reports of TiO₂ as hydrogen sensor concentrate exclusively on the anatase polymorph. Our studies were conducted on films with both structural forms since the rutile polymorph is considered the more stable phase and the higher firing temperature required for its formation affords a stronger substrate-film contact. In order to test the long-term stability of the rutile phase at the sensor operating temperature, a sample of rutile was fired for a period of 5 months at 500°C. Figure 4 shows that no evidence of the anatase polymorph was observed by XRD after this time. This indicates that the rutile form of TiO₂ is stable at the sensor operating temperature and could be used as an alternative H₂ sensor to anatase with the advantage of obtaining mechanically stronger devices than is possible with the anatase form due to the higher temperature at which rutile can be fired.

One final comment is required to address the apparent lack of response of the titania-based sensors when the atmosphere is changed from air to N₂. While the ZrO₂-based sensor clearly shows that the equilibrium P_{O_2} dropped by approximately two orders of magnitude, the thick-film resistance seems to be insensitive to this change, contrary to the prediction of the model mentioned previously. Titania is a well known p-type conductor in air and an n-type conductor under reducing conditions. The change from p-type to n-type is known to occur

Fig. 4. XRD patterns of (a) rutile with no thermal treatment, (b) rutile annealed at 500°C for a period of 5 months.

under slightly oxidizing conditions in the range 500-700°C (8). Because of this, the sum of the p- and n-type conductivity contributions is almost constant within a limited range of P_{O_2} (from air to about 10^{-3} atm). This constancy of conductivity in this range explains the apparent insensitivity of the sensor to the change from air to N_2 . Furthermore, a change of about two orders of magnitude is much smaller than the change of more than 20 orders of magnitude (P_{O_2} decreases to values lower than 10^{-20} atm as shown in Figures 3 and 5) which is registered when H_2 is introduced into the furnace. The relative magnitude of the titania sensor response should therefore be considerably different under each atmosphere change, which is the case.

3.2. Al_2O_3 - and Y_2O_3 - TiO_2 Composites

Films of 10wt.% Al_2O_3 -anatase, 10wt.% Al_2O_3 -rutile, 10wt.% Y_2O_3 -anatase and 10wt.% Y_2O_3 -rutile were similarly tested for sensor resistance and oxygen partial pressure through the series of gas atmospheres: air→ N_2 →10% H_2 in N_2 . The behaviour of all the composite films was similar to that of the pure TiO_2 films; no evidence was provided for the addition of a second phase altering the film sensitivity to hydrogen. Typical examples of data obtained with 10wt.% Y_2O_3 -anatase and 10wt.% Y_2O_3 -rutile films are also presented in Figure 2. Figure 5 shows the $\log(P_{O_2})$ vs. $\log(R)$ plot at a series of temperatures for the composition 10wt.% Y_2O_3 -rutile. Again, the gradient of the slope at each temperature is +1/6, indicating that the hydrogen detection mechanism involves the formation of oxygen vacancies. Although we did not observe any detectable difference between the single-phase and composite films in terms of the response time or magnitude of the resistance change on hydrogen exposure, it should be noted that our experiments involved a rather large concentration of hydrogen (10% H_2 in N_2); previous reports of the effect of second phases relate to much smaller hydrogen levels (ppm range).

Fig. 5. Log of film resistance ($\log R$) and YSZ oxygen sensor (emf) response of a rutile- Y_2O_3 composite thick-film sensor in the temperature range 500-600°C.

4. CONCLUSIONS

The detection mechanism of TiO_2 to hydrogen involves the formation of fully ionised oxygen vacancies for both anatase and rutile TiO_2 polymorphs, as indicated by a gradient of +1/6 for the $\log(R)$ versus $\log(P_{O_2})$ plots at a series of temperatures in the range 500-650°C. The similarity in behaviour of the two modifications suggests that rutile may be a more suitable candidate for sensor fabrication since it is the more stable form and provides a stronger substrate-film contact. The addition of 10wt.% Al_2O_3 or 10wt.% Y_2O_3 to each of the polymorphs did little to affect the film sensitivity at the levels of hydrogen concentration which were tested (10% H_2 in N_2). Composite films were also shown to detect hydrogen by the formation of fully ionised oxygen vacancies.

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