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Effect of oxygen vacancies on transformation of zirconia at low temperatures

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The effect of oxygen vacancy on the stability of phase structures and phase transformation of zirconia at low temperatures was studied using an electrochemical technique. It is suggested that the decrease of oxygen vacancies decreases the stability of metastable tetragonal zirconia and promotes its transformation to the monoclinic phase.

1. Introduction

Although it is known that oxygen vacancies or defect clusters are associated with the structural stability of zirconia at high temperatures [1–5], little is known about the effect of the anion vacancy on the transformation of zirconia at low temperatures.

The tetragonal to monoclinic phase transformation of zirconia is usually considered to be typically martensitic which is diffusionless and displacive. As various workers discovered the degradation phenomenon in zirconia ceramics [6–8], ideas about the low-temperature phase transformation began to change. After investigation of the isothermal propagation of zirconia, Nakanishi and Shigematsu [9, 10] proposed the concept of "bainite-like transformation", which had been found in metals, and they believed that the high diffusibility of oxygen vacancies controlled the propagation rate of the shear transformation in locally distorted tetragonal lattice. Unfortunately, they did not provide the evidence of the vacancies effect.

Some workers [11–13] studied the relationship between the non-stoichiometry and the mechanical properties of certain oxide ceramics; Kaiming Liang *et al.* [14, 15] found that zirconia ceramics can undergo the tetragonal to monoclinic phase transformation in a high-strength electric field at room temperature, and they considered this phenomenon might contribute to the electronic defects produced in the electric field. However, it is difficult to testify to this idea.

To date, no strong evidence of the involvement of the oxygen vacancies in the isothermal transformation of zirconia has been presented. In the present work, the electric field technique has again been used to study the role of the oxygen vacancies in the phase transformation of zirconia.

2. Experimental procedure

ZrO_2 containing 3 mol % Y_2O_3 specimens were provided by China Building Materials Academy. The specimens were sintered at 1550 °C in air for 2h and then cold pressed. The pellets were 30 mm in diameter and 1 mm thick. The samples were ground using SiC-grit papers 120–400, degreased by acetone, cleaned using alcohol, and dried in hot air. Specimens were placed into a specially designed apparatus (see Fig. 1), placed in a furnace and heated. Both the electrodes were made of 1Cr18Ni9Ti stainless steel. When the required temperature was reached, a voltage was applied. After a certain period, the specimen was pulled out and cooled in air without removing the voltage. The phase composition near the two surfaces of the specimen was analysed by X-ray diffraction (XRD) before and after the experiment, using the following equation

$$V_m = \frac{I_m(1\,1\,\bar{1}) + I_m(1\,1\,1)}{I_{c/t}(1\,1\,1) + I_m(1\,1\,\bar{1}) + I_m(1\,1\,1)} \times 100\% \quad (1a)$$

$$V_t = 1 - V_m \quad (1b)$$

where V_m is the volume fraction of monoclinic phase, $V_{c/t}$ is the total volume percentage of tetragonal and cubic phases, $I_i(h\,k\,l)$ is the diffractive X-ray intensity, of the $(h\,k\,l)$ plane of the i phase.

By comparing the phase change near the two surfaces of the specimen with and without an electric field, the role of the oxygen vacancies in the transformation can be investigated.

3. Results and discussion

3.1. Promotion by an electric field of the transformation of zirconia

Two samples with almost the same original phase compositions were chosen for testing in a 300 V cm^{-1} electric field; both were heated to 200 °C for different periods. The phase changes near the anode and the cathode surfaces of each sample are shown in Fig. 2, and the difference in phase change between the two sides is shown in Fig. 3. From these results, it can be seen that (1) isothermal phase transformation from the tetragonal to monoclinic phase can take place with or without an electric field, but the electric field remarkably influences this transformation: (2) the kinetics in

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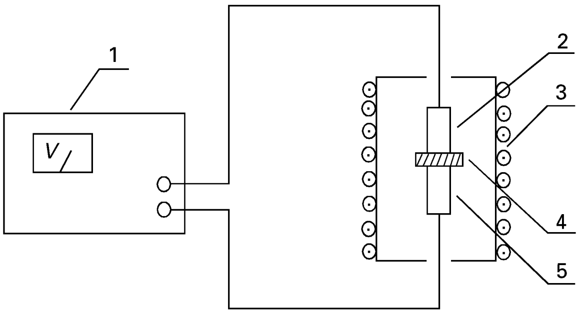

Figure 1 Apparatus for the electric-field induced transformation study. 1, Power source; 2, anode; 3, furnace; 4, specimen; 5, cathode.

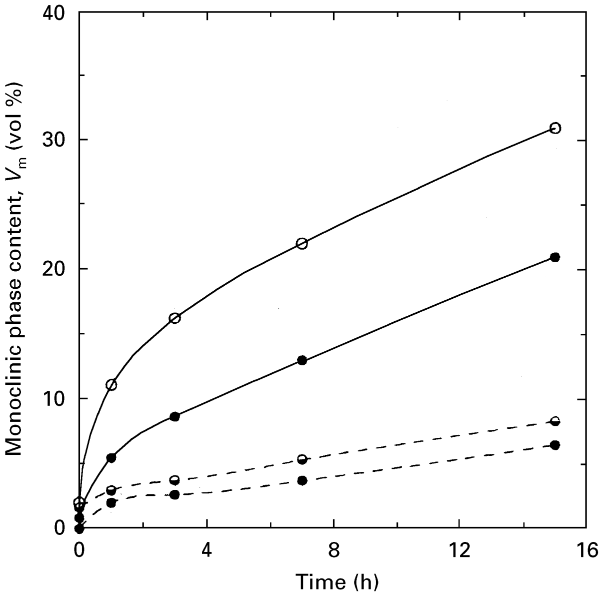

Figure 2 Kinetics of transformation in an electric field, for ZrO_2-3 mol % Y_2O_3 at 200 °C: (—○—, ---◒---) anode, (—●—, ---●---) cathode, at (—○—, —●—) 300 V cm^{-1}, and (---◒---, ---●---) 0 V cm^{-1}.

the electric field obeys a parabolic law, indicating that there might be some diffusion process involved in the transformation; (3) when an electric field exists, the transformed monoclinic phase content near the anode surface is much higher than that near the cathode surface, and the difference again obeys the parabolic law; without the electric field, the transformed monoclinic phase difference between the two sides remains constant. This might be associated with the behaviour of oxygen vacancies in the electric field, because the charged oxygen vacancies can migrate, redistribute and reorder in the sample owing to the electric polarization, non-stoichiometry and charge neutrality. This results in an increased concentration of oxygen vacancy near the cathode side surface, while it decreases near the anode side surface, compared with the original states. More oxygen vacancies near the cathode side surface increase the stability of the tetragonal phase and less oxygen vacancies near the anode side surface decrease the stability of the tetragonal phase, in accordance with the case where more stabilizer content can produce more oxygen vacancies and increase the stability of the high-temperature phases.

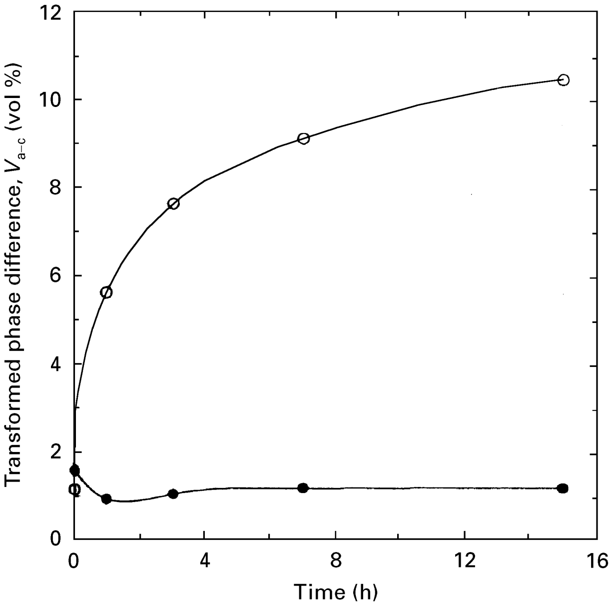

Figure 3 The difference in the transformed phase between the electrodes, for 3 mol % Y_2O_3–ZrO_2: (○) 300 V cm^{-1}, (●) 0 V cm^{-1}, at 200 °C.

Whatever the behaviour of the oxygen vacancy, it can be confirmed that migration, precipitation and reordering of the oxygen vacancies are involved in the transformation process.

3.2. Influence of temperature at constant electric field strength

The influence of temperature at constant electric field strength is shown in Table I. There is a specific temperature range in which electric field promotes the phase transformation, i.e. 200–400 °C above or below which no obvious effect was found. This might be related to the different behaviour of oxygen vacancies at different temperatures. Below 200 °C, oxygen vacancies migrate with difficulty and the electric field cannot separate them from the two specimen surfaces, so it has little effect on the transformation. Above 500 °C, oxygen vacancy migration is quite easy, and heat treatment can cause the oxygen vacancies to distribute uniformly in the specimen; thus no obvious difference is expected at high temperatures with or without an electric field.

3.3. Role of oxygen vacancies in low-temperature transformation of zirconia

According to Ruh and Gariett [1], Rauh and Garg [3], and Hillert [4], the oxygen vacancies in zirconia can lower the phase transition temperatures and enlarge the cubic and tetragonal phase areas in the Zr–ZrO_2 (see Fig. 4) binary phase diagram, so that the high-temperature phases are unstable at low temperatures. If conditions are sufficient, the metastable phases must undergo transformation at low temperatures.

According to the above results the kinetics of the transformation in an electric field is parabolic,

TABLE I Influence of temperature on the t → m transition of 3 mol % Y_2O_3–ZrO_2 in an electric field, $E = 300\ \mathrm{V\,cm^{-1}}$

t (h)	V_m(%)[a]																										
	100 °C			150 °C			200 °C			250 °C			300 °C			350 °C			400 °C			450 °C			500 °C		
	a	*c*	Δ	*a*	*c*	Δ	*a*	*c*	Δ	*a*	*c*	Δ	*a*	*c*	Δ	*a*	*c*	Δ	*a*	*c*	Δ	*a*	*c*	Δ	*a*	*c*	Δ
0	1.0	0.0	1.0	0	0.5	0.5	2.0	0.8	1.2	0.4	0	0.4	0.0	0.0	0.0	0.8	0.5	0.3	0	0	0	0	0	0	0	0	0
1	1.0	0.0	1.0	0	1.3	1.3	11	5.5	5.5	2.7	1.0	1.7	5.5	2.8	2.7	3.1	2.0	1.1	0	0	0	0	0	0	0	0	0
4	–	–	–	0	1.4	1.4	16	8.6	7.4	3.8	2.1	1.7	10	4.7	5.3	5.6	3.9	1.7	0	0	0	0	0	0	0	0	0

[a] *a*, *c* represent the monoclinic phase content at the anode and cathode surface, respectively; Δ is the difference.

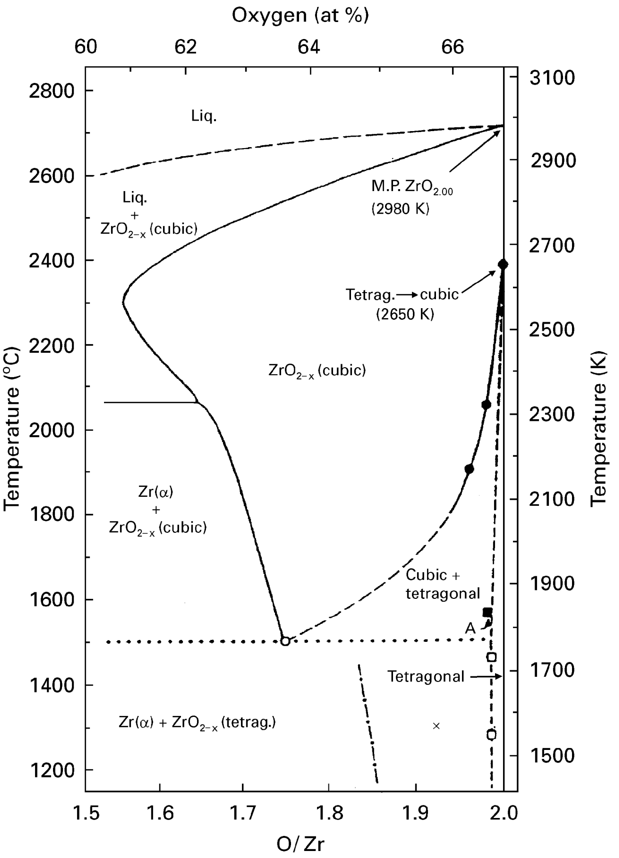

Figure 4 The Zr–ZrO_2, phase diagram after [3].

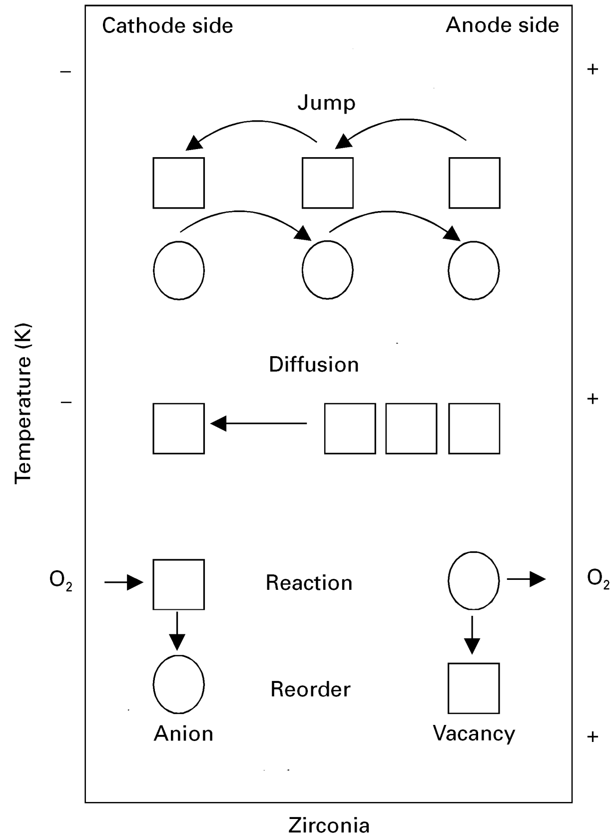

Figure 5 Behaviour of oxygen vacancies in the electric field.

indicating that there was a diffusion process involved in the transition. As in the electric field, only the oxygen vacancies can jump, migrate, redistribute, and make the concentrations near the two surfaces different (see Fig. 5), so the kinetic parabolic law might be reflected in the diffusion behaviour of the oxygen vacancies, and the obvious transformed phase difference might be due to the different oxygen vacancies content near the two surfaces.

When an electric field is applied, the oxygen vacancies migrate from the anode side to the cathode side. The concentration of oxygen vacancies near the anode side decreases, while at the cathode side it increases. According to the Zr–ZrO_2 phase diagram, the decrease in the oxygen vacancies, causes increasing instability of the high-temperature phases at the same temperature. Therefore, some metastable tetragonal phase near the anode side transformed directly to the monoclinic phase at the experimental temperature in the electric field. Otherwise, the increase in the oxygen vacancies near the cathode side might be able to increase the stability of the high-temperature phases at low temperature. However, it also decreased the M_s point at the same time, so some metastable tetragonal phase still underwent isothermal phase transformation, despite the amounts being less than that of the anode.

Although the above explanation may be incorrect, and there is still much work to do, one point which can be confirmed is that the oxygen vacancies play an important role in the transformation process of zirconia, and that they strongly affect the stability of the metastable phase at low temperatures.

4. Conclusion

Oxygen vacancies do have an influence on the stability of the metastable phase structures of zirconia, and play an important role in the isothermal phase transformation at low temperatures.

References

1. R. RUH and H. GARRETT, *J. Amer. Ceram. Soc.* **50** (1967) 257.
2. R. RUH, "Science and technology of zirconia II", edited by N. Claussen, M. Ruhle and A. H. Heuer (The American Ceramic Society, Columbus, OH, 1984). p. 544.
3. E. G. RAUH and S. P. GARG, *J. Amer. Ceram Soc.* **63** (1980) 239.
4. M. HILLERT, *ibid.* **74** (1991) 2005.
5. Y. B. CHENG and D. P. THOMPSON, *ibid.* **76** (1993) 683.
6. T. SATO and M. SHIMADA, *ibid.* **67** (1984) C-212.
7. T. SATO, S. OHTAKI and M. SHIMADA, *J. Mater. Sci.* **20** (1985) 1466.
8. R. M. DICKERSON, M. V. SWAIN and A. H. HEUER, *J. Amer. Ceram. Soc.* **70** (1987) 214.
9. N. NAKANISHI and T. SHIGEMATSU, *J. Mater. Trans. JIM* **32** (1991) 779.
10. *Idem. ibid.* **33** (1992) 318.
11. F. JOLLET, Ph. MAIER, M. GAUTIER, J. P. DURAUD and LEGRESSUA, *J. Amer. Ceram. Soc.* **71** (1988) C-396.
12. G. GANTOZZI, G. ORANGE, K. M. LIANG, *et al. ibid.* **72** (1989) 1562.
13. J. F. BAUMARD and P. ABELARD, in "Science and Technology of zirconia II", edited by N. Claussen, M. Ruhle and A. H. Heuer (The American Ceramic Society, Columbus OH, 1983) p. 555.
14. K. M. LIANG, K. F. GU, G. FANTOZZI and C. LEGRESSUS, "Transformation de phase t-m de la zircone sous champ electrique", presented at the 3rd European Interregion Colloquium on Ceramics, 28–30 May 1991. France, private communication.
15. G. FANTOZZI, C. OLAGNON, C. LECUIR, C. LEFRESSUS, G. BLAISE, K. M. LIANG and K. F. GU, "Electric field induced phase transformation in ceramics", presented at the Conference on Electrical Insulation and Dielectric Phenomena, 20–23 October 1991, Texas, USA, private communication.

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