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# Ageing behaviour of t′-phase in a hot-pressed $ZrO_2$(4 mol % $Y_2O_3$) ceramic

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The ageing behaviour of unequilibrium tetragonal (t′) phase and its resultant effect on the mechanical properties of hot-pressed $ZrO_2$(4 mol % $Y_2O_3$) ceramic have been investigated by means of transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffractometry (XRD). Experimental results show that t′-phase which is the product of diffusionless transformation from cubic (c) phase during rapid cooling after sintering is unstable when aged in a temperature range of 1400–1600°C for up to 80 h in that it decomposes diffusionally into equilibrium tetragonal(t) phase and c-phase. Yttria contents of phases formed during decomposition are basically in agreement with those indicated by phase diagram. The stability of t′-phase characterized by the existence of anti-phase domain microstructure under the microscopic dark field image is significantly associated with the tetragonality(*c*/*a*) measured by XRD and the larger the tetragonality, the more unstable the t′-phase. Metastable precipitates of t-phase are triggered by applied stress to transform to monoclinic (m) phase during which the fracture toughness is enhanced and transformability of t-phase is critically dependent upon the solute content as well as size. It is found that when t′- and m-phase coexist with adequate fractions of c- and t-phase, the fracture toughness of the aged specimen demonstrates a peak value that moves to shorter ageing times with increasing temperature while the Vickers hardness decreases monotonically with ageing time regardless of ageing temperature due to grain growth.

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## 1. Introduction

Zirconia possesses the character of polymorphy, namely cubic (c), tetragonal (t) and monoclinic (m) at high, middle and low temperatures, respectively, among which the stress-induced t- to m-phase transformation is the origin of toughening [1]. The transition from c- to t-phase can be either diffusional or diffusionless in yttria-containing zirconia, depending upon the cooling condition [2, 3]. The precipitates of t-phase in the form of "colony" structure from c-phase are metastable and thus transformable. However, the diffusionless product of c- to t-phase transition, which was termed t′-phase by Miller and Smielek [4], possesses the same yttria content as the c-phase and is stable against transformation to m-phase no matter how large the applied stress is; therefore, no transformation toughening can occur. The stability of t′-phase arises from the smaller tetragonality compared with that of t-phase with the same yttria content as well as the relaxation of transformation strain energy by the existence of coordinating twins [5, 6]. The appearance of anti-phase domain microstructure typical of t′-phase in the dark field image taken by the {1 1 2} type forbidden spot can be attributed to the shift of oxygen ions in the opposite direction along the same axis. Theoretically speaking, t′-phase is the transitional phase between the c- and t-phases, and is thermodynamically unstable. The aim of the present paper is to investigate the changes of microstructure and mechanical properties of $ZrO_2$(4 mol % $Y_2O_3$) ceramic with ageing techniques by carrying out the ageing treatment of t′-phase in the region of c- plus t-phase to ensure that the diffusional phase separation can take place.

## 2. Experimental procedure

Powders of $ZrO_2$(4 mol % $Y_2O_3$) ceramic with an average diameter of about 0.1 μm were hot-pressed into a pellet 120 mm in diameter and 6 mm thick, followed by water cooling with nitrogen as the protective atmosphere, during which a pressure of 25 MPa was simultaneously imposed and a holding time of 1 h was maintained. The specimen for TEM observation was prepared by conventional ion thinning to perforation and coated with a thin film of carbon. The fractions of c-, t-, t′- and m-phase were calculated using the following formulas [7] :

$$\frac{M_m}{M_{c\bar{t}}} = 0.82\,\frac{I_m(1\,1\,\bar{1}) + I_m(1\,1\,1)}{I_{c\bar{t}}(1\,1\,1)}$$

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$$\frac{M_{\mathrm{c}}}{M_{\bar{\mathrm{t}}}} = 0.88\ \frac{I_{\mathrm{c}}(4\,0\,0)}{I_{\bar{\mathrm{t}}}(4\,0\,0) + I_{\bar{\mathrm{t}}}(0\,0\,4)}$$

$$\frac{M_{\mathrm{t}}}{M_{\mathrm{t}'}} = \frac{I_{\mathrm{t}}(0\,0\,4) + I_{\mathrm{t}}(4\,0\,0)}{I_{\mathrm{t}'}(0\,0\,4) + I_{\mathrm{t}'}(4\,0\,0)}$$

and

$$I_{\bar{\mathrm{t}}}(4\,0\,0) = I_{\mathrm{t}}(4\,0\,0) + I_{\mathrm{t}'}(4\,0\,0)$$

$$I_{\bar{\mathrm{t}}}(4\,0\,0) = I_{\mathrm{t}}(0\,0\,4) + I_{\mathrm{t}'}(0\,0\,4)$$

where $I$ refers to relative peak intensity and where $M_{\mathrm{m}}$, $M_{\mathrm{c}}$, $M_{\mathrm{t}}$ and $M_{\mathrm{t}'}$ represent the fractions of m-, c-, t- and t′-phase, respectively and $M_{\mathrm{c}\bar{\mathrm{t}}}$ refers to the addition of c-, t- and t′-phase fraction, while $M_{\bar{\mathrm{t}}}$ is the addition of the fraction of t- and t′-phases. The tetragonality ($c/a$) of t′-phase was calculated using the plane distances of the (0 0 4) and (4 0 0) peaks, i.e. $c/a = d(0\,0\,4)/d(4\,0\,0)$. The yttria content of t′-phase was simultaneously calculated using the following formula [7]:

$$\mathrm{wt\,\%\ Y_2O_3} = 408.37 - 396.7\,c/a\,(\pm 0.2\,\mathrm{wt\,\%\ Y_2O_3})$$

The Vickers hardness was measured using the Hv-50 type indentor with 10 kg as indenting load and 5 s as acting time. At the same time, the fracture toughness was also calculated using the indentation method [8].

## 3. Results and discussion

### 3.1. Microstructure of sintered specimen

TEM observation of $ZrO_2$(4 mol % $Y_2O_3$) ceramic sintered at 1700°C reveals the lath-like contrast in the bright field image which is characteristic of low carbon steel martensite as shown in Fig. 1a and d. The formation of coordinating twins by different variants to minimize the strain energy is responsible for the appearance of this kind of contrast, which is composed of alternating bright and dark bands. Miller and Smielek [4] refer to the above microstructure as the unequilibrium tetragonal phase or t′-phase, which is the product of diffusionless transformation from cubic (c) phase. The dark field image as shown in Fig. 1c taken by {1 1 2} type forbidden spot for a fcc lattice along the [1 1 0] direction also appears to consist of twin variants in which the microstructure of the anti-phase domain can be observed. Fig. 2 shows the XRD profiles in which only two peaks of (0 0 4) and (4 0 0) planes can be found in a large angle area from 72° to 76° without any peaks of monoclinic phase appearing in a small angle area, which further confirms the results of TEM

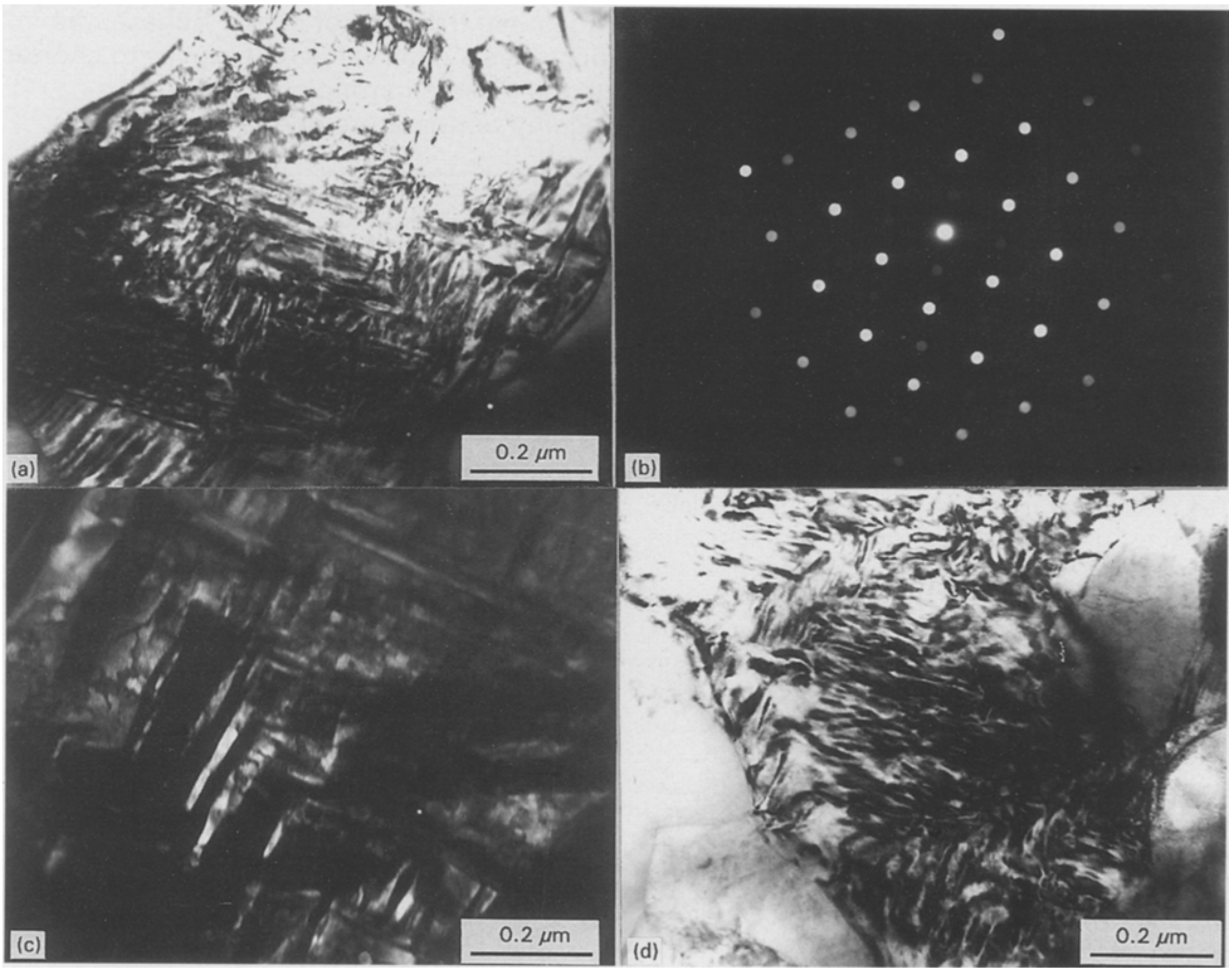

*Figure 1* TEM photographs of $ZrO_2$(4 mol % $Y_2O_3$). Ceramic hot-pressed at 1700 °C. (a) bright field image; (b) diffraction pattern of [1 1 0] direction; (c) dark field image taken by using (1 1 2) spot; (d) bright field image of another grain.

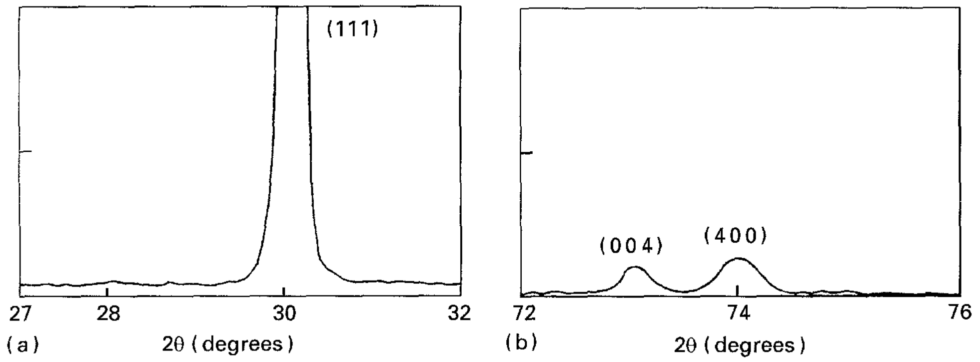

*Figure 2* XRD profiles of $ZrO_2$(4 mol % $Y_2O_3$) ceramic sintered at 1700 °C. (a) Small angle area; (b) large angle area.

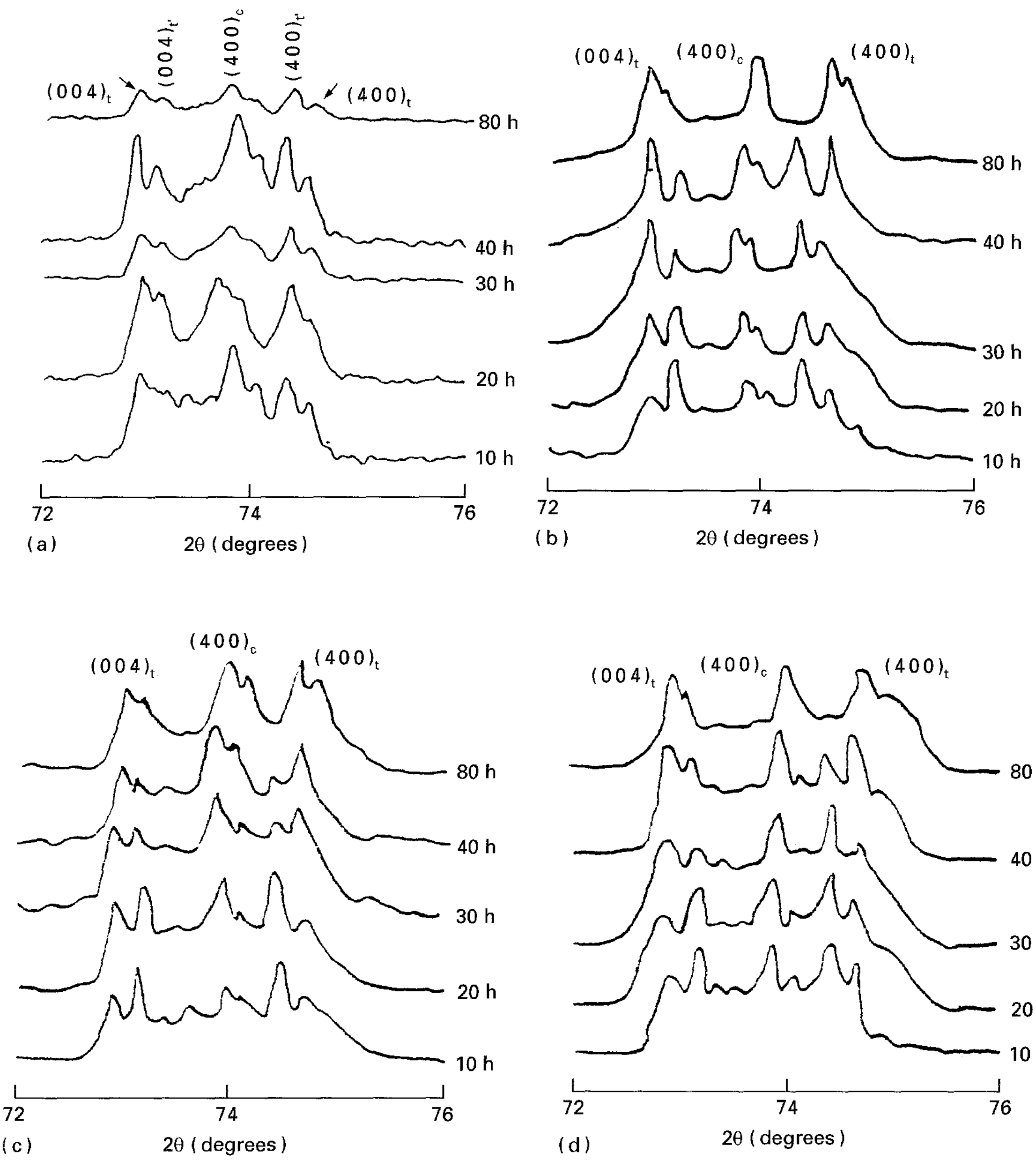

*Figure 3* XRD profiles of hot-pressed $ZrO_2$(4 mol % $Y_2O_3$) ceramic aged at different temperatures for different times. (a) 1300 °C; (b) 1400 °C; (c) 1500 °C; (d) 1600 °C.

observation that only t′-phase exists in the sintered specimen.

## 3.2. Effect of ageing techniques on constituents of phases

XRD profiles of $ZrO_2$(4 mol % $Y_2O_3$) ceramic aged at different temperatures for different times and the variation of constitutents are of phases with ageing times at different temperatures shown in Figs 3 and 4, respectively, from which it is clear that fractions of both c- and t-phases increase while that of the t′-phase decreases after ageing. Results indicate that diffusional phase separation has taken place in that the t′-phase decomposes into the yttria-rich c-phase and yttria-poor t-phase. The rate of decomposition increases obviously with increasing temperature, which can be attributed to the fact that the role of temperature is more effective than that of time. As for ageing at 1300°C, no m-phase is detected even if the ageing time is extended to 80 h. The case is quite different for ageing at higher temperatures because small amounts of m-phase can be found beyond a certain ageing time depending on the ageing temperature. Results of XRD measurements for $Y_2O_3$ content in

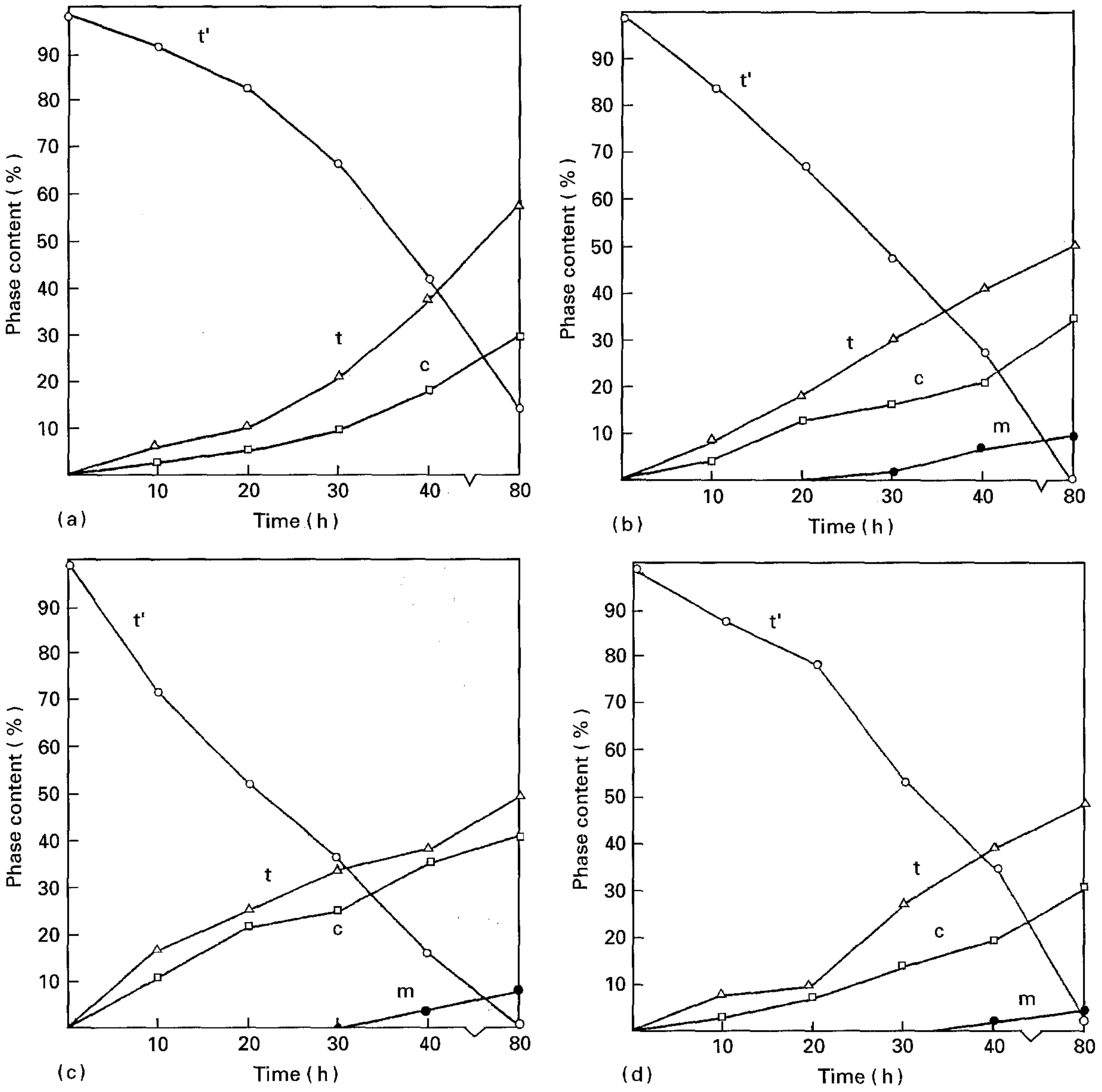

*Figure 4* Changes in phase composition with ageing times for hot-pressed $ZrO_2$(4 mol % $Y_2O_3$) ceramic aged at different temperatures. (a) 1300 °C; (b) 1400 °C; (c) 1500 °C; (d) 1600 °C.

TABLE I Results of XRD measurements for $Y_2O_3$ content and tetragonality ($c/a$) for specimen aged at different temperatures for different times

| Temperature | 1300 °C | | | 1400 °C | | | 1500 °C | | | 1600 °C | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (h) | Wt % $Y_2O_3$ | $\frac{d(004)}{d(400)}$ | $c/a$ | Wt % $Y_2O_3$ | $\frac{d(004)}{d(400)}$ | $c/a$ | Wt % $Y_2O_3$ | $\frac{d(004)}{d(400)}$ | $c/a$ | Wt % $Y_2O_3$ | $\frac{d(004)}{d(400)}$ | $c/a$ |
| 10 | 6.75 | $\frac{1.3031}{1.2874}$ | 1.0124 | 6.59 | $\frac{1.3027}{1.2864}$ | 1.0128 | 6.41 | $\frac{1.3031}{1.2862}$ | 1.0132 | 5.76 | $\frac{1.3047}{1.2855}$ | 1.0149 |
| 20 | 6.56 | $\frac{1.3033}{1.2868}$ | 1.0129 | 6.35 | $\frac{1.3035}{1.2862}$ | 1.0134 | 6.16 | $\frac{1.3037}{1.2857}$ | 1.0139 | 5.56 | $\frac{1.3051}{1.2853}$ | 1.0154 |
| 30 | 6.43 | $\frac{1.3034}{1.2866}$ | 1.0132 | 6.19 | $\frac{1.3038}{1.2861}$ | 1.0138 | 5.79 | $\frac{1.3044}{1.2854}$ | 1.0148 | 5.36 | $\frac{1.3062}{1.2851}$ | 1.0164 |
| 40 | 6.32 | $\frac{1.3035}{1.2861}$ | 1.0135 | 6.08 | $\frac{1.3038}{1.2857}$ | 1.0141 | 5.61 | $\frac{1.3051}{1.2854}$ | 1.0153 | 5.21 | $\frac{1.3066}{1.2851}$ | 1.0167 |
| 80 | 6.24 | $\frac{1.3035}{1.2859}$ | 1.0137 | — | — | — | — | — | — | — | — | — |

the t′-phase and the tetragonality of the t′-phase of specimen aged at different temperatures for different times are given in Table I, which reveals that the yttria content decreases while tetragonality increases with either increasing temperature at a certain time or prolonging time at a certain temperature. In addition, the results imply that the influence of temperature is more evident than that of time. In view of the fact that the t′-phase is the product of a diffusionless transition from the c-phase, it is understandable that the yttria content of the t′-phase is the same as that of the c-phase and the tetragonality shows the minimum value. It should be noted that both the reduction of yttria content and increase in tetragonality result from the decomposition of t′-phase aged in the temperature range 1300–1600 °C. The tetragonality directly reflects the severity of distortion of the lattice and the higher the former, the larger the latter. It is argued by some literature [9] that when tetragonality is larger than 1.016, the tetragonal phase will become transformable. It is apparent from Table I that tetragonality has already exceeded the proposed value when the specimen is aged beyond 30 h at 1600°C with the t′-phase still remaining untransformable. The divergence between the present results and the previous study can only be accounted for by the deduction that tetragonality is not the sole criterion that defines whether a phase belongs to the t′- or the t-phase. Actually, the difference between the t- and the t′-phase first lies in their morphologies as well as the submicrostructures, i.e. the t′-phase usually takes the form of parallel lathes arising from the presence of inter-compensating twin variants in the bright field image; furthermore, the appearance of an anti-phase domain structure in the dark field image taken by {1 1 2} type forbidden spot is always accompanied by the existing twins. By contrast, there is no particular feature for t-phase in the bright field image which corresponds exactly to the dark field image taken by the {1 1 2} spot with the implication that the whole grain itself is one of variants of t-phase. Second, t′-phase is so stable against transition to m-phase that no transformation toughening takes place no matter how large the applied stress is. The inertness of this unequilibrium phase can be attributed on the one hand to a high yttria content, and on the other hand to the formation of coordination twins by the variants to partly relieve the distortion stress. However, t-phase is metastable and t → m phase transformation can be rendered to produce a toughening effect. Considering that the kinetics of the decomposition of t′-phase is mainly controlled by the volume diffusion of yttrium ions, it is reasonably understood that the process of disintegration will become slower as time goes on, which is in good agreement with our experimental results. This phenomenon can be further explained by the fact that the diffusion coefficient of yttrium ions itself is rather small because yttria possesses the character of both ionic and covalent bonds; apart from this, the motivation for the diffusion, which comes mainly from the concentration gradient of yttria between the t- and t′-phase, decreases considerably with the decrease in the yttria content of the t′-phase.

## 3.3. TEM observation of aged specimen

TEM photographs of 1500 °C, 40 h aged specimen are shown in Fig. 5, which reveals that t-phase precipitates within the original territory of t′-phase and EPMA results indicate that yttria content of precipitates is almost identical to that of the equilibrium phase governed by the phase diagram [10]. There also exists a tendency for t-phase to preferentially precipitate within the t′-phase close to the grain boundaries, probably due to the comparatively larger diffusion coefficient of yttrium along grain boundaries, while the inner part of the grain still remains t′-phase as shown in Fig. 5a. Fig. 5b is a dark field image taken by {1 1 2} type forbidden spot, in which the untransformed t′-phase shows the twinning contrast corresponding to Fig. 5a. TEM photographs of a 1500 °C, 80 h aged specimen are shown in Fig. 6, from which it can be seen that the t′-phase has almost completely decomposed to form the microstructure of c- plus t-phase. Some precipitates of t-phase have transformed martensitically to m-phase during cooling as shown in Fig. 6c. In some cases, the distribution of precipitates demonstrates some degree of orientation

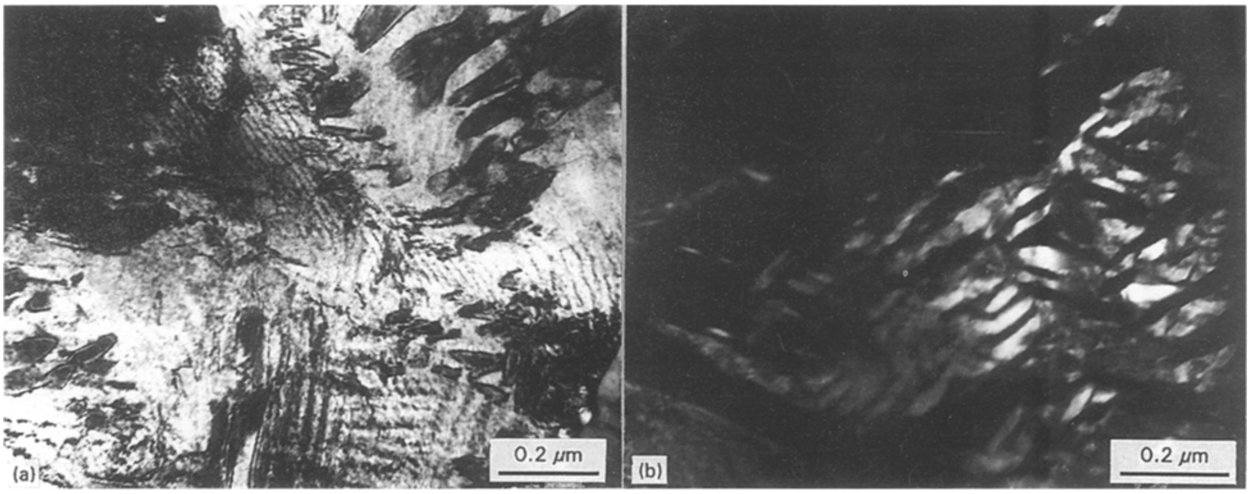

*Figure 5* TEM photographs of hot pressed $ZrO_2$(4 mol % $Y_2O_3$) ceramic aged at 1500 °C for 40 h. (a) bright field image; (b) dark field image taken by using (1 1 2) spot.

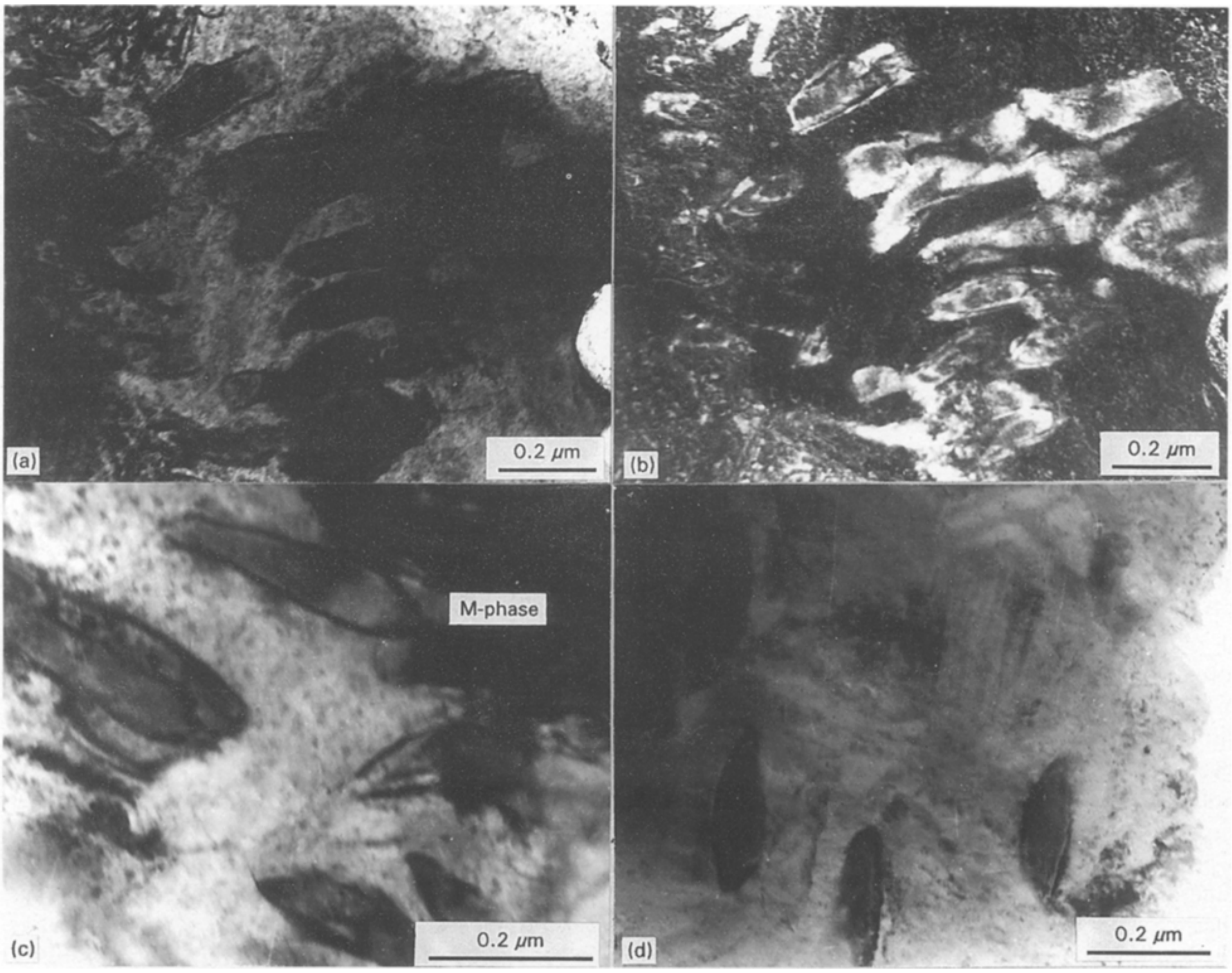

*Figure 6* TEM photographs of hot-pressed $ZrO_2$(4 mol % $Y_2O_3$) ceramic aged at 1500 °C for 80 h. (a) bright field image; (b) dark field image corresponding to the area in (a) showing the precipitation of t-phase; (c) formation of m-phase; (d) directional distribution of t-phase precipitates.

in correlation with the matrix phase to minimize the interfacial energy, as shown in Fig. 6d.

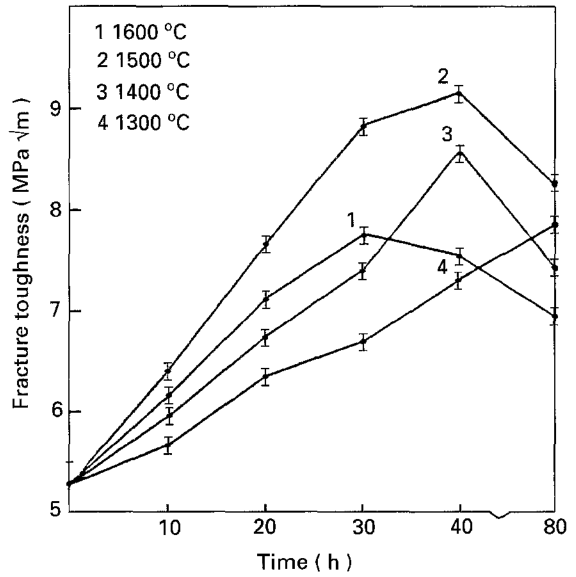

*Figure 7* Changes of fracture toughness with ageing times for hot-pressed $ZrO_2$(4 mol % $Y_2O_3$) ceramic aged at different temperatures.

## 3.4. Effect of ageing techniques on mechanical properties

Fig. 7 shows the changes of fracture toughness with ageing time at different temperatures. Owing to the lack of a toughening effect of t'-phase, the fracture toughness is low in the sintered state. As the fraction of t-phase that can be stress-triggered to transform to m-phase increases, the fracture toughness improves steadily. Except for the case of ageing at 1300°C, in which the fracture toughness increases monotonically with ageing times, the fracture toughness approaches a peak value which moves to shorter times as the temperature goes up. It is found that t'- and m-phase coexist with a medium fraction of c- and t-phase at peak-aged time and in addition m-phase formed spontaneously during cooling can just be detected. The appearance of the peak value of the fracture toughness in the context of the coexistence of four phases might be caused by the improved stress state of the peak-aged specimen. A deeper insight into this new finding needs further investigation both experimentally and theoretically. The drop in fracture toughness for an over-aged specimen can well be explained by the fact that the fraction of precipitates whose sizes are larger than the critical sizes for spontaneous t → m phase transformation increases and the toughening effect accordingly becomes less obvious. The Vickers hardness decreases monotonically with ageing times regardless of temperature, as shown in Fig. 8. Both the coarsening of grains as shown in Fig. 9 for over-aged

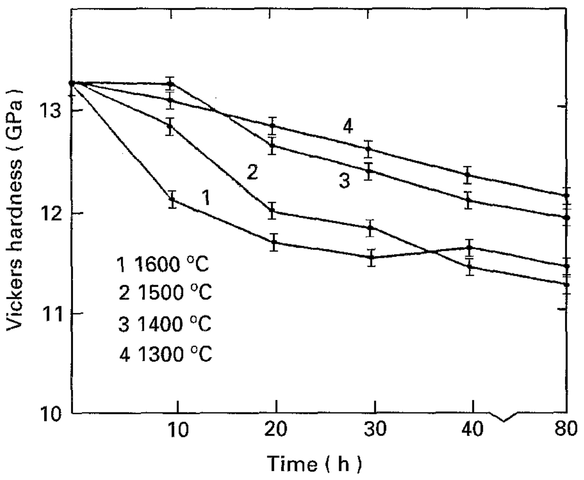

*Figure 8* Changes of Vickers hardness with ageing times for hot-pressed $ZrO_2$(4 mol % $Y_2O_3$) ceramic aged at different temperatures.

specimens and microcracks produced by spontaneous transformation of t-phase contribute to the decrease in the Vickers hardness.

## 4. Conclusions

1. There exists only unequilibrium tetragonal (t′) phase, which is the product of diffusionless transformation from cubic (c) phase in the sintered specimen. The t′-phase is significantly different both in morphology and stability from the equilibrium tetragonal (t) phase.

2. The t′-phase decomposes diffusionally into c- and t-phase during ageing in the temperature range 1300–1600 °C for up to 80 h. The tetragonality and yttria content of t′-phase increases and decreases, respectively, with ageing times.

3. The fracture toughness reaches a peak value when t′- and m-phase coexist with a medium fraction of

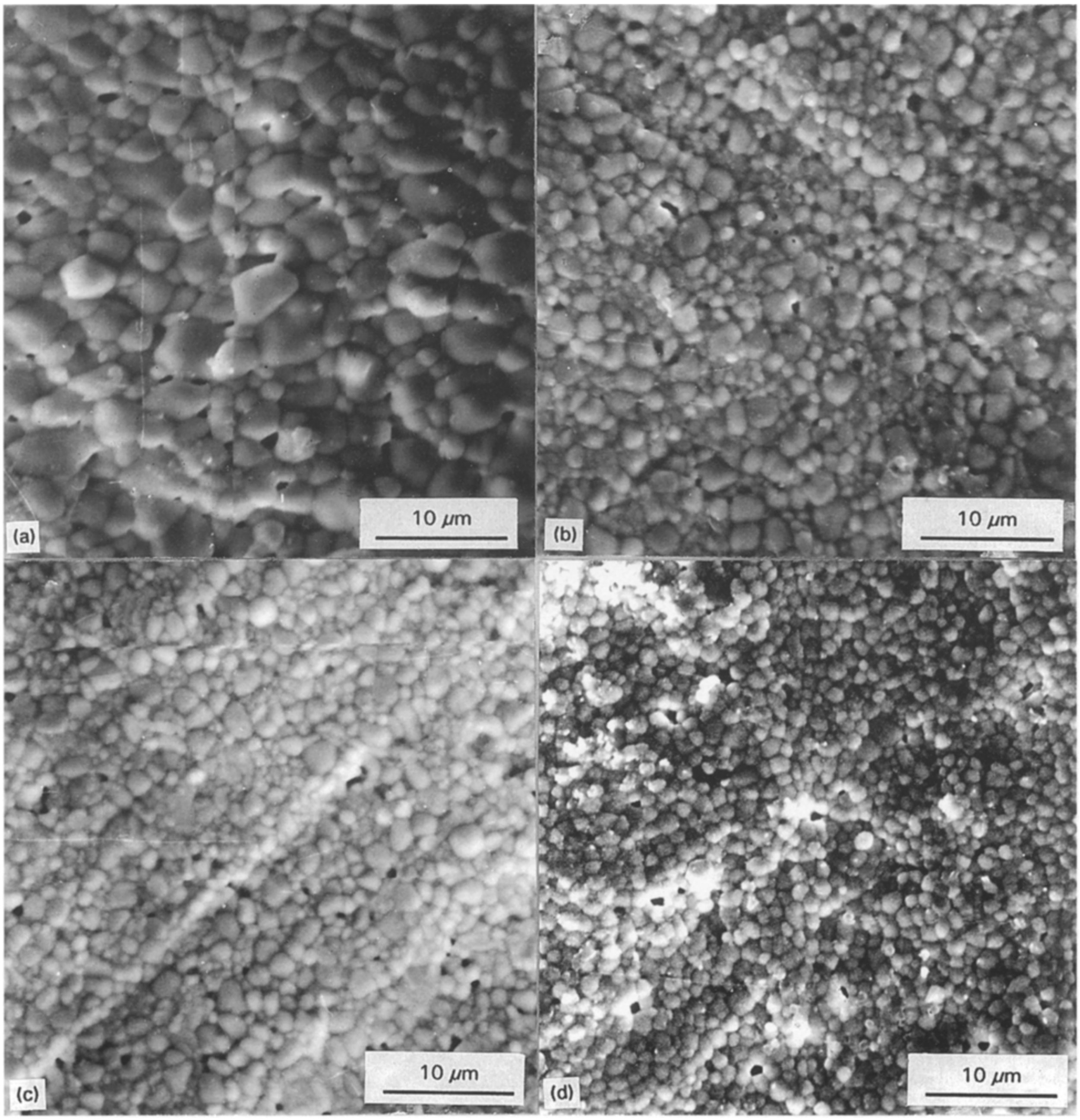

*Figure 9* SEM photographs showing the surface of hot-pressed $ZrO_2$ (4 mol % $Y_2O_3$) specimen aged at different temperatures for 40 h. (a) 1600 °C; (b) 1500 °C; (c) 1400 °C; (d) 1300 °C.

c- and t-phase, while the Vickers hardness decreases monotonically with ageing times.

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