

Low-temperature ageing map for 3 mol % $Y_2O_3-ZrO_2$

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The ageing behaviour of 3 mol % $Y_2O_3-ZrO_2$ at 100–500°C in a water-containing atmosphere was studied. A critical grain size of $\sim 0.37 \mu m$ and a lower temperature limit of $\sim 80^\circ C$ for retaining the tetragonal symmetry were deduced from the kinetic study. An "ageing map" constructed on the grain size (G) against ageing temperature (T) plot is proposed to describe the low-temperature ageing behaviour of 3 mol % $Y_2O_3-ZrO_2$.

1. Introduction

Low-temperature, 150–400°C, ageing of Y_2O_3 -TZP resulting in mechanical property degradation has been extensively studied [1–4, 7, 9]. The ageing behaviour was found to be strongly dependent [1, 3, 4] on the grain size of the ceramic. When aged in air, critical grain size for the (t) \rightarrow (m) transformation was reported [3] to increase from 0.2 to $0.6 \mu m$ between a Y_2O_3 -content of 2 to 5 mol %. A critical grain size of $\sim 0.5 \mu m$ [1, 4] was also found from low-temperature ageing studies of a sintered 3 mol % $Y_2O_3-ZrO_2$. Correlation between density and bending strength of the aged samples further suggested [1–3, 5] that the (t) \rightarrow (m) transformation is responsible for the property degradation observed. The property degradation due to ageing in air observed only in the temperature range of 150–400°C [3] was interpreted by an infinite incubation time for the lower temperature limit and the martensite start temperature (M_s) for the upper limit [4].

The presence of water [2, 6, 9, 10] in the ageing environment plays a definite role in accelerating the degradation. Although stress corrosion [6] of glassy grain boundary phase, the formation of α -Y(OH)₃ [6, 10] or Zr(OH)₄ [2, 10], autocatalysis [7, 9] and, shortening the incubation time [9] were proposed to account for the acceleration effect; no mechanism has so far evolved to describe the ageing behaviour. We propose here an "ageing map" to describe the effect of water on the ageing behaviour of 3 mol % Y_2O_3 -TZP.

2. Experimental procedures

Toyo Soda (Tokyo, Japan) TZ3Y- ZrO_2 powder containing trace impurities of SiO₂ (100 p.p.m.), Fe₂O₃ (20 p.p.m.) and Na₂O (70 p.p.m.) was die-pressed at a pressure of ~ 100 MPa to discs and sintered at 1500°C for 0.5–20 h to yield different grain-size ceramics. Ageing treatment was conducted in air at 100–400°C [4], in an atmosphere of ~ 0.1 MPa water vapour at 100–500°C for 2 min to 30 h, and in water at 80–100°C for 0.5 h to a period of one week. XRD was used for the analysis of phase content and SEM for microstructure. Kinetic data of the (t) \rightarrow (m) transformation

were accumulated by determining the (m)- ZrO_2 content after each ageing treatment. Experimental details were described previously [4, 9] in the literature.

3. Results and discussion

3.1. General kinetics

The as-sintered sample contained $\sim 100\%$ tetragonal phase irrespective of the sintering schedule. The representative (t) \rightarrow (m) transformation kinetics is given in Fig. 1 for ageing of different grain-size samples at 180°C in water atmosphere. The characteristic sigmoidal shape (e.g. $0.49 \mu m$) signifies the existence of an incubation time before a measurable (m)- ZrO_2 content due to the (t) \rightarrow (m) transformation emerges [4]. When the incubation time became negligible, the kinetic curve (e.g. $1.15 \mu m$) can be approximated to a logarithmic function [2, 9]. The (t) \rightarrow (m) transformation rate, $(d/dt)(\Delta m)$, was taken as the first derivative of the kinetic curve. For $G_{av} = 0.83$ and $1.15 \mu m$, the transformation reached a maximum rate at 10 min when aged at 180°C in water, and its rate then decreased as the ageing proceeded. While for other four samples of $G_{av} = 0.49 \mu m$, $0.52 \mu m$, $0.58 \mu m$ and $0.69 \mu m$ respectively, the transformation rate increased to a maximum value before decreasing a negligible value after ageing for a longer period of 3–4 h (Fig. 2). That an incubation time [4] elapsed before appreciable transformation was detected for these four different grain-size samples, can again be evidenced. As for samples of $G_{av} = 1.15 \mu m$ and $0.83 \mu m$, the incubation times were too short to be recorded (indicated in Fig. 2). Considering the procedure of loading sample into the furnace, however, they were definitely less than 10 min.

Temperature had the same effect on the ageing kinetics. For the sample of $G_{av} = 1.15 \mu m$, the incubation time was not detected. The kinetics of $G_{av} = 0.83 \mu m$ sample changed from a sigmoidal to a logarithmic type when the ageing temperature was raised from 180 to 320°C. Similar extensive microcracks appeared on the sample surface after ageing to those observed previously [4].

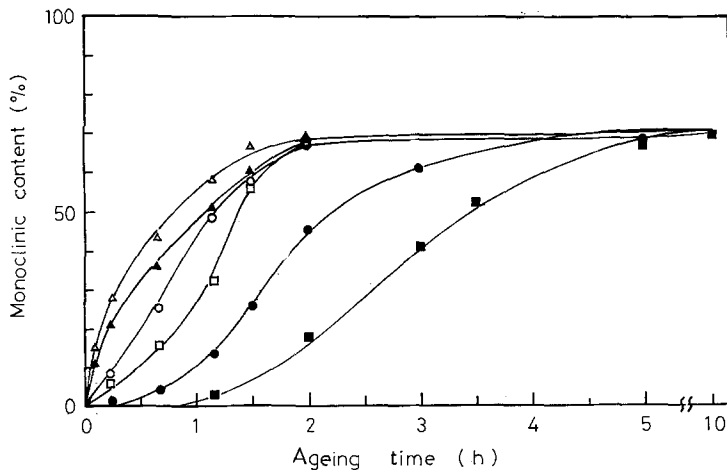


Figure 1 Representative ageing kinetics of 3 mol % Y_2O_3 -TZP at 180°C in water-containing atmosphere. (Δ 1.15 μm , \circ 0.69 μm , \square 0.58 μm , \blacktriangle 0.83 μm , \bullet 0.52 μm , \blacksquare 0.49 μm .)

3.2. Degradation temperature range

A plot of the monoclinic content against ageing temperature yielded the martensitic start temperature (M_s) for different grain size 3 mol % Y_2O_3 -TZP [4], as indicated in Fig. 3. The M_s here refers to the “constraint” rather than the “unconstraint” martensite start temperature usually addressed in phase diagrams. As shown in Fig. 3, the M_s for ceramic of 0.83 μm and 1.15 μm has apparently exceeded 500°C. For 3 mol % Y_2O_3 -TZP samples of grain size 0.52–1.15 μm aged at 500°C in air, no ageing-induced (t) \rightarrow (m) transformation was detected by XRD in the previous study [4]. The higher M_s for sample of similar grain size (e.g. 0.58 μm at 430°C, 0.69 μm at 500°C) was found in this study. The indication is that the martensite start temperature was affected by the presence of water in the ageing atmosphere. For the ageing in air, a G_{av} of 0.52 μm was reported to be the critical grain size for ageing degradation to occur. The fact that the M_s for sample of $G_{av} = 0.52 \mu m$ appeared at $\sim 280^\circ C$ (Fig. 3) when aged in water-containing atmosphere has again indicated the water effect on the M_s of the ceramic.

Water affecting the ageing behaviour in triggering off the (t) \rightarrow (m) transformation at a higher temperature is clear. In consequence, it resulted in a higher upper temperature limit [4] of ageing degradation.

3.3. Critical grain size and lower temperature limit

Extrapolation of the plot of maximum transformation rate, $[d/dt(\Delta m)]_{max}$, against average grain size, G_{av} , intersects with the abscissa at a critical grain size, $G_{critical} \sim 0.37 \mu m$ (Fig. 4). When the average grain size, $G_{av} < G_{critical}$, and the (t) \rightarrow (m) transformation rate was zero, the ageing degradation was then inhibited. Adopting the idea of infinite incubation time [4], $G_{critical} \sim 0.37 \mu m$ can also be deduced. The lower temperature limit of $\sim 80^\circ C$ was, furthermore, obtained by plotting $(\ln t)$ against ageing temperature (Fig. 5). The presence of water in ageing atmosphere has not only increased the upper temperature limit but also reduced the critical grain size and the lower temperature limit. The indication is that water has expanded the temperature range of ageing degradation when compared with the ageing in air.

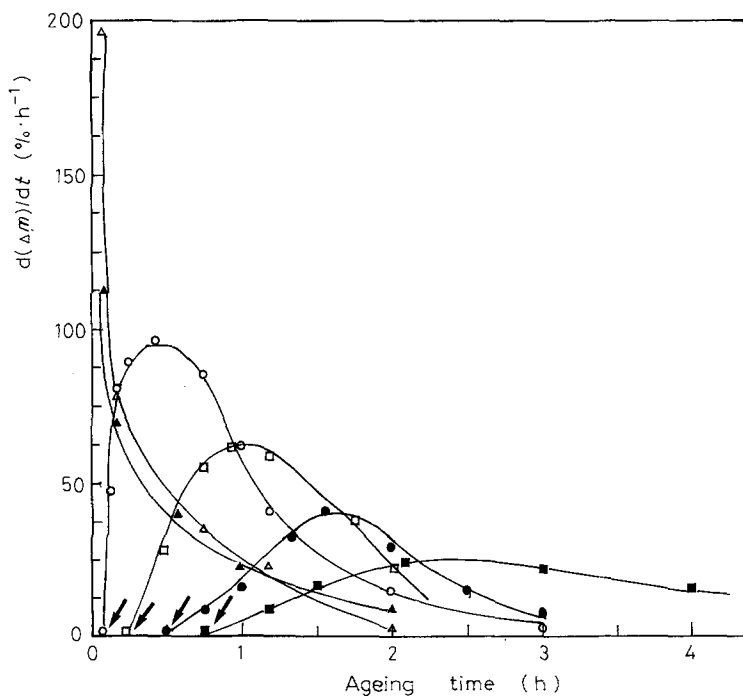


Figure 2 The (t) \rightarrow (m) transformation rate corresponding to the ageing kinetics in Fig. 1. (Symbols as for Fig. 1.)

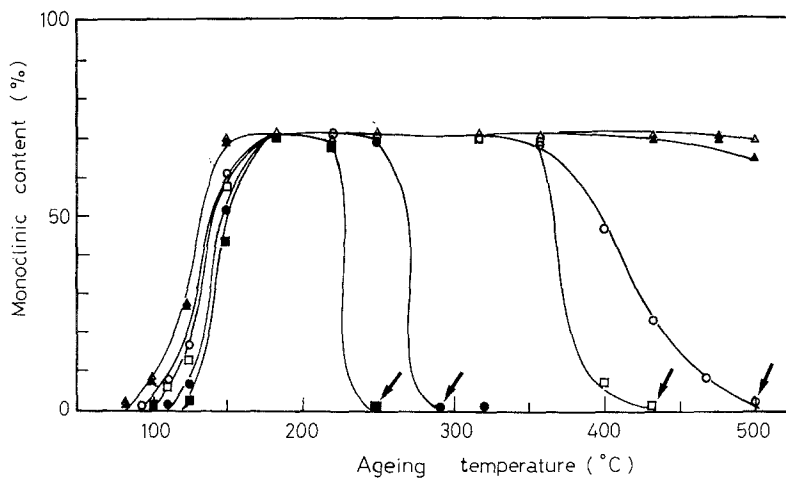


Figure 3 The lower transformation temperature and the M_s for aged 3 mol% Y_2O_3 -TZP samples aged 5h. (Symbols as for Fig. 1.)

3.4. Ageing map

The plot of G_{av} against ageing temperature presented in Figs 6 and 7 is addressed as the "ageing map" of 3 mol% Y_2O_3 -TZP aged in air and in water atmosphere. Plotting M_s and lower transformation temperature for ageing in air resulted in two regions denoted as I and II (Fig. 6). The lower transformation temperature was the temperature at which measurable $(t) \rightarrow (m)$ transformation was detected by XRD for a particular G_{av} sample aged in air [4]. Dotted line parallel to the abscissa (ageing temperature axis), is the extrapolation of the M_s dependence on grain size; since the critical grain size of $\sim 0.52 \mu m$ [2, 4] implies no M_s temperature for sample of $G_{av} < 0.52 \mu m$. For samples treated in Region II, no $(t) \rightarrow (m)$ transformation was induced, the low temperature degradation was then inhibited. Only the ageing treatment in Region I resulted in $(t) \rightarrow (m)$ transformation, and consequently, the property degradation occurred. The ageing kinetics was of the sigmoidal type in Region I, an incubation time was necessary.

When the same plot was constructed for ageing in water atmosphere, three regions, I, II and III of different significance as denoted in Fig. 7 were obtained. Similarly, the $(t) \rightarrow (m)$ transformation induced became appreciable only after a certain period of incubation time, is represented in Region I. Region III where ageing occurs with zero incubation time signifies that ageing kinetics is logarithmic. The dotted extension of the M_s dependence extrapolation became parallel to the abscissa (ageing temperature axis) at $G_{av} = 0.37 \mu m$ which was the critical grain size of infinite incubation time when aged in water atmosphere. The total region where ageing induced transformation occurs, has been expanded by the water presence in the ageing environment. For 3 mol% Y_2O_3 -TZP samples of relatively larger grain-size, low-temperature ageing degradation can only be prevented at temperature below $\sim 80^\circ C$ or at a much higher temperature than $500^\circ C$, due to the high M_s (Fig. 3).

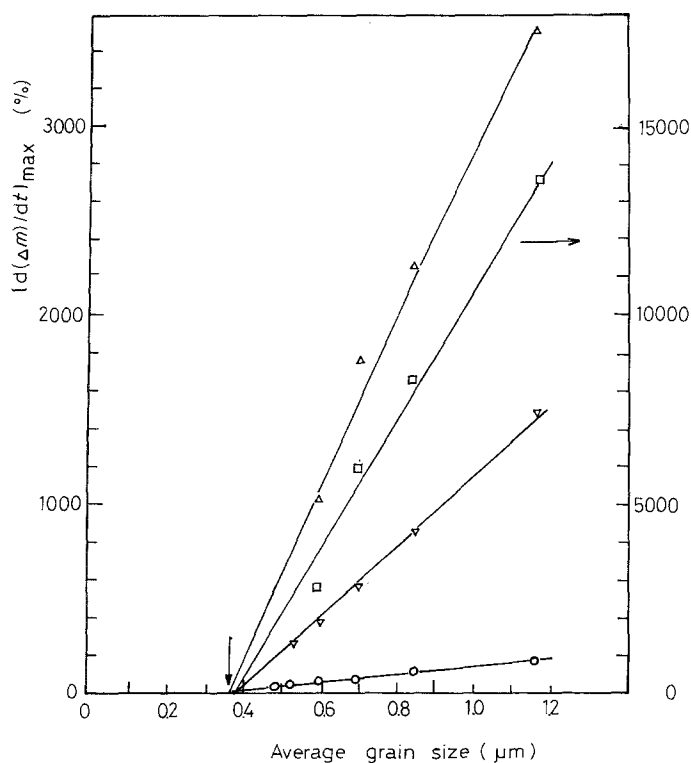


Figure 4 The critical grain size falls at $G_{av} \sim 0.37 \mu m$. (\circ $180^\circ C$, ∇ $250^\circ C$, Δ $320^\circ C$, \square $360^\circ C$.)

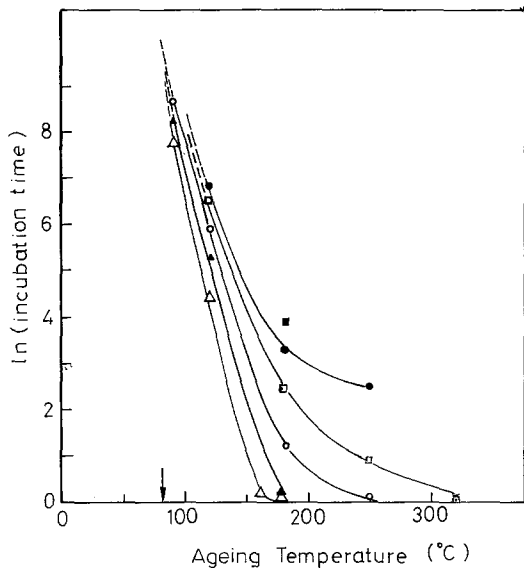


Figure 5 The lower temperature limit of $\sim 80^\circ\text{C}$ is deduced. (Symbols as for Fig. 1.)

4. Conclusions

(1) Water affected the ageing of 3 mol% Y_2O_3 -TZP by reducing the critical grain size to $\sim 0.37\ \mu\text{m}$, and the lower temperature limit to $\sim 80^\circ\text{C}$.

(2) The "constraint" M_s was increased by the presence of water in the ageing atmosphere.

(3) Low-temperature ageing behaviour of 3 mol% Y_2O_3 -TZP can be described by constructing an "ageing map" on the ageing temperature and grain size plot.

(4) Three regions of different significance in the ageing map were identified.

(5) The region where ageing property degradation

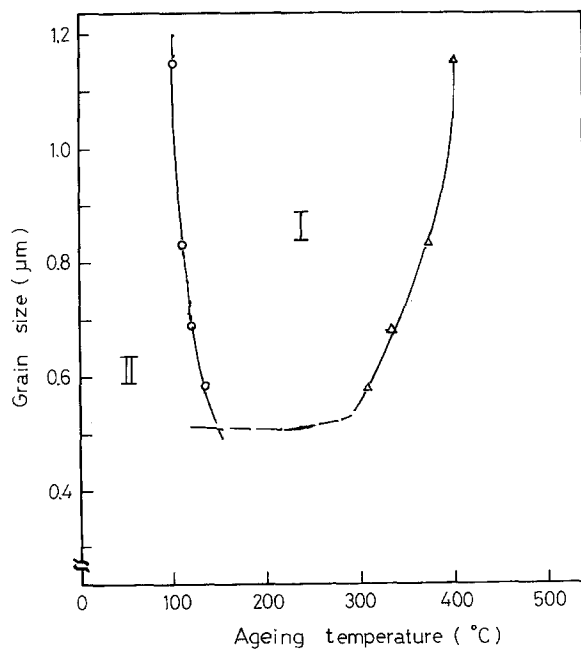


Figure 6 The ageing map for 3 mol% Y_2O_3 -TZP aged in air. (ΔM_s , \circ Lower transformation temperature.)

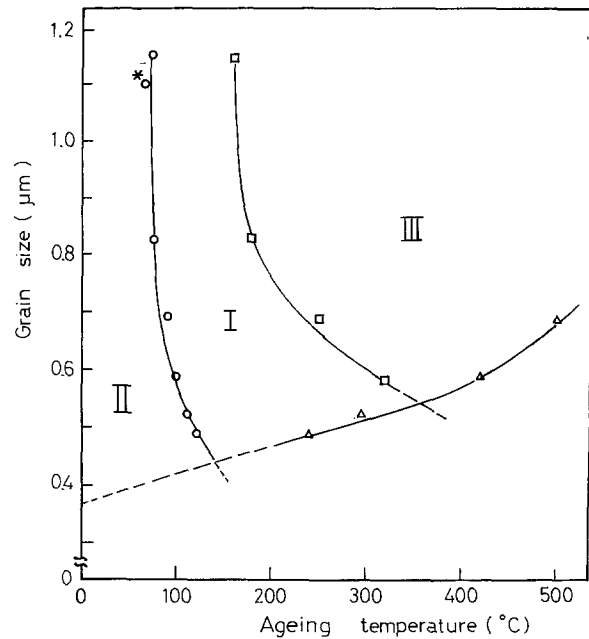


Figure 7 The ageing map for 3 mol% Y_2O_3 -TZP aged in water-containing atmosphere. *Indicates data from [2]. (\circ Lower transformation temperature, \square incubation time ≈ 0 , ΔM_s .)

occurred was expanded by the presence of water; the upper temperature limit was increased.

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