Isothermal Tetragonal-to-Monoclinic Phase Transformation in a Zirconia–Yttria System

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1. Introduction

Zirconia ceramics containing a small amount of yttria stabilizer are known to have excellent mechanical properties of strength and toughness. These properties are also known to be strongly related to the stress-induced transformation from the metastable tetragonal (T) to the stable monoclinic (M) phases.1-5) This transformation is usually called a martensitic transformation and is affected by many factors, e.g., yttria content, grain size, water environment, thermal history, third oxide addition and so on.6-14) The nature of this transformation is thus so complex that no clear view has been obtained. Furthermore, this transformation has hitherto been believed to proceed via an athermal mode particularly in pure zirconia and zirconia–yttria ceramics with low yttria content, i.e., a diffusionless mechanism.15,16) However, several studies have reported that the transformation proceeds isothermally in low yttria content ceramics of less than 3 mol%,17-25) though this isothermal mode has not been apparent. The control of the transformation is therefore fairly difficult though it should be very important for improvement of the mechanical properties of this ceramic.

The addition of a small amount of alumina to zirconia–yttria ceramics is known to lead to much higher bending strength, fracture toughness and other beneficial mechanical properties.26-30)

This article summarizes the isothermal transformation behavior in this zirconia–yttria system with and without alumina addition and discusses the transformation mechanism related to the mechanical properties.

2. T-to-M Transformation during Heating and Cooling Stages

Dilatation curves during heating and cooling stages at different rates in various yttria content ceramics are shown in Figs. 1-4. The curves for zirconia-1 and 1.5 mol% yttria

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Fig. 1 Dilatation curves accompanying the tetragonal–monoclinic phase transformation of zirconia-1 mol% yttria (1Y) (a) and 1.5 mol% yttria (1.5Y) (b) at various heating and cooling rates.
specimens (denoted 1Y and 1.5Y) show similar dilatation changes with temperature, i.e., a shrinkage during the heating stage at the temperature denoted As and an expansion at Ms during the cooling stage (Fig. 1). Furthermore, the amounts of this expansion and shrinkage in the two specimens are also similar, regardless of different heating and cooling rates. These dilatation changes around As and Ms are due to the \( M \to T \) and \( T \to M \) transformations, respectively. However, the curves of zirconia-2, 3 and 4 mol% yttria (denoted 2Y, 3Y and 4Y) sintered at 1973 K for 54 ks are greatly different from those in Fig. 1, i.e., their dilation changes depend strongly on the heating and cooling rates (as shown in Figs. 2, 3 and 4). The amounts of shrinkage and expansion accompanying \( T \to M \) transformation become less or disappear with an increase in the heating and cooling rates. The dilatation curves for specimens sintered at lower temperature, 1673 K for 18 ks, showed no change (not shown here) even though the specimens were cooled at a slower rate. The grain size of the T-phase increases as the yttria content decreases and the sintering temperature increases, as shown in Fig. 5. It is generally found that the smaller the grain size of the T phases, the more difficult is the transformation,\(^{28,31–35}\) so the transformation in the specimens sintered at 1673 K does not proceed. The \( T \to M \) transformation in the as-sintered specimens (forced-air-cooled from the sintering temperature) has been found to occur at a lower yttria content of less than 1.5 mol% but not in higher yttria specimens, as shown in Fig. 6. The amount of transformation (M%) was estimated by the relative X-ray diffraction (XRD) intensities of (111)\( _t \), (111)\( _m \) and (111)\( _h \).\(^{36}\) Based on Fig. 6, people may believe that the transformation would have occurred by the athermal mode, i.e., diffusionless transformation, in specimens with less than 1.5 mol% yttria.

Interestingly, during the heating stage in the specimens of higher yttria contents, the expansion around 500–600 K can be observed in Figs. 2–4. These phenomena are related to an isothermal \( T \to M \) transformation mode described in the next section.

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**Fig. 2** Dilatation curves of zirconia-2 mol% yttria (2Y) at various heating and cooling rates.

**Fig. 3** Dilatation curves of zirconia-3 mol% yttria (3Y) at various heating and cooling rates.

**Fig. 4** Dilatation curves of zirconia-4 mol% yttria (4Y) at various heating and cooling rates.
3. Isothermal T-to-M Transformation

Isothermal aging transformation curves at various temperatures obtained by XRD are shown in Fig. 7. Even in the as-sintered 1Y and 1.5Y (Fig. 7(a),(b)) the transformation has proceeded to about 83% and 8%, respectively, but there is no transformation in other as-sintered specimens (Fig. 7(c)–(e)). In all specimens, the amount of transformation increased obviously with an increase in isothermal aging time. The change in M% with aging time is represented as a sigmoidal curve at all temperatures. The time-temperature-transformation (T-T-T) curves obtained from Fig. 7 show a typical C-shape with a higher nose temperature in lower yttria content, as shown in Fig. 8; these results suggest that some thermally activated processes act in this transformation, based on the literature.\(^{37}\) The C-curves under the same sintering condition shift to shorter aging time and higher temperature as the yttria content decreases, resulting in a high speed transformation following the T-T-T diagrams. Even in 0.5Y sintered at lower temperature (1473 K), M% was 95% in the as-sintered condition (Fig. 6) but it increased to 100% on aging at 573 K, so all the zirconia–yttria ceramics containing yttria down to 0.5 from 4 mol% yttria shown here do transform isothermally.

In Fig. 8, the starting temperatures of this transformation (Ms) during the cooling stage obtained from the dilatation curves in Figs. 1–4 are also superimposed on each cooling rate curve. The Ms temperatures coincide well with the C-
curves above the nose temperature in all specimens. Therefore, the T ⇒ M transformation during the cooling stage over 1 mol% yttria must be closely related to these T-T-T curves, but the transformation during the cooling stage at high rates is suppressed in the ceramics with higher yttria content. It is suggested from these results that the T-to-M transformation during the cooling stage proceeds by an isothermal mode. In general, when the cooling curve intersects with the C-curve at higher M% with lower yttria content, the expansion due to the T ⇒ M transformation can be observed; at lower M% with higher yttria content, however, the dilatation curve at higher rates than 0.66 K/min was almost linear, as shown in Fig. 4. This is because the transformation proceeds from the specimen surface to the specimen interior, as shown in Fig. 9; the transformation takes place easily with increasing time in the thermal cycling of heating and cooling. The isothermal aging curve obtained by conventional XRD indicates the transformation at the specimen surface including about an 8 μm depth. At lower M%, the transformation of the specimen interior then does not transform within this period of aging, resulting in no dilatation change in the specimens with higher yttria content.

Isothermal aging curves in different environments, in air, vacuum (8 mPa) and water, are shown in Fig. 10. The results in which M% increases sigmoidally with aging time in different environments also indicate similar C-shaped curves, although they shift to a shorter time in water and to a longer time in vacuum. It has been reported that the transformation does not occur in vacuum, but it does occur in the specimens with larger grain size such as 1.4 μm even in vacuum. It is well-known that a water environment accel-

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Fig. 8 T-T-T curves obtained from isothermal aging curves. Ms temperatures obtained from dilatation curves are superimposed on various cooling rates of 10.7, 5.33, 2.67, 1.33, 0.66 and 0.17 K/min.

Fig. 9 Relationship between the amount of monoclinic phase and depth from the surface after various heating and cooling cycle times between room temperature and 1073 K, indicating that the T-to-M transformation proceeds from the specimen surface to the interior.

Fig. 10 Isothermal aging curves at 400 and 473 K in 3Y aged in water, air or vacuum (8 mPa) environment. (Mean grain size is about 1.4 μm.)
erates the transformation and results in the degradation of mechanical properties. Several degradation mechanisms have been proposed: a disbonding of the Zr-O-Zr(Y) binding couples or the formation of Y(OH)$_3$ due to the penetration and diffusion of H$_2$O, OH$^-$, or O$^2-$ through the zirconia matrix, though the model has not yet been clarified.

Apparent activation energy was estimated to be 88–100 kJ/mol from the T-T-T curves below the nose temperature, irrespective of different environments. These values are coincident with published activation energies obtained from impedance conductivity measurements in ZrO$_2$. 1–5 mol%Y$_2$O$_3$ (91 kJ/mol in 1Y, 43) 48–91 kJ/mol in 1.4Y, 44) 95 kJ/mol in 2Y, 45) 60–113 kJ/mol in 3Y, 46) 89 kJ/mol in 2.8Y, 47) 102 kJ/mol in 5Y and 80–105 kJ/mol in 3Y), i.e., those for diffusion of oxygen ion vacancies in partially stabilized zirconia. Another results by the impedance conductivity measurements show that the activation energy in the M-phase is smaller than that in the T-phase. So, the activation energies in PSZ are different depending on the existing different phases. Then, it can be considered that this T $\Rightarrow$ M transformation proceeds by a thermally activated diffusion process.

Many time-transformation isotherms in alloy systems have been described by the Johnson-Mehl equation:

$$f = 1 - \exp(-bt^n)$$

(1)

where $f$ is the fraction transformed, $t$ is time, and $b$ and $n$ are constants. An approximately linear relationship between log log(1/(1 $-$ $f$)) and log $t$ is found, as shown in Fig. 11. Similar results were obtained in other aging specimens. From the slope of the straight lines, about 1.4 is obtained as the $n$-value, independent of different environments. The value of $n$ in the kinetic law of eq. (1) varies with the shape of the transformation products and nucleation sites, i.e., $n = 1$ means the thickening of long cylinders or needles in a homogeneous reaction or the grain boundary surface nucleation in a heterogeneous reaction, and $n = 1.5$ means growing of spherical particles in a homogeneous reaction or further grain edge nucleation in a heterogeneous reaction. Figure 11 shows that the value of $b$ decreases with the change from water to a vacuum environment but is almost the same $n$-value irrespective of different environments; this means that the nucleation rate increases in a water environment, i.e., the water environment affects the nucleation stage. Namely, a water environment acts as a trigger for the initiation stage of transformation but not the growth stage, based on the obtained $b$ and $n$-values and the activation energy. Very similar results were observed in different yttria content specimens aged even under the same condition; the $b$-value increases but the $n$-value is almost the same as the yttria content decreases. These results mean that the nucleation of the transformation laths is accelerated in the specimens with lower yttria content.

4. Growth Mode of Transformation Lath

Typical AFM micrographs are shown in Fig. 12. Thermally etched grain boundary grooves can be clearly seen. Each micrograph in this figure shows the same area of the specimen surface at various aging times. With an increase in aging time, the bright parts that are surface reliefs raised due to the expansion caused by the transformation spread to the surrounding grains. Detailed observations of each bright part are composed of twinned transformation laths, and they start from the grain boundaries, advance into the grain interiors as noted by the arrows, and then propagate to the adjacent grains. These transformation phenomena are fundamentally similar to the results of in-situ transmission electron microscopic (TEM) studies on the martensitic transformation in ZrO$_2$.3–5 mol%Y$_2$O$_3$.1 mol%MgO and ZrO$_2$.2.5 mol%–Y$_2$O$_3$ ceramics. They have shown that the transformation occurred by the nucleation and growth of monoclinic laths. In these studies, TEM observations of the transformation were performed by adjusting the current and illumination conditions of the electron beam, i.e., they should be the strain-induced martensite mode; however, the isothermal transformation mode is shown in these AFM observations.

The propagation rate of martensitic laths was estimated from AFM micrographs using the 3Y aged at 473 K in water and vacuum environments. The estimated growth rate was 0.4–1.7 $\times$ 10$^{-10}$ m/s, obtained from various AFM micrographs under the assumption that the laths propagate continuously at a constant rate, i.e., the lath growth distance in 1 ks is equivalent to about 0.04–0.17 $\mu$m, irrespective of the environments. The diffusion distance in 1 ks is calculated to be 0.001–0.05 $\mu$m using the diffusivity extrapolated down to 473 K from the published diffusivity of the oxygen ion in ZrO$_2$.15 mol%MgO. The estimated growth rates are not very different in order from the values calculated from the extrapolated diffusivity, though the actual values in the former are relatively larger than those in the latter. However, the estimated growth rates are scattered dependent on the grain boundaries, and the rate was not obtained from the specimen interior but from the surface reliefs due to the laths transformed at the specimen surface. The mechanism-controlled propagation rate will then be relatively complex. The propagation rate in the grain interior should be much slower than that at the specimen surface as suggested from Fig. 9, so the propagation is presumably controlled by the diffusion of oxygen ion vacancies in partially stabilized zirconia.

Therefore, this transformation will be a heterogeneous
nucleation-controlled reaction, i.e., nucleating at the grain boundaries with the growth being controlled by the diffusion of oxygen ion vacancies. From macro-scale observations, the advanced transformation area was observed as a round shape. Thus, the transformed area is constrained from the surrounding matrix, and the stress occurring due to the transformation may be a very important factor in inducing further propagation of the transformation, i.e., presumably the trans-

Fig. 12  AFM micrographs showing the same area of 3Y aged at 473 K for various times. The surface reliefs due to T-to-M transformation advance from the grain boundaries into the grain interiors, as shown by the arrows. As-sintered (a), aged at 473 K for 7.2 ks (b), 14.4 ks (c), 21.6 ks (d).

Fig. 13  Effect of alumina addition of 2 mass% (2A) and 5 mass% (5A) on the critical stress intensity factor \((K_{IC})\) in 3Y sintered at various sintering temperatures \((T_s)\) for 18 ks.

Fig. 14  Plots of the ratio of two XRD intensities \((111)m\) and \((11\bar{1})m\) against aging time in 2Y and 2Y containing alumina (2Y-5A, -30A). Aging temperature is 500 K.
formation stress induces further nucleation of the transformation.

5. Effect of Alumina Addition

There have been many reports\textsuperscript{26–30} that the addition of alumina improved the mechanical properties, hardness,\textsuperscript{27} bending strength,\textsuperscript{27,30} fracture toughness,\textsuperscript{27,30} thermal shock resistance\textsuperscript{26} and so on.\textsuperscript{28} Figure 13 shows the typical improvement in mechanical properties, the critical stress intensity factors, by a small addition of alumina to 3Y. The effect of alumina addition on the transformation is a very important factor in the improvement of mechanical properties. However, the actual effect of a small amount of alumina addition on the transformation behavior has not yet been clarified.

The T-T-T curves, the transformation kinetics and the apparent activation energies for the transformation in the alumina containing ceramics are very similar to those in the zirconia–yttria ceramics without alumina addition.\textsuperscript{55}

There is a big difference between the observed XRD intensity ratio ($(111)_m/(11\bar{1})_m$) and the theoretical value, 0.64,\textsuperscript{56} as shown in Fig. 14.\textsuperscript{57,58} This value of 0.64 was obtained in a powder specimen of 2Y but the ratio in the sintered 2Y is very smaller than the theoretical value, and the ceramic containing alumina approaches the theoretical value. Thus, the preferred orientation of the transformed monoclinic phase in PSZ without alumina, i.e., the big anisotropic tendency of the transformed monoclinic phase, occurs but is decreased by the addition of alumina. These results are

\begin{table}
\centering
\begin{tabular}{|c|c|c|}
\hline
 & 2Y(1923 K, 54 ks) & 2Y-5A(1923 K, 54 ks) & 2Y-30A(1923 K, 54 ks) \\
\hline
(a) & (b) & (c) \\
\hline
\end{tabular}
\caption{Fig. 15 Pole figures of 2Y and 2Y containing alumina (2Y-5A, -30A). (a)–(c): as-sintered, (d)–(l): aged at 573 K for 100 ks.}
\end{table}
related to a large constrained effect existing for the formation of the monoclinic phase in PSZ but no or a less constrained effect from the surrounding matrix in PSZ containing alumina. Figure 15 shows a pole figure of the tetragonal and these two monoclinic phases with and without alumina addition. It has been confirmed that 2Y shows a strong preferred orientation of the M-phase but alumina addition introduces the relaxation role for the formation of the monoclinic phase, which results in easier transformation when a crack occurs and results in the introduction of greater mechanical properties.

Detailed AFM observations indicate that the advancing morphology in alumina-containing ceramics is different from that in 2Y and 3Y. Namely, the laths advance in many directions via a branching morphology in alumina-containing specimens because of the presence of undissolved alumina particles. The alumina-containing ceramics show the formation of an amorphous grain boundary phase in 3Y-5A and commercial 3.5Y, so much stronger cohesion between grains is expected, resulting in the transformation being restricted to a thin surface of the specimen with alumina, as shown in Fig. 16. Therefore, the actual effect on the transformation due to the addition of alumina is that the T → M transformation in alumina-containing ceramics proceeds relatively easily at the surface because of small constrained effect from the surrounding matrix, but the propagation into the specimen interior is relatively difficult. The improvement mechanism due to the addition of alumina will be related to these effects, and furthermore, the slight dissolution of alumina in the zirconia shown in the phase diagram may be important.

6. Summary

The T-to-M transformation in a zirconia–yttria ceramic system has been believed to be a diffusionless transformation mode. However, this article based on our studies shows that this transformation proceeds by a diffusion mode; a nucleation-controlled mode, and its growth stage is controlled by some kinds of diffusion, for example, oxygen ion vacancies. The transformation kinetics and detailed AFM observations indicate that martensitic laths nucleate at the grain boundaries and advance into the grain interiors with aging and spread out to adjacent grains in a round shape, irrespective of different environments. Water does not affect on growth stage but on nucleation stage. In alumina-containing ceramics, however, the propagation mode and preferred orientation are very different from those of non-alumina-containing ceramics, though the transformation kinetics are very similar in both ceramics with and without alumina.

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REFERENCES