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Kinetics of Athermal Martensitic Transformation in Yttria Doped Zirconia

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ABSTRACT

The high temperature tetragonal phase of zirconia containing 1.40~1.60 mol% of yttria can be fully retained at room temperature by rapid cooling. The metastable tetragonal phase transforms into the monoclinic phase athermally upon subzero cooling. The transformation exhibited an athermal burst transformation. The effects of yttria content and grain size on the athermal martensitic transformation were studied in detail. The burst temperature linearly decreased with increasing yttria content or decreasing grain size. To consider the distribution of martensite nuclei, the Weibull modulus of the athermal martensitic transformation was evaluated from the distribution of the burst transformation temperature. From the Weibull analysis, the distribution of embryos appears to be more homogeneous than that of the defects responsible for the fracture of similar material.

Key words **: *Athermal martensitic transformation, Burst type martensitic transformation, Yttria doped zirconia, Embryo***

1. Introduction

As first demonstrated by Gupta and co workers for ZrO_2-Y_2O_3 compositions, Y_2O_3 is an important solid-solution additive to ZrO_2, helping in the retention of the tetragonal phase.[1,2] Retention of the tetragonal phase requires certain grain size and Y_2O_3 content.[3] Zirconia doped with a small amount of yttria (less than 1.75 mol% yttria) had been considered to undergo a typical athermal transformation. However, it was shown that the high temperature tetragonal phase of zirconia containing ~1.60 mol% of yttria can be fully retained at room temperature by rapid cooling, through the use of a small spherical specimen.[4,5] The metastable tetragonal phase obtained by such a fast cooling readily transformed into the monoclinic phase by heating at approximately 550 K. More interestingly, the metastable tetragonal phase underwent a burst-type martensitic transformation into the monoclinic phase during subzero cooling to the liquid nitrogen temperature. The occurrence of both isothermal and athermal transformation in a sample of the same chemical composition is very rare and little is known about these transformations. Notably, a deep bay in the TTT diagram separates these two modes of transformation, as shown in Fig. 1.[4]

The appearance of the athermal transformation was found recently and thus little is known about its general characteristics. As such, quantitative measurement of this transformation is necessary to clarify the differences, or whether there are in fact any differences, between the isothermal and athermal transformations. The objective of the present study is to elucidate the general characteristics of the athermal burst-type transformation at subzero temperatures, including the composition and grain size dependence on the burst transformation temperature (M_b).

2. Experimental Procedure

Powders having an average composition of 1.35~1.60 mol% Y_2O_3-ZrO_2 (1.35~1.60Y) were prepared from pure zirconia and

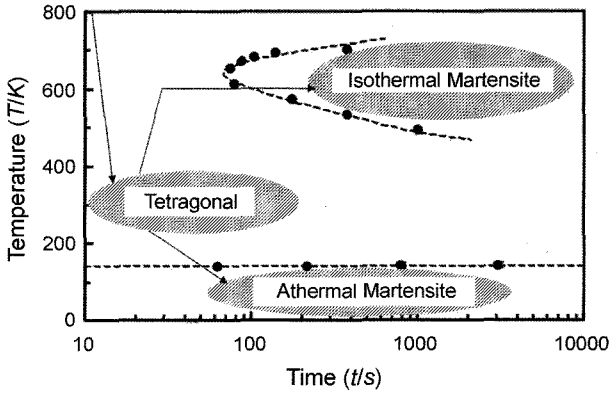

Fig. 1. A TTT diagram showing a C-Curve for the isothermal transformation and M_b for the athermal transformation for rapid cooled specimens of 1.50Y. (Tetragonal : tetragonal phase, Martensite: Monoclinic phase)

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ZrO_2-3.0 mol%Y_2O_3 powders (TZ-0Y and TZ-3Y, TOSOH, Japan), both having 99.9% purity. The prepared powders were ball milled with ethanol for 50h. After being dried, they were pressed by a uniaxial load in a steel die (200 MPa) into a ~1 mm thick sheet. The pressed sheet was cut with a knife-edge to cubes of 0.5~1 mm size. The cubes were placed in a rotary granulator lined with emery paper and turned at a speed of 50 rpm for 24~48 h. Small spherical specimens were prepared such that a metastable tetragonal phase was obtainable by rapid cooling without excessive quenching stress. Granulated small spherical specimens were sintered at 1723~1923 K for 1h followed by furnace cooling to 1273 K. They were then quickly taken out from the furnace and the bottom half of the crucible was immersed in water.

After rapid cooling, we confirmed the phase constitution by the X-Ray Diffraction method (XRD) (Cu Kα radiation, 40 kV and 30 mA). The volume fraction of monoclinic phase was estimated from the relative intensities of the two monoclinic peaks $(111)_m+(\bar{1}11)_m$ and the tetragonal peak $(111)_t+(111)_m+(\bar{1}11)_m$ and calculated using following formulae.[6]

$$V_m = \frac{1.311X_m}{1+0.311X_m} \tag{1}$$

$$X_m = \frac{I_m(\bar{1}11)+I_m(111)}{I_m(\bar{1}11)+I_m(111)+I_t(111)} \tag{2}$$

where $I_{m,t}(hkl)$ denotes the integrated intensities of the hkl-peak of the monoclinic or tetragonal phase corrected for the background. Although zirconia powders having various yttria content were prepared, a 100% tetragonal phase by rapid cooling from more than 1.40Y could be obtained. The density of the sintered samples was higher than 98%, as measured by the Archimedes method in deionized water. Grain size was measured on SEM micrographs of cross-sections of the samples after polishing and thermal etching, using more than 600 grains for each sample. The linear intercept method was used to obtain the average grain size with a conversion factor of 1.54.[7] The average grain sizes increased with increasing sintering temperature by nearly independently of the composition. For 1.55Y specimens, the grain sizes of 0.51~2.88 μm were obtained by sintering at 1723~1923 K, respectively. Samples of approximately 700 μm diameter for M_b measurement were selected for the present experiment, as shown in Fig. 2.

An apparatus for M_b measurement, as shown in Fig. 3, was manufactured by modifying a XRD specimen cooling stage, which consisted of a liquid nitrogen reservoir at the top and a specimen holder connected to the bottom of the liquid nitrogen reservoir by a heat conducting rod. On a copper plate of 25 mm width, 20 mm height and 2 mm thickness, ten vertical grooves of 1mm in width and depth were milled so that small spherical specimens could be placed at the bottom of each groove. The copperplate was fixed on the holder plate. The cooling rate was maintained at −10 K/min by controlling the amount of liquid nitrogen and amount of

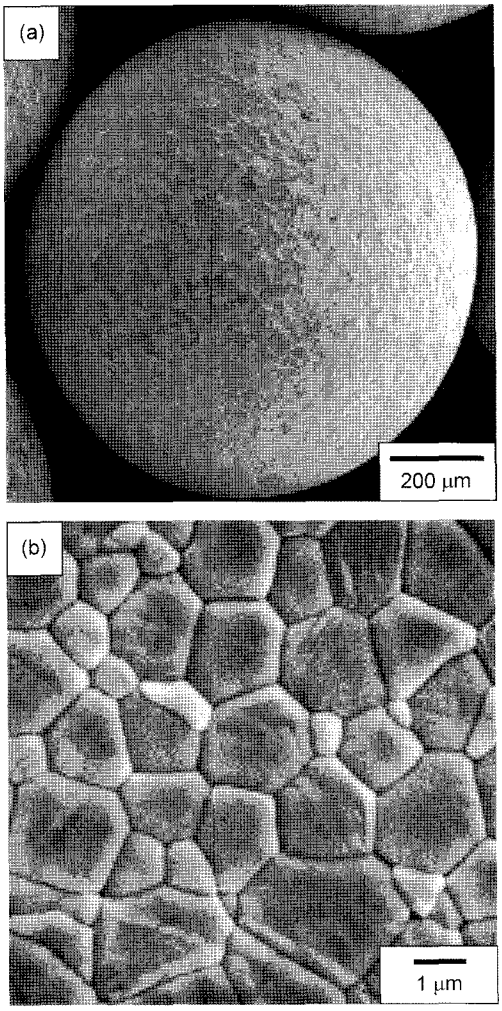

Fig. 2. SEM micrographs of a dense spherical specimen of 1.50Y prepared for M_b measurement; (a) low magnification and (b) microstructure of a spherical specimen.

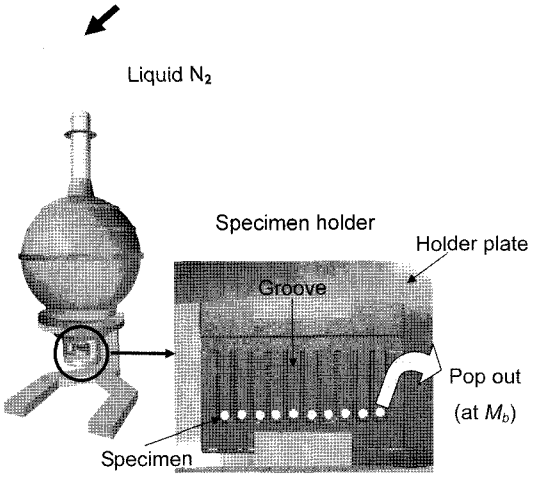

Fig. 3. A schematic view of the apparatus for M_b measurement. It was manufactured by modifying a specimen cooling stage, and consists of a liquid nitrogen reservoir at the top and a specimen holder.

insertion. The temperature in the vicinity of the specimens was measured by a thermocouple (Type K) for low temperature. The specimen holder was placed in a vacuum chamber with a glass-covered window so that the specimens could be observed without frost on the window. When a specimen underwent a burst type transformation, it popped out from the bottom of the groove and fell on the bottom of the vacuum chamber. The M_b was determined when it popped out from the groove. The specimens were monitored with a video recorder along with the temperature of the specimen holder. Thus, M_b of 10 specimens could be accurately read by a single cooling experiment.

3. Results and Discussion

A small spherical specimen jumped as high as nearly 10 mm and fell on the bottom of the vacuum chamber when it transformed. The samples that fell on the bottom of the chamber were not cooled to the M_b. The volume fraction of martensite associated with the first burst transformation was measured on numerous specimen used for the measurement of M_b. It was found that 78% of the monoclinic phase was formed on average by the first burst transformation. Further cooling of these specimens by soaking in liquid nitrogen resulted in only a 3% increase as shown in Table 1. Thus the martensitic transformation of the present specimens is characterized by a large single burst; this is an extreme form of autocatalysis.

Although the M_b of an individual specimen could be measured accurately with the present equipment, the data for identical specimens exhibited considerable scatter. This was not unexpected as nucleation takes place at the most potent embryo among the many distributed in the specimen. In order to facilitate statistical consideration of the embryos distribution, the distribution of the M_b was measured for more than 100 essentially identical 1.50Y-1823K specimens. The results are summarized as a histogram in Fig. 4. The curve is the normal distribution fitted to the histogram, resulting in a mean value of M_b= 211 K and a standard deviation of 9.1 K. The standard deviation might be larger than that observed for metal martensite, but no comparable data exist.

Table 1. Volume Fraction of Monoclinic Phase Depends on the Cooling Condition

Cooling condition	V_m (%)
M_b temperature	78.2
LN_2 temperature	81.2
Holding for 24 h at LN_2 temperature	81.4

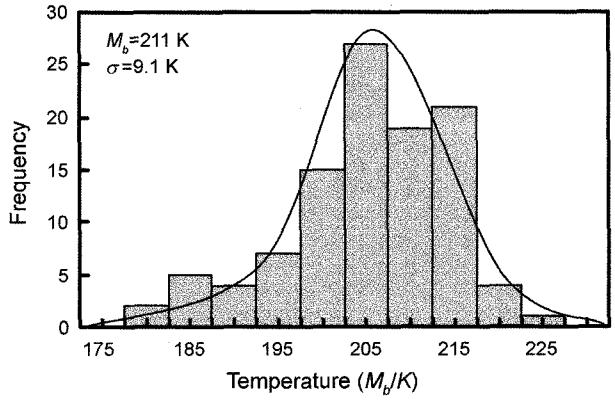

Fig. 4. Distribution of M_b for the specimen 1.50Y sintered at 1823 K for 1 h.

The burst phenomenon of martensitic transformation is generally considered to take place by the activation of the most potent embryo. The phenomenon is analogous to the fracture of a brittle material, and is initiated at the weakest point or at the largest defect. Similar defects might be operating as the embryos of martensite nuclei. The distribution of such defects is often analyzed by means of a Weibull plot.[8] Thus, a similar analysis is possible by replacing the failure at stress σ with the burst at driving force ΔG. Because reliable data do not exist for the driving force ΔG, the degree of super-cooling at the burst for each specimen was used, i.e., $\Delta T_i = T_0 - M_{bi}$ with T_0 = 853 K (equilibrium temperature between tetragonal monoclinic phase) as before. $F(\Delta T) = 1 - \exp(-(\Delta T/T_0)^m)$, where $F(\Delta T)$ is the probability of transformation, m is the Weibull modulus, and ΔT is super-cooling from T_0. In order to obtain the m value, nature logs were taken twice. Thus, a plot of $\ln\ln(1/(1-F))$ against $\ln(\Delta T/T_0)$ is a straight line having a slope m. From the slope of the Weibull plot in Fig. 5, m = 81 was obtained for the Weibull modulus. The value is considerably higher than the value for the fracture of Y-TZP (m~6), for which defects comparable to grain sizes are generally considered to be responsible for the fracture.[8,9] The considerably higher m value for M_b suggests a narrower distribution of embryos than that of the defects responsible for the fracture.

These measurements were conducted for specimens of different compositions and grain sizes in order to assess the

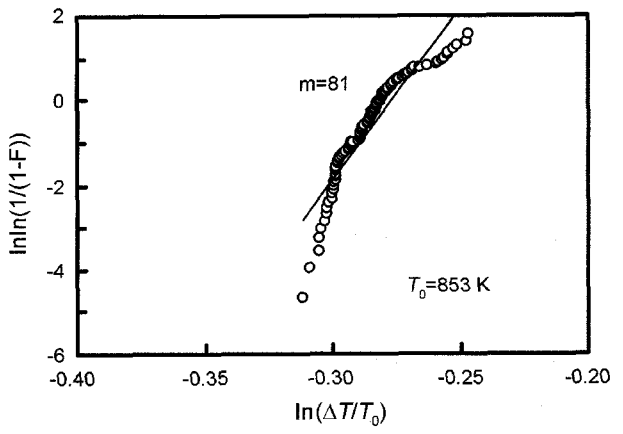

Fig. 5. Weibull plots for M_b of 1.50Y sintered at 1823 K for 1 h. The Weibull moduli are high, indicating a narrow distribution of martensitic transformation.

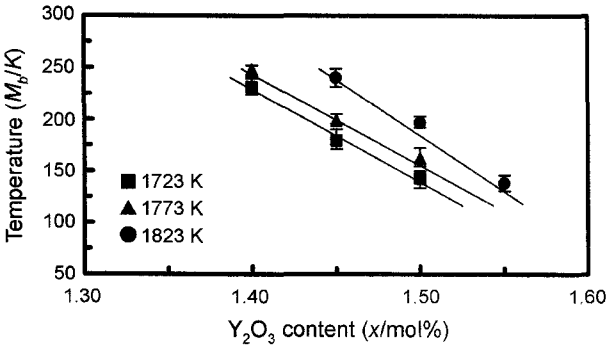

Fig. 6. Composition dependence of M_b for specimens sintered at different temperatures.

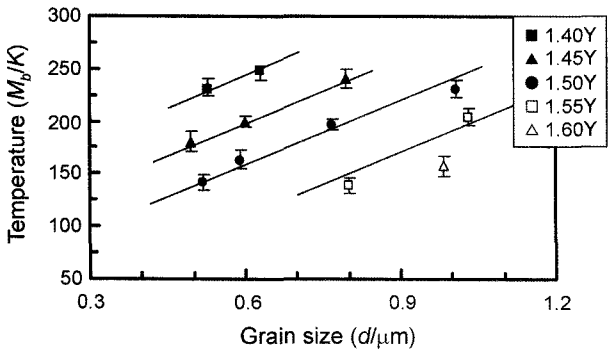

Fig. 7. Grain size dependence of M_b for specimens with various yttria content.

effects of the two factors on the kinetics of the athermal transformation. The results are summarized in terms of M_b in TTT diagrams. Fig. 6 shows the composition dependence of the M_b for specimens sintered at different temperatures. The mean size diameter of the specimens was 700 μm. Each marked point represents the average of 10 measurements and the error bar indicates the range of scatter. M_b under the same sintering temperature decreased with increasing yttria content. It is seen that the composition dependence is quite large, and thus it was possible to observe a burst transformation at subzero temperature region only for a limited composition range.

The dependence was nearly linear for the specimens sintered at 1723~1823 K, but non-linearity of M_b appeared for the specimens sintered above 1873 K. Although this indicates that uniform grain growth could be obtained by raising the sintering temperature, grain sizes became non-uniform at higher sintering temperatures. The non-linearlity of the results for higher sintering temperatures might be attributable to the non-uniform grain size distribution. M_b under the same composition increased with increasing grain size and the dependence was also quite large. Although the grain size dependence is nearly linear in Fig. 7, where M_b was plotted against grain size $1/d$, re-plotting against d, $1/d^{0.5}$ also showed linear dependence. Thus, it is not possible to identify the exact functional form of the dependence. A stabilizing effect due to yttria content is expected through the reduction of T_0. Similarly a stabilizing effect due to grain refinement must occur through the increased driving force required for triggering the transformation. However, these effects on M_b were indistinguishable.[10]

4. Conclusions

Metastable tetragonal phase of zirconia doped with 1.40~1.60 mol% of yttria exhibits a burst type martensitic transformation at subzero temperatures. The burst temperature strongly depends on yttria content and grain size. The transformation occurs essentially by a single large burst, in with a manner similar to that yielded by large super-cooling from the equilibrium temperature. From the Weibull analysis, the distribution of embryos appears to be more homogeneous than that of the defects responsible for the fracture of similar material.

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