A Dilatometric Study of the Martensitic Transformation of Zirconia Containing 1.8~2.0 mol% Yttria*1

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The martensitic transformation during a continuous cooling was monitored by the dilatometric and HT-XRD method for the samples of zirconia containing 1.8~2.0 mol% \( Y_2O_3 \). The alloys exhibited distinctly different \( M_t \) (martensite start temperature) for the surface and bulk martensite when the cooling rate was relatively low. From the dilatometric data, the thickness of the surface martensite was estimated to be about 90 \( \mu \)m. With increasing cooling rate, the \( M_t \) tended to decrease and the transformation was eventually completely suppressed, in agreement with the isothermal nature of the transformation suggested earlier.

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1. Introduction

The transformation from the \( t \) (tetragonal) phase to the \( m \) (monoclinic) phase in zirconia has long been known to be martensitic.\(^{11}\) The \( M_t \) (martensite start temperature) of pure zirconia is located at around 1050°C, but this can be lowered by doping with some oxides, such as \( Y_2O_3 \) and \( CeO_2 \).\(^{3}\) A typical transformation-toughening zirconia, known as TZP (Tetragonal Zirconia Polycrystals), contains 2.5~3.0 mol% \( Y_2O_3 \) and consists entirely of the tetragonal phase at room temperature. Because of the relatively high stability of the metastable phase, the martensitic transformation does not take place on subzero cooling, but it does so in a high stress field such as that around a propagating crack tip. The TZP undergoes the isothermal transformation when it is kept at a temperature between 200~300°C.\(^{4-9}\) On the other hand, zirconia containing \( \sim 1.6 \) mol% \( Y_2O_3 \) exhibits both athermal and isothermal modes of martensitic transformation.\(^{10}\) However, it is not known clearly how the transformation mode changes from the athermal to the isothermal mode in the range of \( ZrO_2:1.8~2.0 \) mol% \( Y_2O_3 \). In this study, the dilatation (DL) and high temperature X-ray diffraction (HT-XRD) methods were used to investigate the phase transformation behavior of this composition range.

2. Experimental Procedure

The samples of \( \text{ZrO}_2:1.8~2.0 \) mol% \( Y_2O_3 \) were prepared by the combination of wet ball-mill mixing (BM) and mechanical alloying (MA) with the raw materials of pure \( \text{ZrO}_2 \) (Tosoh Co., Japan) and pure \( \text{Y}_2\text{O}_3 \) (Shinetsu Chemical, Japan). With wet ball-mill mixing, the powders were mixed in a polypropylene pot containing \( \phi 10 \) mm and \( \phi 5 \) mm zirconia balls and ethanol, while a planetary type ball mill was used with an alumina container and \( \phi 10 \) mm or \( \phi 5 \) mm zirconia balls and was rotated by the rate of 450 min\(^{-1}\). The mixing time for each process was 72 and 4.5 h, respectively. The mixing procedure is as follows:

\[
\text{BM}(24 \text{h}) \rightarrow \text{MA}(2 \text{h}) \rightarrow \text{BM}(24 \text{h}) \rightarrow \text{MA}(2.5 \text{h}) \rightarrow \text{BM}(24 \text{h})
\]

The powders made as above were dried and shaped into a cylinder of \( \phi 6 \text{mm} \times \phi 15 \text{mm} \) under the uniaxial compression of 100 MPa in hardened steel dies. Samples of \( \phi 19 \text{mm} \times \phi 3 \text{mm} \) were also made under the uniaxial compression of 20 MPa. All samples were subsequently press by the isostatic pressing at 200 MPa. The samples were sintered at 1450°C~2h and then air-cooled to room temperature after furnace cooling to 1100°C. The density was measured by Archimedes' method and phase composition was measured by XR (MacScience, model MO3X-HF). The relative density was about 98% and the phase composition was nearly 100% \( t \)-phase. Dilatometer (Shinku-Riko, model DL9800) was mostly used for monitoring the phase transformation with cooling rate ranging from 200°C/h to about 5.8°C/h. High Temperature XR was also supplementarily used.

3. Results

Figure 1 shows the DL curve of zirconia containing 1.8 mol% \( Y_2O_3 \) with the cooling rate of 4.13°C/h. The DL curve was nearly straight above 300°C, but a large expansion of about 1.1% occurred in the range of 300~200°C. It is obvious in this figure that the \( t \)-\( m \) transformation took place at around 250°C. However, as illustrated in the enlarged graph in Fig. 2, the DL curve exhibited a slight deviation from the straight line at around 400°C. In order to examine this particular feature of dilatation, HT-XRD was used. The volume fractions of the \( m \)-phase (\( V_m \)) obtained by HT-XRD are shown in Fig. 2. The point of slight deviation matched to the increasing point of the \( V_m \). Since XR data reflects the state of top surface, the slight deviation in the DL curve was interpreted as the beginning of the surface transformation. Thus, for this sample, the slight deviation at 290°C and the large deviation at around 400°C were interpreted as the transformation start temperatures for the surface \( M_s \) (surf.) and for the bulk \( M_t \).
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Fig. 1. A dilatation curve for ZrO$_2$–1.8 mol% Y$_2$O$_3$ with the cooling rate of 41.3°C·h$^{-1}$.

Fig. 2. An enlarged section of Fig. 1 showing the dilatation due to the surface martensite along with the volume fraction of the m-phase measured by HT-XRD for ZrO$_2$–1.8 mol% Y$_2$O$_3$ with the cooling rate of 41.3°C·h$^{-1}$.

(bulk), respectively.

The $M_s$ (bulk) and $M_s$ (surf) were conveniently defined as the minimum point of the DL curve and the departure point from the linear portion through the high temperature region as illustrated in Fig. 2. Similar DL measurements were made for the specimens of other compositions and with different cooling rates.

In Fig. 3, $M_s$ (surf) and $M_s$ (bulk) are plotted against cooling rate for the specimens containing 1.8~2.0 mol% Y$_2$O$_3$. Data points missing at some cooling rates in the figure indicate that there was no evident transformation under the corresponding cooling rate. For example, when the specimen of ZrO$_2$–1.9 mol% Y$_2$O$_3$ was cooled at 41.3°C·h$^{-1}$, the surface transformation took place, but not the bulk transformation.

In Fig. 4, $V_m$ is plotted against the cooling rate, where the $V_m$ was estimated from the strain measured by DL, assuming the complete transformation results in a 1.5% linear expansion. The $V_m$ significantly decreased with increasing cooling rate. For example, the $V_m$ fell into zero at a cooling rate higher than 97°C·h$^{-1}$ for the specimen containing 1.8 mol% Y$_2$O$_3$ and at a cooling rate higher than 11.2°C·h$^{-1}$ for the specimen with 1.9 and 2.0 mol% Y$_2$O$_3$. Thus, there was a critical cooling rate above which the bulk or surface transformation was fully restrained.

4. Discussion

The presently obtained $M_s$ (bulk) for the specimen containing 1.8~2.0 mol% Y$_2$O$_3$ are plotted against Y$_2$O$_3$ content in Fig. 5 along with the previously obtained $M_s$. The present $M_s$ (bulk)’s obtained with slow cooling lie on the extrapolated line of the previous data. At higher cooling rates, $M_s$ (bulk) decreased and the amount of transformation decreased and eventually the transformation became fully suppressed. As shown in Fig. 3, the reduction of $M_s$ with increasing cooling rates was moderate and did not account for the complete suppression of the martensitic transformation. Instead, the data in Figs. 3 and 4 were consistent with an isothermal trans-
formation, which exhibits a C-curve behavior in the TTT diagram. Referring to the TTT diagram previously obtained for 1.6 mol% Y$_2$O$_3$ (Fig. 4 in Ref. 10), the present specimens with slightly higher Y$_2$O$_3$ contents should have the C-curve shifted toward the long-time direction and $M_s$ toward a lower temperature. Thus with a slow cooling rate, the cooling curve would intersect the C-curve and result in a partial transformation. While with a faster cooling rate, the cooling curve would avoid the C-curve and retain the $t$-phase at room temperature. A subsequent subzero cooling may or may not trigger athermal transformation depending on the location of $M_t$. A normal TZP contains 2.5~3.0 mol% Y$_2$O$_3$ and has its C-curve in a long-time region and $M_s$ below the liquid nitrogen temperature. Thus, with a normal cooling rate, $t$-phase is always retained as a metastable phase and this undergoes only isothermal transformation during a prolonged isothermal holding at an intermediate temperature. So the martensitic transformations of the present alloys are essentially the same as those observed in Y-TZP. They are all isothermal in nature and different only in the rate of reaction.

Another interesting feature of the present results is a clear distinction between the surface martensite and bulk martensite. Even though, it is well known that the isothermal martensitic transformation of TZP occurs from the surface, the transformation was considered to continually proceed into a bulk body. The dilatometric data in Fig. 2 shows that the $M_s$ (surf) was considerably higher than $M_s$ (bulk). Furthermore, the surface martensite nearly saturated before the bulk martensite started.

The thickness of the surface martensite can be estimated from the dilatometric data. In Fig. 3 the expansion $\Delta d$ just above $M_s$ (bulk) was ascribed to the surface martensite. It was assumed that only the martensite in the top and bottom surface layer contribute to the longitudinal expansion. The volume fraction of the $m$-phase in these layers was estimated to be 0.85 from the XRD data. Then considering that the specimen length=13.5 mm, the linear expansion of the $t$-$m$ transformation=1.5% and $\Delta d = 0.0164\%$, the following equation should hold for the thickness of the transformed layer $\delta$: $28 \times 0.85 \times 1.5\%/13.5 = 0.0164\%$. Then 86 $\mu$m was obtained for $\delta$. The thickness is two orders of magnitude larger than the grain size.

It is not known presently what factor is actually controlling the thickness of this layer. One of the possibilities is the free energy balance influenced by the stress field caused by the transformed layer and the constraining stress of the bulk. It is well known that the isothermal transformation of TZP initiates on the surface. The stress field generated by the transformation would trigger further transformation in the subsurface region. With increasing thickness of the transformed layer, the front layer ahead of the transformation will experience higher constraint stress from the bulk material. This would eventually become so high as to suppress further transformation. Further study is necessary to make a quantitative account for the thickness of the surface martensite.

5. Summary

(1) Zirconia containing 1.8~2.0 mol% Y$_2$O$_3$ exhibited distinctly different transformation kinetics for the surface and bulk martensite when the cooling rate was relatively small. The surface martensite started at a temperature about 100°C above that of bulk martensite. The thickness of the surface martensite was estimated to be 90 $\mu$m.

(2) The $M_t$ for both surface and bulk martensite decreased with increasing cooling rate and there was a critical cooling rate above which the phase transformation did not take place. The observation is consistent with the nature of the isothermal martensitic transformation, which prevails in a wide range of Y$_2$O$_3$ contents.

REFERENCES