Martensitic Transformations in Zirconia Ceramics

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Martensitic (shear displacive) phase transformations of the tetragonal to monoclinic and the reverse transformations in Y_2O_3 doped tetragonal ZrO_2 ceramics, which are thought to be included in the displacive phase transformations, were found to propagate isothermally, while in contrast, in CeO_2 doped ZrO_2 a burst-like (athermal type) propagation was observed.

One of the reasons for the isothermal nature, which occurred in the tetragonal to monoclinic transformation and also upon thermal cycles in a few mol% Y_2O_3 doped ZrO_2 , is believed to be due to a fairly large amount of oxygen vacancies produced by ionic replacement of Zr^{4+} by Y^{3+} ions. In other words, a high diffusibility of oxygen ions through their vacancies controls the propagation rate of the shear transformation in locally distorted tetragonal lattice. In the CeO_2 doped ZrO_2 , on the other hand, a typical athermal nature is expected because of a small amount of oxygen vacancies which exists thermodynamically in the tetragonal lattice

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I. Introduction

Martensitic transformation is usually included in the so-called displacive phase transformations. Some examples of the displacive transformation observed in oxide ceramics are as follows; (i) $\alpha \leftrightarrow \beta$ phase transformation in quartz⁽¹⁾, where the low temperature α structure can be formed by a small ionic displacement from the high temperature β structure without breaking any bonds of the basic SiO_4 tetrahedra, (ii) displacive phase transformations in perovskite oxides, such as $SrTiO_3$ and $BaTiO_3$ ⁽²⁾, in which the so-called soft phonon mode exerts an important influence on the transformation mechanism, and (iii) displacive cubic-tetragonal transformations in ZrO_2 ceramics⁽³⁾, in which the transformation requires very small oxygen-ion displacements and is diffusionless-type. Although these displacive transformations are also recognized to be diffusionless, a little discussion will be needed to decide whether they are martensitic or not.

Recently, the martensitic (shear dominated) transformations in zirconia ceramics have been widely noticed because of a close relation between the stress-induced martensite and high toughness found in Y_2O_3 doped PSZ (Partially Stabilized Zirconia and TZP (Tetragonal Zirconia Polycrystals)⁽⁴⁾). This transformation, tetragonal to monoclinic, requires a fairly large volume change and its kinetics and morphology are influenced by the associated strain energy, as already observed in the ferrous martensites.

On the other hand, a serious degradation phenomenon⁽⁵⁾ has been observed in Y_2O_3 doped PSZ and TZP, and it is believed that an isothermal propagation of the tetragonal to monoclinic martensitic transformation is

deeply related to this degradation. Therefore, studying of the martensitic transformation behavior in ZrO_2 ceramics surely contributes toward the improvement of their mechanical properties.

In this paper, isothermal and athermal characteristics associated with the martensitic tetragonal to monoclinic transformations which occurred in Y_2O_3 - ZrO_2 and CeO_2 - ZrO_2 , respectively, were comparatively adopted as a subject for discussion.

II. Experimental Procedure

The raw materials, for preparing the 2.2, 3.0 mol% Y_2O_3 , 3.0 mol% Y_2O_3 3.0 mol% CeO_2 , and 12.0 mol% CeO_2 contained ZrO_2 specimens, were 2.0 mol% Y_2O_3 - ZrO_2 TZP powders (3.53 wt% Y_2O_3 and impurities content (Al, Si, Fe) is less than 0.085 wt%, Tosoh Co. Ltd.), 12.0 mol% CeO_2 - ZrO_2 TZP powders (16.69 mass% CeO_2 and impurities (Al, Si, Fe) less than 0.013 mass%, Tosoh Co. Ltd.), and 99.99% Y_2O_3 and ZrO_2 powders. These powders were milled and pressed at 100 MPa, and calcined for several hours at 1673 and 1873 K in air. Their average grain sizes after sintering were in the range of 0.3 ~ 5.0 μm . X-ray diffraction, TG-DSC and thermal expansion methods were used to measure the amount of the monoclinic phase transformed from the tetragonal phase during isothermal holding and upon cyclic thermal treatments.

III. Experimental Results

1. Isothermal martensitic characteristics in Y_2O_3 doped ZrO_2

Although the martensitic transformations in metals and alloys usually propagate athermally, even with burst-type in iron alloys⁽⁶⁾, the authors have found an isothermal propagation of martensite in ZrO_2 specimens doped

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with trivalent Y^{3+} ions. Here, some experimental results so far obtained are mutually compared among Y_2O_3 , Er_2O_3 (trivalent ions) and CaO (divalent ions) doped ZrO_2 specimens.

In Fig. 1, a part of the Y_2O_3 - ZrO_2 phase diagram⁽⁷⁾ is shown, in which so-called PSZ and TZP are noticed. The isothermal expansion curves against the aging time in the temperature range of 493 ~ 573 K in air were obtained in the specimens of 3.0 mol% Y_2O_3 -3.0 mol% CeO_2 - ZrO_2 (3Y-3Ce-TZP), as shown in Fig. 2(a). Then, Fig. 2(b) shows the C-curve behavior of isothermal martensite in T-T-T diagram obtained by this thermal expansion technique in 3.0 mol% Y_2O_3 (3Y-TZP) and 3Y-3Ce-TZP specimens, where the middle points between the start and the finish curves of the transformation were plotted. In the figure, a nose point for the former C-curve (3Y-TZP) corresponds to the holding time of about 27 ks at 550 K, while the other curve is delayed to a longer holding time (~180 ks), the nose temperature being unchanged. This is because of the effect of CeO_2 addition.

According to Dickerson *et al.*⁽⁸⁾, a 7.8 mol% CaO - ZrO_2 specimen was fired at 2143 K, subsequently aged at 1573 K for 345.6 ks, and the tetragonal phases which had precipitated during aging were then held for several days (up to 50 days) at room temperature.

Figure 3 shows the monoclinic % against the holding time at room temperature, using X-ray diffraction, where the monoclinic phase increased from 24% to 30%, and then saturated. It is supposed that these tetragonal precipitates closest to the critical size can undergo the

Fig. 1 A partial phase diagram of ZrO_2 - Y_2O_3 ⁽⁷⁾, showing TZP and PSZ regions.

Fig. 2 (a): Change in thermal expansion during isothermal aging at 493 ~ 573 K in 3Y-3Ce-TZP. (b): T-T-T diagram of 3Y-TZP and 3Y-3Ce-TZP after isothermal aging.

Fig. 3 Monoclinic % vs. aging time at room temperature after being aged at 1573 K for 96×3.6 ks in 7.8 mol% CaO - ZrO_2 ⁽⁸⁾.

isothermal transformation. Moreover, since the M_s temperature was reported to be about 523 K just after the 345.6 ks-holding at 1573 K, it is possible that the

monoclinic phase can be induced by coherency stresses in the tetragonal precipitates surrounded by the matrix during room temperature ageing. This behavior is related to the migration of oxygen-ion vacancies.

In order to study the isothermal character of the tetragonal $\leftrightarrow$ monoclinic martensitic transformation, a cyclic thermal treatment, using 2.2 mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ TZP specimens, was carried out and the change in thermal expansion and contraction associated with the tetragonal $\leftrightarrow$ monoclinic transformation was plotted against temperature (see Fig. 4). In the figure, where the grain size is $2\sim 3\text{ }\mu\text{m}$ and the cycle-rate $2.1\times 10^{-2}\text{ K s}^{-1}$, an extraordinary expansion is observed in the first heating process (at $523\sim 573\text{ K}$) which is due to the appearance of the monoclinic phase, and a subsequent contraction due to the reverse monoclinic tetragonal transformation is followed at about 823 K . In the second and third cycles similar expansion and contraction are also remarkably observed, where the transformation temperatures, M_s and A_s , increase with increasing the cycle number, i.e., $M_s=673\text{ K}$ at the second, $M_s=723\text{ K}$ at the third, and $M_s=753\text{ K}$ at the fourth rising curve, while $A_s=723\text{ K}$ at the second and $A_s=823\text{ K}$ at the third falling curve. It is noticed in this experiment that when the cycle-rate is increased to $8.4\times 10^{-2}\text{ K s}^{-1}$ (four times larger), no expansion and contraction occur both during heating and cooling, because of its isothermal character, and if the athermal character controls the transformation, the expansion due to the tetragonal to monoclinic transformation can't appear during the first heating (RT to high temperature), but is observed during the first cooling. Moreover, the amount of thermal expansion

increases with the cycle number, suggesting the gradual increase in the monoclinic phase accompanying a small amount of cracks. As seen in Fig. 5⁽⁹⁾, a similar dilatation behavior is dominant in 2.0 mol% $\text{Er}_2\text{O}_3\text{-ZrO}_2$ specimen, where the first expansion due to the forward (t-m) transformation appears at $\sim 523\text{ K}$ and the reverse transformation which associates a contraction is completed at $\sim 923\text{ K}$. In this case, the M_s temperatures upon these cycles are observed at about 823 K , except the first one, and the amount of thermal expansion associated with the tetragonal to monoclinic transformation shows only slight increase upon an increase in the number of thermal cycle, compared with that observed in the 2.2 mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (Fig. 4). From this result, the isothermal nature was also clearly shown in the $\text{Er}_2^{3+}\text{O}_3\text{-ZrO}_2$ specimen.

It must be, however, noticed that the isothermal propagation of the tetragonal to monoclinic transformation always occurred in the atmosphere of air in the temperature range from 473 to 523 K and enhanced by moisture in $\text{Y}_2\text{O}_3\text{-ZrO}_2$ ceramics. This fact means that the existence of surface water may act as a trigger for the transformation⁽¹⁰⁾.

2. Typical athermal character of the tetragonal to monoclinic transformation in $\text{CeO}_2\text{-ZrO}_2$

The authors studied the transformation behavior upon the thermal cycles, using DSC and thermal expansion, in 12 mol% $\text{CeO}_2\text{-ZrO}_2$ specimens (an average grain size of $2\sim 3\text{ }\mu\text{m}$), and the results obtained were compared with those in the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ specimens. Figure 6 exhibits a phase diagram of $\text{CeO}_2\text{-ZrO}_2$ ⁽¹¹⁾, in which it must be noticed that the tetragonal phase region extends up to the con-

Fig. 4 Thermal expansion vs. temperature associated with thermal cycles in 2.2 mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$.

Fig. 5 Thermal expansion vs. temperature associated with thermal cycles in 4.0 mol% $\text{ErO}_{1.5}\text{-ZrO}_2$ ⁽⁹⁾.

Fig. 6 Phase diagram of ZrO₂-CeO₂⁽¹¹⁾.

centration about 20 mol% CeO₂, comparing to that of about 3 mol% Y₂O₃ in the Y₂O₃-ZrO₂ system. In Fig. 7(a), is shown the thermal change associated with the tetragonal to monoclinic transformations upon the thermal cycles, and sharp peaks of heat evolution at the transformation appeared in a very narrow temperature range (~ 2 K). It is interesting to note that in the figure the tetragonal to monoclinic transformations exhibited the athermal or even burst-like character, and upon increasing the number of thermal cycles, the M_s temperatures (the first peaks of each cycle) gradually moved to higher temperature side (because of change in the distribution of transformation stresses retained in the tetragonal regions adjacent to the cracks), and the sharp peaks split and their height became small. The splitting of sharp peaks is thought to be due to the generation of cracks caused by a large volume change associated with each burst-type transformation. In contrast, as shown in Fig. 7(b), the peaks of heat change in the reverse transformation were not so sharp and became more and more wider with increasing thermal cycle. The reason seems that stress distributions produced by the forward transformation can be changed by relaxation processes occurring during heating up to the reverse transformation, this exerting the influence upon the process of reverse transformation.

When the monoclinic specimen was heated up to 1073 K through the A_s temperature and then cooled, the measured heat evolution peaks at the forward transformation were also very sharp, as shown in Fig. 7(c), and the shift of each M_s temperature was not observed between the first and the fifth cycles. This result suggests that after the transformation stress was completely released or the retained elastic strain energy was annealed out during heating up to 1073 K, a fresh and burst martensite

can be formed whenever the M_s temperature was reached. In this case, the reverse transformations also occurred at the same temperatures (A_s), and their peak-widths were ~ 10 K. A similar transformation behavior was observed in the dilatational change during thermal cycles between 150–550 K in the 12 mol% CeO₂ doped ZrO₂, as shown in Fig. 8. An abrupt expansion due to the burst formation and its reverse contraction were observed in the first thermal cycle.

IV. Discussion

The stabilized zirconia of CaF₂-type structure is well known as a superionic conducting material⁽¹²⁾, where only O²⁻ ions have a high mobility in the lattice.

When Zr⁴⁺ ions are replaced by a few mol% di- and trivalent cations, Ca²⁺ and Y³⁺ (or Er³⁺), in the lattice of ZrO₂, a fairly large amount of oxygen vacancies will be formed to keep charge neutrality. This is expressed as, $\text{ZrO}_2 + \text{Y}_2\text{O}_3 \rightarrow \text{ZrO}_2 + 2\text{Y}_{\text{Zr}} + \text{V}_\text{o} + 3\text{O}_\text{o}$. It is therefore important to consider that the martensitic shear displacement can be modified by the diffusibility of oxygen ions through their vacancies and also by the formation of clusters⁽¹³⁾ composed of displaced oxygen ions and vacancies in the tetragonal lattice of these CaO- or Y₂O₃ doped ZrO₂.

Catlow *et al.*⁽¹⁴⁾ and Uehara *et al.*⁽¹⁵⁾ have pointed out, based on their EXAFS studies, that in the cubic phase of Y₂O₃-ZrO₂ specimens, oxygen vacancies produced by the addition of Y₂O₃ have a tendency to preferentially locate in the vicinity of Zr⁴⁺ ions, which are smaller in ionic-radius than Y³⁺ ions, thus resulting in an ionic configuration of Zr⁴⁺-O₇ similar to that often observed in the monoclinic phase. A similar tendency has been recognized in the system of $(1-x)\text{ZrO}_{2-x}\text{GdO}_{1.5}$ ($0.2 \leq x \leq 0.62$), where the number of Zr-O₈ configuration decreased and changed into the configuration "Zr-O₆" with increasing Gd content⁽¹⁶⁾.

Since the existence of high concentration of oxygen vacancies and of the O²⁻ ion-oxygen vacancy clusters controls the rate of propagation of the tetragonal to monoclinic transformation, the activation energy for the isothermal propagation can be accordingly influenced in the zirconia ceramics doped with di-and/or trivalent cations. This is supported by the experimental fact that the athermal character of the tetragonal to monoclinic transformations so far observed in pure ZrO₂ and Ce⁴⁺O₂ doped ZrO₂ was changed into the isothermal one in Ca²⁺O and Y₂O₃ doped ZrO₂.

From this point of view, the authors named the isothermal tetragonal to monoclinic transformation observed in Y₂O₃-ZrO₂ "Bainite-like" transformation⁽¹⁷⁾, in the analogy with the lower-bainitic transformation in steel, which requires not only the shear process but also the movement of carbon-atoms and the activation energy for the growth of lower-bainite is nearly equal to that for the carbon-diffusion in the ferrite phase.

In order to elucidate the character of transformation behavior depending upon the oxygen vacancy concentra-

Fig. 7 (a): Change in transformation heat at M_s temperatures associated with thermal cycles between 133.2 K and 723 K in 12 mol% CeO₂-ZrO₂. (b): A_s temperatures after thermal cycles in the same specimens. (c): Burst-like peaks at M_s temperatures after re-cooling from 1073 K in the same specimens.

tion, a deoxidization ($\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$) study was carried out. ZrO₂ containing 12 mol% CeO₂ sintered specimens were found to be efficiently deoxidized in a hydrogen atmosphere at 1073 K (for one hour) with a weight loss.

According to reduction time at 1073 K, the increase in

the unit cell volume and the decrease in the tetragonality of the unit cell occurred, meaning that the tetragonal symmetry was decreased into cubic one. At the same time, the M_s temperature of the tetragonal to monoclinic transformation shifted to fairly lower temperature⁽¹⁸⁾. It

Fig. 8 Dilatation vs. temperature associated with thermal cycles in 12 mol% $\text{CeO}_2\text{-ZrO}_2$.

is of interest, therefore, to observe whether the isothermal transformation character appears or not in the temperature range from about 423 K to 573 K in the specimens containing 6 ~ 8 mol% CeO_2 (Ce^{3+}), this being under study.

V. Summary

To make clear the basic reason of different martensitic behavior, i.e., isothermal character in Y_2O_3 doped and athermal one in CeO_2 doped ZrO_2 , the following experiments have been carried out and their results are:

(1) An isothermal behavior similar to one already observed in 3.0 mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ sintered specimens was also found in 3.0 mol% $\text{Y}_2\text{O}_3\text{-3.0 mol% CeO}_2\text{-ZrO}_2$, although the tetragonal to monoclinic transformation was considerably delayed to a longer holding time.

(2) In cases of Er_2O_3 (Er^{3+}) and $\text{CaO}(\text{Ca}^{2+})$ doped ZrO_2 sintered specimens, the isothermal martensitic character was also dominated and the one of the reasons of this isothermal behavior may depend on the high concentration of oxygen vacancies generated to keep the charge neutrality.

(3) In 12 mol% $\text{CeO}_2\text{-ZrO}_2$, on the other hand, a typical nature of athermal, even burst-like, martensitic transformation was observed.

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