JOURNAL OF MATERIALS SCIENCE **32** (1997) 1149–1153

Influence of a small amount of Al_2O_3 addition on the transformation of Y_2O_3-partially stabilized ZrO_2 during annealing

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Tetragonal-to-monoclinic phase transformations in 2 and 3 mol% Y_2O_3–ZrO_2 ceramics and their composites with 5 vol% Al_2O_3 during annealing in water and in vacuum at 353–623 K were investigated to explore the effect of a small quantity of Al_2O_3 addition on the transformation. The dispersion of Al_2O_3 particles into the $ZrO_2(Y_2O_3)$ matrix was found to be effective to suppress the transformation directly induced by the attack of H_2O during annealing in water, even though the amount was as small as 5 vol%. However, the transformation predominantly caused by thermal activation during annealing in vacuum was not affected by the limited amount of Al_2O_3 addition. The effect of suppression of Al_2O_3 on the water-induced phase transformation was considered to be realized through the hydroxydation of Al_2O_3 particles, by which the sample surface was effectively "protected" from further attack of H_2O, which accelerated the low-temperature degradation transformation.

1. Introduction

Partially stabilized zirconia (PSZ) ceramics have been extensively studied and used in many applications because of their high strengths and fracture toughnesses benefited from the well known stress-induced tetragonal-to-monoclinic transformation toughening echanism [1, 2]. Y_2O_3-dopped ZrO_2 (Y-PSZ) has received special attention among the zirconia ceramics due to its excellent mechanical properties and good sinterability. However, a drawback is that the strength and fracture toughness decrease greatly when it is annealed or used at around 470 K, particularly in environments containing water or its vapour [3–10]. This problem, usually called low-temperature degradation, has been found to be caused by the tetragonal-to-monoclinic transformation that takes place spontaneously during annealing without applied stresses. The low-temperature degradation can be suppressed by increasing the content of the oxide stabilizer [4, 7], but strength and fracture toughness will be lowered simultaneously due to a decreasing contribution from the transformation-toughening [11].

It has been found that the addition of Al_2O_3 particles to Y–PSZ effectively suppresses low-temperature degradation [12–14], and fortunately the mechanical properties can also be improved to some extent through a composite effect [15–17]. The suppression effect of Al_2O_3 addition has been believed to be caused by combined contributions of the inhibited grain growth of tetragonal $ZrO_2(Y_2O_3)$ and the increase in the composite elastic modulus resulting from the dispersion of Al_2O_3 particles [12, 13]. Such an argument is usually verified when Al_2O_3 particles are added in sufficiently large amounts. However, as has recently been reported [14], low-temperature degradation during annealing in water at 353 K is also remarkably suppressed, even though the Al_2O_3 addition is as small as 1.2 mass% and the grain sizes have been confirmed to be independent of the limited amount of Al_2O_3 addition. Therefore, further investigation is needed to obtain a full understanding of the role of Al_2O_3 particles in the Y–PSZ matrix in suppressing the low-temperature degradation transformation.

In the present work, 2 and 3 mol% Y_2O_3–ZrO_2 ceramics were dispersed with 5 vol% (approximately equal to 3.4 mass%) Al_2O_3 particles. The transformations during annealing in water and in vacuum were investigated to explore the effect of a small quantity of Al_2O_3 addition on suppressing the low-temperature degradation transformation.

2. Experimental procedure

Commercial powders of 2 and 3 mol% Y_2O_3–ZrO_2 (abbreviated as 2Y and 3Y) and Al_2O_3 were used as the starting materials. The Y_2O_3–ZrO_2 solid-solution powder produced by a coprecipitation method has an average crystallite size of 26 nm and high purity (< 0.002 mass% SiO_2, < 0.02 mass% Fe_2O_3, 0.013 mass% NaO_2). Some 5 vol% Al_2O_3 powder (purity > 99.8%), with an average particle size of 0.4 μm, was mixed with 2Y and 3Y powders, respectively. The samples with Al_2O_3 additions were

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abbreviated as 2Y5A and 3Y5A for the 2Y and 3Y matrices, respectively. The $\mathrm{Y_2O_3}$–$\mathrm{ZrO_2}$ and $\mathrm{Al_2O_3}$ powders were mixed in distilled water by ball milling for 12 h using a plastic pot and high-purity $\mathrm{Al_2O_3}$ milling balls. Cylinder-shaped green powder compacts of a diameter of 10 mm were made by die-pressing at 100 MPa and subsequently by cold-isostatic pressing at 200 MPa. The green compact was sintered in air at 1673 K for 2 h and cooled as fast as possible to avoid the tetragonal-to-monoclinic phase transformation during the cooling process. The sintered densities were near 100% of the theoretical values as confirmed by Archimedes' method, using water as the immersion medium. Disc-shaped specimens about 0.6 mm thick used for the annealing experiments were cut from the sintered pellets, and one side of each specimen was ground and polished to achieve a mirror-like surface finish. The microstructure was observed by scanning electron microscopy (SEM) with the samples polished and then thermally etched at 1623 K for 2 h to show the grain boundaries clearly.

The annealing treatments were performed separately in water and in vacuum with the disc specimens sealed in a Pyrex® glass tube of about 20 ml. For the annealing in water, distilled water of a half of the tube volume was put into the glass tube before sealing; and for the vacuum annealing the tube was evacuated by rotary and oil diffusion pumps to the level of 0.133 Pa. The sealed tubes were heated in an electric furnace and quickly cooled to room temperature after the annealing treatment.

X-ray diffraction (XRD) using Cu-radiation (30 kV, 15 mA) was done on the polished surfaces of the disc specimens before and after annealing to investigate the phase transformation caused by the annealing treatment. The monoclinic intensity fraction was determined from the relative XRD intensities of the two monoclinic peaks $(1\,1\,1)_{\mathrm{m}} + (1\,1\,\bar{1})_{\mathrm{m}}$ and the tetragonal peak $(1\,1\,1)_{\mathrm{t}}$ [18].

3. Results

Fig. 1 shows the monoclinic intensity fractions formed in the monolithic 2Y samples during annealing in water and in vacuum, respectively, as a function of annealing temperature. For annealing in water, no tetragonal-to-monoclinic phase transformation occurred below approximately 330 K, whereas the amount of monoclinic phase increased rapidly as annealing temperature was raised. As a special case, the disc-shaped specimen was spalled after annealing at 393 K for 100 h due to crack formation caused by a large amount of phase transformation accompanied by volume expansion [3, 4]. On the other hand, no phase transformation was detected when the annealing was done in vacuum below 373 K, even when the annealing time was three times as prolonged as that in water. Similar to the early experiment by Sato and Shimada [6], it is clear from Fig. 1 that the tetragonal-to-monoclinic phase transformation is greatly accelerated by the presence of water.

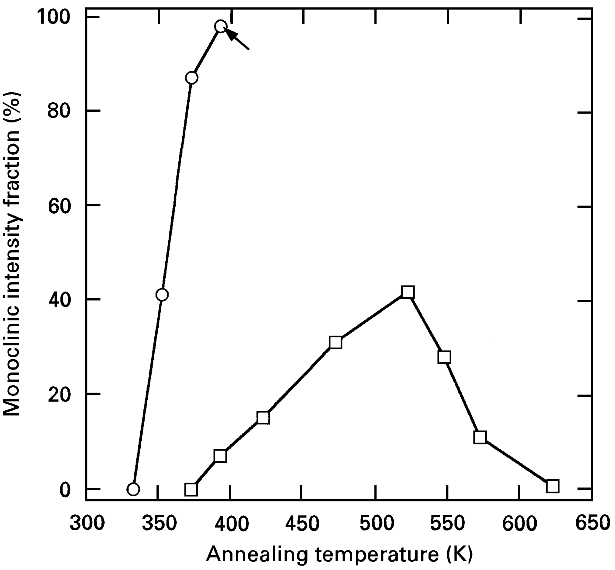

Figure 1 Monoclinic intensity fraction formed in the 2Y samples during annealing in water for 100 h (–○–) and in vacuum for 300 h (–□–) as a function of annealing temperature. Arrow points to spalled sample.

To clarify the effect of $\mathrm{Al_2O_3}$ addition on the low-temperature degradation transformation induced in the presence of water, the annealing in water was first conducted at 353 K, where the transformation during annealing in vacuum was not observed. Fig. 2 shows typical XRD patterns of the monolithic 2Y and its 5 vol % $\mathrm{Al_2O_3}$-containing composite specimens before and after annealing in water at 353 K for 100 h. Almost only tetragonal phases were contained in the two specimens before annealing. After annealing in water for 100 h, a strong peak assigned to the monoclinic $(1\,1\,\bar{1})$ reflection appeared in the annealed 2Y specimen, but no apparent change was found in the XRD pattern for the 2Y5A specimen. Furthermore, the low-temperature annealing in water was prolonged to 500 h, the amount of monoclinic phases formed during annealing was determined to see the time dependence of the transformation. As shown in Fig. 3, the monoclinic intensity fractions for the 2Y and 3Y specimens monotonously increased with annealing time, whereas almost no transformation occurred in the $\mathrm{Al_2O_3}$-containing composites even when the duration was prolonged to 500 h. These results clearly show that the phase transformation during annealing in water is effectively suppressed by the small addition of $\mathrm{Al_2O_3}$ particles.

Fig. 4 shows the temperature dependence of the monoclinic intensity fraction formed in the monolithic 2Y and 2Y5A composite samples during annealing in water. Below 400 K, the tetragonal-to-monoclinic transformation was effectively suppressed by the addition of 5 vol % $\mathrm{Al_2O_3}$ particles. Whereas, the monoclinic intensity fraction increased rapidly above 400 K. It seems that the tetragonal-to-monoclinic transition temperature was raised by 50 K by the addition of 5 vol % $\mathrm{Al_2O_3}$ particles. However, as shown in Fig. 5, the small $\mathrm{Al_2O_3}$ addition showed no suppression effect on the tetragonal-to-monoclinic phase transformation during annealing in vacuum. Regardless of the $\mathrm{Al_2O_3}$ addition, the transformation during

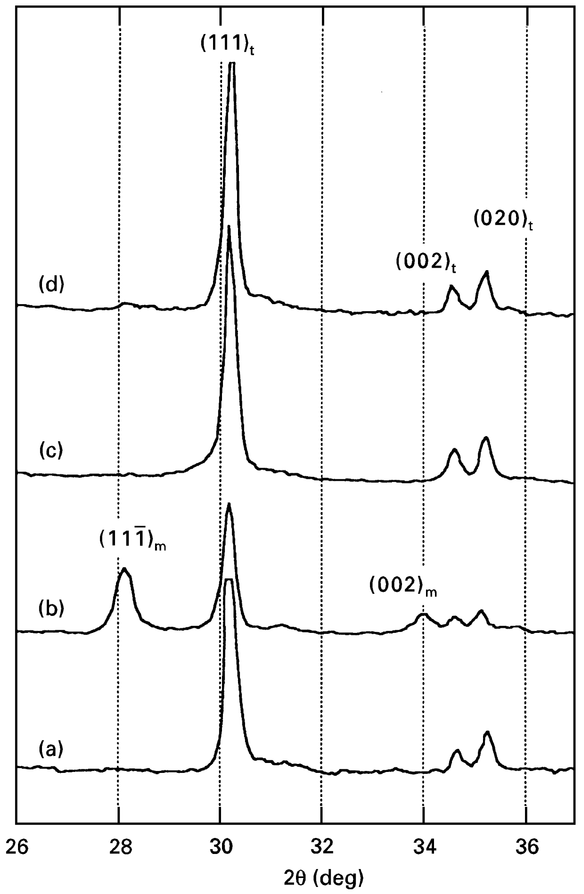

Figure 2 X-ray diffraction patterns: (a) 2Y before annealing, (b) 2Y after annealing in water at 353 K for 100 h, (c) 2Y5A before annealing, and (d) 2Y5A after annealing in water at 353 K for 100 h.

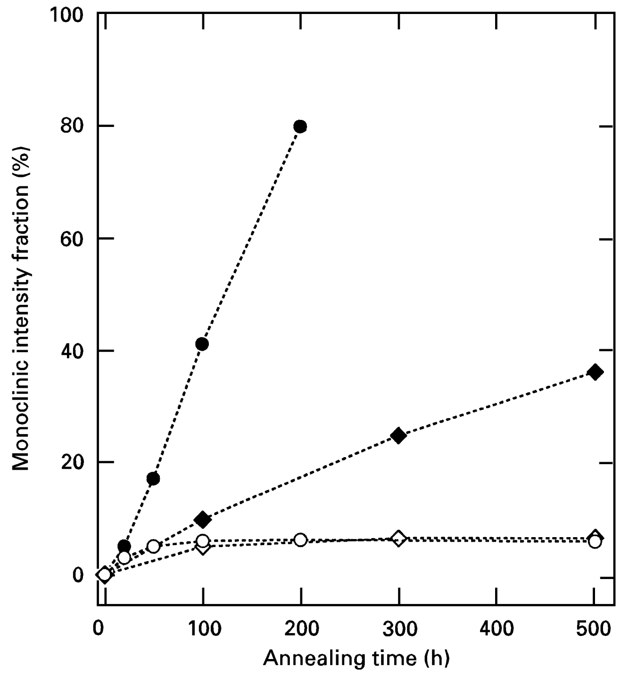

Figure 3 Monoclinic intensity fraction formed during annealing in water at 353 K as a function of annealing time: (●) 2Y, (◆) 3Y, (○) 2Y5A, (◇) 3Y5A.

annealing in vacuum increased with increasing annealing temperature from 373 K and exhibited a maximum at about 520 K, and then decreased to zero at about 623 K.

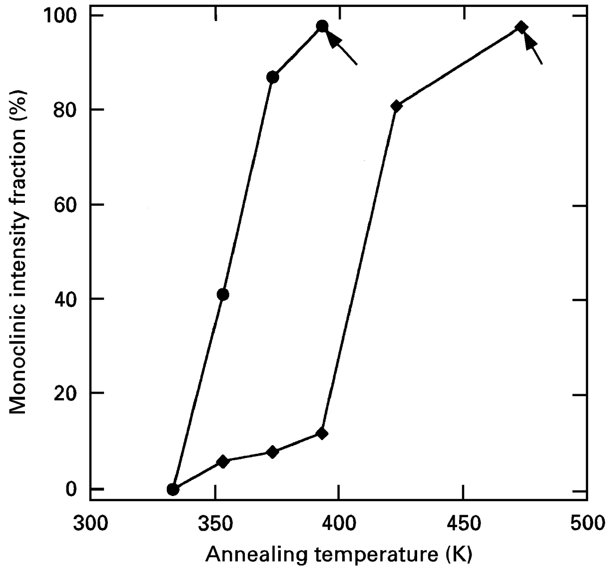

Figure 4 Variation of monoclinic intensity fraction formed in the 2Y (–●–) and 2Y5A (–◆–) samples during annealing in water for 100 h as a function of annealing temperature. Arrows point to spalled samples.

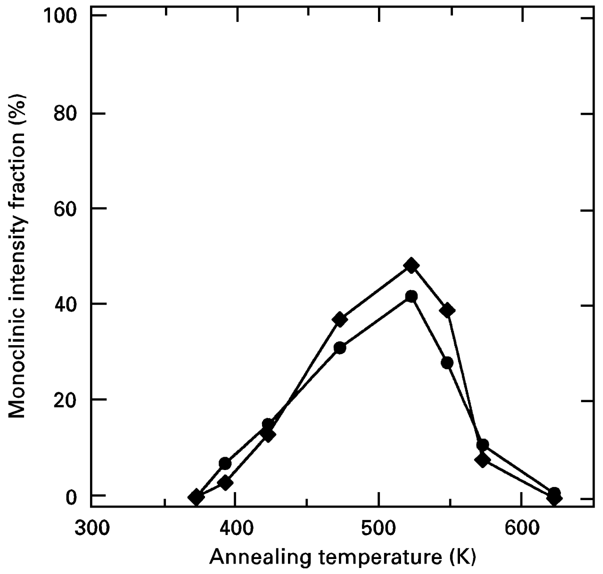

Figure 5 Variation of monoclinic intensity fraction formed in the 2Y(–●–) and 2Y5A (–◆–) samples during annealing in vacuum for 300 h as a function of annealing temperature.

Because the grain size of $ZrO_2(Y_2O_3)$ is usually considered to be an important factor in influencing the phase transformation, the grain sizes of the monolithic 2Y and its 5 vol % Al_2O_3-containing composite samples were investigated to clarify this point. As shown in Fig. 6, the grain sizes of $ZrO_2(Y_2O_3)$ are almost the same for both samples.

4. Discussion

The phase transformation during annealing in vacuum is considered to be due to the intrinsic property of partially stabilized zirconia. That is, the metastable tetragonal phase transforms to the relatively stable monoclinic phase by thermal activation in the absence

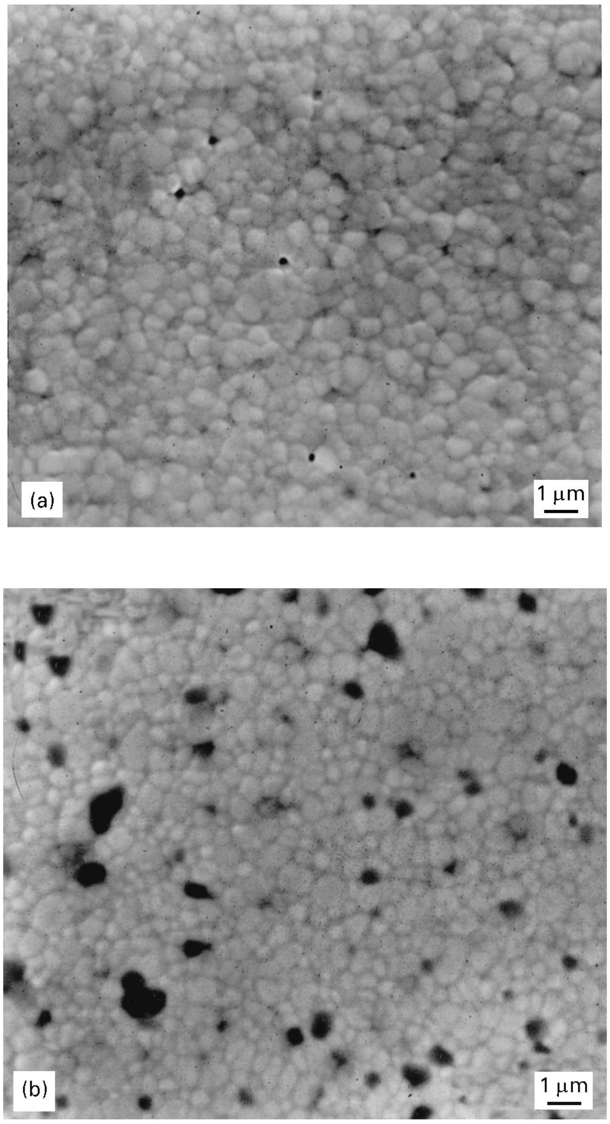

Figure 6 SEM micrographs of thermally etched surfaces of (a) 2Y, and (b) 2Y5A samples. The dark grains in (b) are Al_2O_3 particles.

of water. The tetragonal phase is retained metastably near room temperature because the thermal activation energy is not enough to overcome the strain energy at low temperature [19]; when annealing temperature is high enough, the tetragonal-to-monoclinic transformation becomes difficult as a consequence of the decrease in the free energy of the tetragonal phase. Therefore, the intensity fraction of the monoclinic phase formed during annealing in vacuum shows a peak at 523 K, as shown in Figs 1 and 5. The fact that the transformation during annealing in vacuum is not suppressed suggests that the intrinsic phase stability was not influenced by the small addition of Al_2O_3 particles.

On the other hand, the phase transformation during annealing in water is directly caused by the presence of water at low temperature, where the transformation during annealing in vacuum takes place with difficulty, as shown in Fig. 1. Comparison of Figs 4 and 5 suggests that the small Al_2O_3 addition only effectively suppresses such a phase transformation induced by water. Of course, the transformation during annealing in vacuum may be retarded by a large amount of Al_2O_3 addition, but in that case changes in elastic modulus and grain size, and so forth, should be taken into consideration [12, 13]. Because the present work was intended to explore the effect of the presence of Al_2O_3 on the suppression of the low-temperature degradation transformation, only 5 vol % Al_2O_3 particles were added so that the property change was negligible. Indeed, because of the limited addition of Al_2O_3 the sizes of the ZrO_2 grains both in the monolithic 2Y–PSZ and 2Y–PSZ/5 vol % Al_2O_3 composite are the same, as shown in Fig. 6. This result also gave an explanation why the phase transformation during annealing in vacuum was not suppressed by the small amount of Al_2O_3 addition. According to the other investigations [20, 21], Al_2O_3 does not dissolve into the ZrO_2 matrix under the present sintering condition. If dissolution had occurred, if any, its influence on the transformation during the annealing in vacuum would have appeared.

Clearly, transformation during annealing in vacuum was not retarded because the essential phase stability of tetragonal phases does not change with the small amount of Al_2O_3 addition. Therefore, it seems that the small amount of Al_2O_3 addition displays the suppression effect on the phase transformation during annealing in water through its interaction with water. The effect of the small Al_2O_3 addition on the phase transformation during annealing in water must be examined in connection with the presence of water. At the surface of Al_2O_3-dispersed Y–PSZ samples soaked in water, it is possible that Al_2O_3 particles dispersed in the $ZrO_2(Y_2O_3)$ matrix react with H_2O to form aluminum hydroxide. A recent investigation [22] has also revealed the formation of aluminium hydroxide [$Al(OH)_3$] from α-Al_2O_3 particles in aqueous solutions. In a similar way, it has been proposed that yttrium hydroxide is formed by the dissolution of yttrium ions in $ZrO_2(Y_2O_3)$ as a key process responsible for the low-temperature degradation transformation [7]. Because the existence of $Y(OH)_3$ needs higher pressure than that of $Al(OH)_3$ in the water-containing system [23–25], it is reasonable to presume that the hydro-reaction of Al_2O_3 occurs more easily than that of Y_2O_3 under the same conditions. The solubility of $Al(OH)_3$ into water or basic solutions (pH 7.2–9.3) was also confirmed to be very limited [22]. Therefore, the surface of the $ZrO_2(Y_2O_3)$ matrix is "protected" from further attack of H_2O by the preferably formed $Al(OH)_3$; as a result, the transformation was suppressed in the initial step. On the other hand, as shown in Fig. 4, the small addition of Al_2O_3 lost the suppression effects on the phase transformation during annealing in water above 400 K. Two reasons are considerable to be related to that result. First, $Al(OH)_3$ is difficult to form on the specimen surface because $Al(OH)_3$ is not thermodynamically stable above 400 K according to the phase diagram in the alumina–water system [23]. Second, the phase transformation is increasingly thermally activated with an increase in annealing temperature, whereas such a transformation determined by the intrinsic phase stability cannot be suppressed by the small addition of Al_2O_3 as shown in Fig. 5.

5. Conclusions

The tetragonal-to-monoclinic phase transformation during annealing in water can be directly induced in the presence of water at a temperature, where the thermally activated transformation is difficult to occur. Even though the amount is as small as 5 vol %, the dispersion of Al_2O_3 particles into the Y–PSZ matrix is effective in suppressing such water-accelerated transformations. However, the limited amount of Al_2O_3 addition does not exhibit a suppression effect on the transformation during annealing in vacuum and that in water at high temperatures. Because the small addition of Al_2O_3 particles did not influence the phase stability or transformability of tetragonal $ZrO_2(Y_2O_3)$ at least under the present experimental conditions, the suppression effect of Al_2O_3 on the water-induced phase transformation is considered to be realized through its interaction between H_2O and Al_2O_3 particles. Namely, hydroxydation of Al_2O_3-dispersed particles is preferably formed and the sample surface is consequently "protected" from the further interaction of H_2O with the $ZrO_2(Y_2O_3)$ matrix, which causes the low-temperature degradation transformation.

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Received 25 March
and accepted 17 July 1996