JOURNAL OF MATERIALS SCIENCE **35** (2000) 3053 – 3057

Effect of calcining temperature on the tetragonal-to-monoclinic phase transition characteristics in 2 mol% yittria-doped zirconia ceramics

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Two types of tetragonal-to-monoclinic (t-m) phase transition characteristics were observed in the 2Y-TZP powder samples. In the sample calcined below 1200°C, the t-m phase transition occurred below 200°C, and the fraction of the monoclinic phase increased sigmoidally. At the beginning of the transition, the fraction of the monoclinic phase increased gradually, and the lattice strain remained unchanged. The abrupt increase in the monoclinic phase accompanying the increase in the lattice strain of the tetragonal phase followed this. Finally, the fraction of the monoclinic phase was saturated, and the lattice strain dropped to 0%. The reaction between the adsorbed water and 2Y-TZP was essential for the t-m phase transition of 2Y-TZP to occur in air at around room temperature. The lattice strain stored in the tetragonal lattice assisted the phase transition. On the other hand, the fraction of the monoclinic phase increased, accompanied by a decrease in the lattice strain in the 1400°C calcined powder. After the fraction of the monoclinic phase was almost saturated, the lattice strain dropped to 0%. A gas-solid reaction between the water vapor in air and 2Y-TZP and the diffusion of OH^- ion into the 2Y-TZP lattice were essential for this type of t-m phase transition. © *2000 Kluwer Academic Publishers*

1. Introduction

The tetragonal-to-monoclinic (t-m) phase transition in yittria-doped tetragonal zirconia polycrystals (Y-TZP) and partially stabilized zirconia (Y-PSZ) is closely connected to their good bending strength and high toughness and also their degradation around 200°C in air [1–5]. The formation of OH^- ion during the gas-solid reaction between water vapor and Y-TZP or Y-PSZ and the diffusion of OH^- ion in Y-TZP or Y-PSZ lattice are essential for the t-m phase transition to occur during low temperature annealing in air [6].

For the 2 mol% yittria-doped TZP (2Y-TZP) powder calcined at temperatures below 1200°C, the isothermal t-m phase transition occurs in air even at room temperature [7]. The transition takes place after a certain retardation time, and the amount of monoclinic phase increases abruptly. On the other hand, no isothermal t-m phase transition occurs in air at room temperature in the powder samples calcined above 1300°C. In the Fourier-transformed infrared (FT-IR) diffuse scattering spectra of the samples calcined below 1200°C, a broad band at around 3300 cm^{-1} was observed, although this band disappears after the calcination above 1300°C. This broad band indicates the existence of adsorbed water on the surface of the 2Y-TZP powder samples after calcination below 1200°C. In the present study, we have tried to understood the effect of calcining temperature on the t-m phase transition behavior.

2. Experimental

Two mol% yittria-doped zirconia powders (Sumitomo-Osaka Cement) were used in the present study. The impurities were 0.001 mass% Al_2O_3, 0.0015 mass% SiO_2, 0.0006 mass% Fe_2O_3, and 0.0014 mass% TiO_2, according to the supplier's analysis. The as-received powders were calcined in air for 24 h at temperatures of 1100–1400°C and were removed from the furnace at 1000°C in order to avoid the t-m phase transition. The annealing treatments were performed in air.

The as-calcined and annealed samples were characterized by X-ray diffraction (XRD), utilizing graphite monochromated Cu K radiation, and FT-IR diffuse scattering measurements in order to investigate the phase transition caused by the annealing treatment. The amount of monoclinic phases was estimated from the relative peak-area of the monoclinic peaks $(11\bar{1})_m + (111)_m$ and the monoclinic plus tetragonal peaks $(111)_m + (111)_m + (111)_t$. The lattice strain of the tetragonal phases in the 2Y-TZP powder samples was determined by using the Voigt function in single line method for the analysis of XRD line broadening [8].

3. Experimental results

The XRD measurements of the as-calcined samples indicated that the obtained powder samples were the tetragonal single phase. The mean crystallite size of the as-calcined powders increased with the increase in the calcining temperature and ranged from 37 (at 1100°C) to 57 nm (at 1400°C). Rapid growth of the crystallite size with increasing calcining temperature was not observed in the present study. The lattice strain of the as-calcined powders was about 0.1% and did not depend on calcining temperature.

Figs 1–4 show the increase in the fraction of the mono clinic phase after annealing in air at 77°C, 140°C, 200°C and 280°C for the 2Y-TZP powder after being calcined at temperatures of 1100–1400°C, respectively. For the 2Y-TZP powder after being calcined at temperatures below 1200°C, the t-m phase transition occurred below 200°C, and the fraction of the monoclinic phase increased sigmoidally. At the beginning of the phase transition, the fraction of the monoclinic phase increased gradually up to about 10%. The fraction of the monoclinic phase abruptly increased thereafter but finally became saturated. The saturated values of the monoclinic phase were about 95%. This value did not depend on the calcining temperature or on the annealing temperature. Similar isothermal t-m phase transition behavior was observed even at room temperature [7] in the 2Y-TZP powder samples after being calcined at temperatures below 1200°C. The transition rate increased with increasing annealing temperature up to 140°C, but the rate slowed down at 200°C. Finally, this t-m phase transition characteristic was not observed when the powder sample was annealed in air above 280°C, and only a few percent of the monoclinic phase was formed after a long period of annealing.

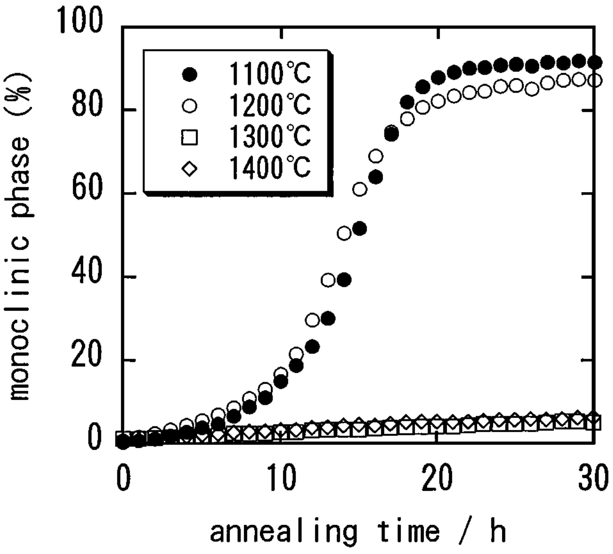

Figure 1 The amount of the monoclinic phase in the 2Y-TZP powder formed during the isothermal annealing in air at 77°C. The calcining temperatures is indicated in the figure.

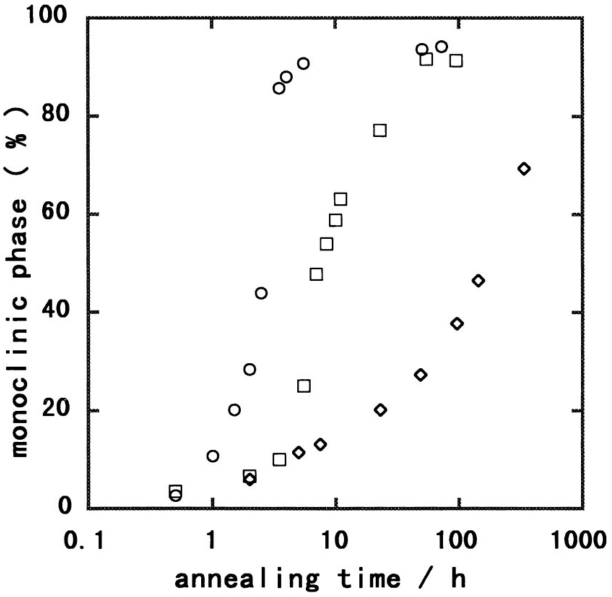

Figure 2 The amount of the monoclinic phase in the 2Y-TZP powder formed during the isothermal annealing in air at 140°C. For calcining temperature key, see Fig. 1.

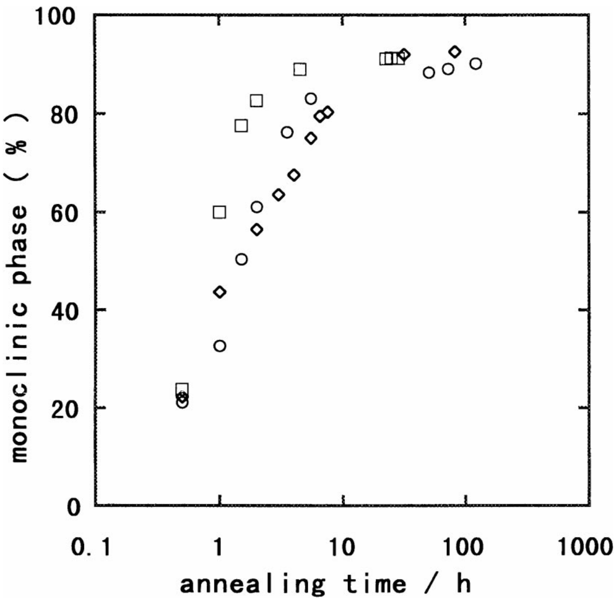

Figure 3 The amount of the monoclinic phase in the 2Y-TZP powder formed during the isothermal annealing in air at 200°C. For calcining temperature key, see Fig. 1.

On the other hand, in the 2Y-TZP powder samples calcined at 1400°C, only a small percent of the tetragonal phase was transformed to the monoclinic phase after a long period of annealing in air at 77°C. The fraction of monoclinic phase increased when the 2Y-TZP powder samples were annealed at a temperature above 140°C in air and the transition rate increased with the increase in annealing temperature. The t-m phase transition of the 1300°C calcined samples showed an intermediate characteristic. After a low temperature annealing, i. e., at 77°C, the phase transition characteristics

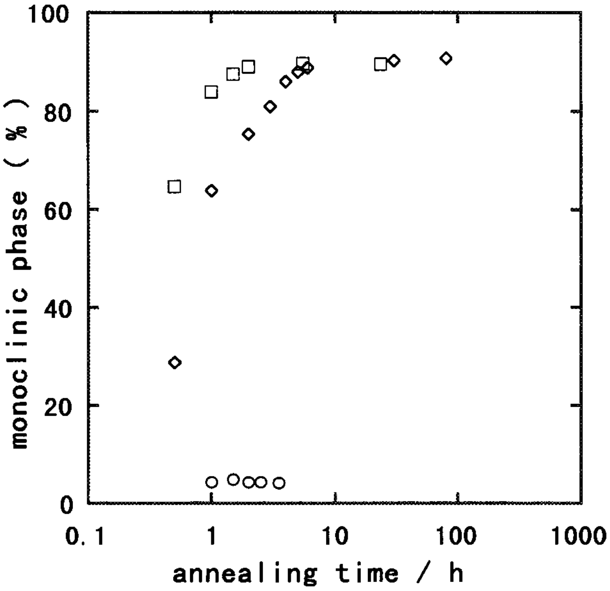

Figure 4 The amount of the monoclinic phase in the 2Y-TZP powder formed during the isothermal annealing in air at 280°C. For calcining temperature key, see Fig. 1.

were similar to those of sample calcined at temperatures above 1400°C, and a small percent of the monoclinic phase was formed after a long period of annealing. On the other hand, the t-m phase transition occurred after annealing above 140°C, and the fraction of monoclinic phase increased sigmoidally.

Fig. 5 shows the change in the lattice strain of the 1100°C calcined 2Y-TZP powder at room temperature with the increase in the monoclinic phase. On these isotherms, three distinctive stages of annealing time were clearly recognized. At the first stage of annealing up to 500 h, the lattice strain was 0.1% and remained unchanged. The fraction of the monoclinic phase increased gradually from 0% to about 10% at this stage. The increase in the lattice strain up to about 0.2% was observed at the second stage of annealing (500–1100 h), and the slope of the isotherm became steep as the annealing time proceeded. The fraction of the monoclinic phase increased abruptly to about 95% at this stage. A sudden drop in the lattice strain to 0% was observed at the beginning of the third stage of annealing, and the lattice strain of 0% remained unchanged during this stage. At this stage of annealing, some of the tetragonal phase was transformed to the monoclinic phase, and the fraction of monoclinic phase reached the saturated value.

Fig. 6 shows the change in the lattice strain of the 1400°C calcined 2Y-TZP powder annealed at 177°C in air with the increase in the monoclinic phase. In this case, only two stages of annealing time were recognized on these isotherms. At the first stage of annealing up to 90 h, the lattice strain was decreased from 0.1% to about 0.05%. After this annealing stage, the lattice strain suddenly dropped to 0% and remained unchanged (second stage of annealing). The fraction of monoclinic phase increased gradually, and about 80% of the tetragonal phase was transformed to the monoclinic phase after 90 h of annealing in air. The fraction of the monoclinic phase still increased thereafter, but the transition rate slowed down at the second stage of annealing and finally the fraction of the monoclinic phase was saturated (about 95%).

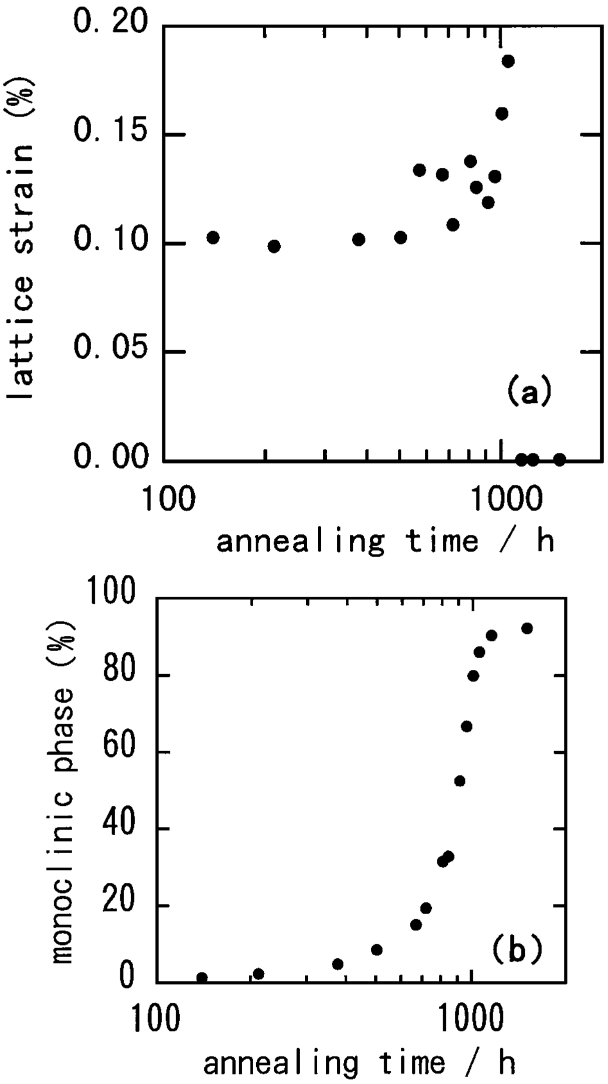

Figure 5 The change in the lattice strain of the 1100°C calcined 2Y-TZP powder at room temperature (a) with the increase in the monoclinic phase (b).

4. Discussion

The obtained results strongly suggested that two types of the t-m phase transition exist in the 2Y-TZP powder samples when annealed in air. In the FT-IR diffuse scattering spectra of the 2Y-TZP powder samples calcined at 1100 and 1200°C, a broad band around 3400 cm^{-1} and around 1550 cm^{-1} was clearly observed. These bands around 3400 cm^{-1} and 1550 cm^{-1} correspond to the stretching vibration and deformation vibration mode of H_2O, respectively. The existence of these bands indicated the existence of adsorbed water on the surface of the 2Y-TZP powder. On the other hand, these bands were not observed in the samples calcined above 1300°C. This means that no water vapor can adsorb on the surface of the 2Y-TZP powder after being calcined at 1300°C or higher temperatures. The existence of adsorbed water on the surface of the 2Y-TZP powders may have affected the t-m phase transition characteristics.

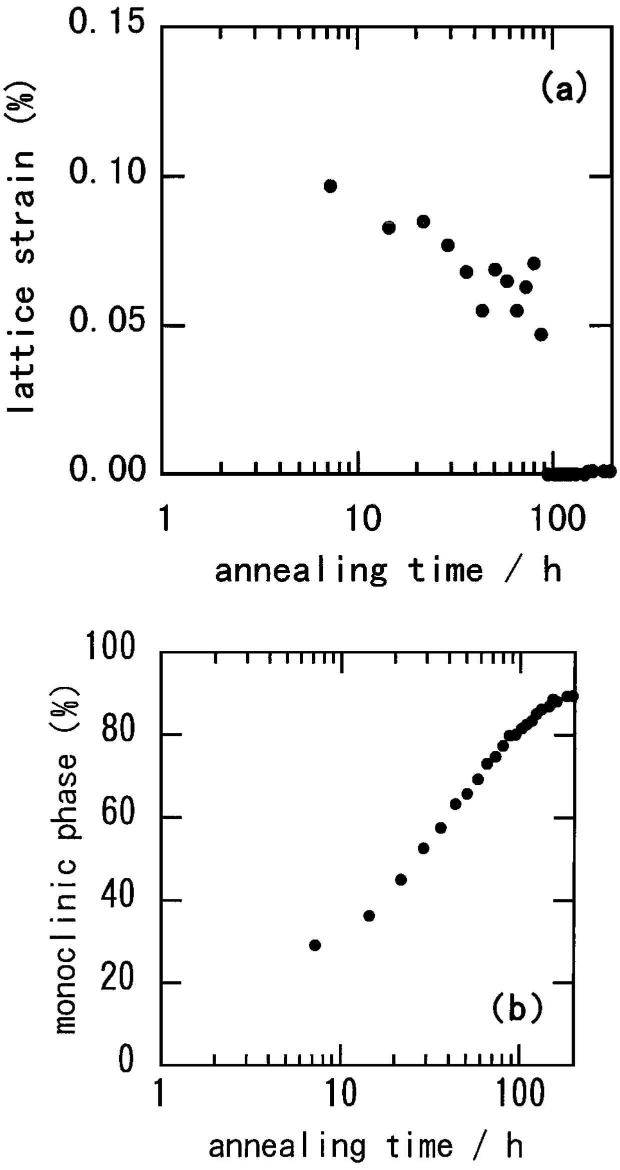

Figure 6 The change in the lattice strain of the 1400°C calcined 2Y-TZP powder at 177°C (a) with the increase in the monoclinic phase (b).

In the case of the 2Y-TZP powder after being calcined at 1400°C, the t-m phase transition occurred without a retardation time, and this phase transition proceeded accompanying the relaxation of the lattice strain. After the t-m phase transition was nearly finished, the lattice strain dropped to 0%. Fig. 7 shows the "C"-type behavior in the time-temperature-transformation (T-T-T) diagram of the 2Y-TZP powder after calcination at 1400°C. In this T-T-T diagram, each annealing time when half of the saturated monoclinic phase was attained was plotted against the annealing temperature. A similar "C"-type curve was observed in the T-T-T diagram of 2.2Y-TZP, 3.3Y-TZP and 5.0Y-TZP [6]. In the FT-IR diffuse scattering spectra of the 1400°C calcined 2Y-TZP powder after annealing in air (about 80% of monoclinic phase), a rather sharp band at 3340 cm^{-1} which is ascribed to the stretching vibration mode of Me-O-H bonds was observed [7]. It is noted that this rather sharp band was always observed whenever the Y-TZP and Y-PSZ powders were transformed to the monoclinic phase by isothermal annealing in air [6]. The appearance of this band strongly suggests a gas-solid reaction between the water vapor in air and the 2Y-TZP powder. The reaction between the water vapor and 2Y-TZP and the formation of OH$^-$ ion may be the rate determining step, because the diffusion of OH$^-$ ions into the 2Y-TZP lattice is fast around 200°C. This gas-solid reaction may occur first in the powders with higher lattice strain, and these powder are transformed to the monoclinic phase. This gas-solid reaction and the subsequent phase transition proceed to the powder with lower lattice strain. After the 2Y-TZP powder with a lattice strain of about 0.05% is transformed to the monoclinic phase, a small amount of the tetragonal phase with 0% lattice strain remains. These powders cannot be transformed to the monoclinic phase. Thus, the fraction of the monoclinic phase is saturated during the second stage of annealing.

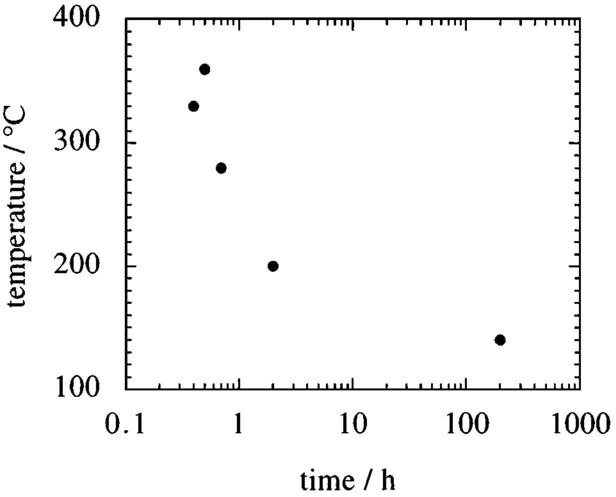

Figure 7 The T-T-T diagram of the 2Y-TZP powder after calcination at 1400°C.

On the other hand, in the 2Y-TZP powder calcined below 1200°C, some tetragonal phase may have higher lattice strain and is unstable even at room temperature. In these powders, the adsorbed water can react with the ZrO_2 (Y_2O_3) and can form Me-O-H bonds even at room temperature. Thus, several percent of the as-calcined 2Y-TZP powder was transformed to the monoclinic phase without a significant increase in the lattice strain at the first stage of annealing. During this t-m phase transition, the lattice strain began to be stored in the tetragonal phase due to the volume expansion of neighboring transformed particles. This stored lattice strain in the tetragonal phase assists the reaction between the adsorbed water and ZrO_2 (Y_2O_3) and the subsequent t-m phase transition. The increase in the monoclinic phase fraction accelerates the increase in stored lattice strain in the tetragonal phase. Thus, a sigmoidal increase in the monoclinic phase fraction accompanying the abrupt increase in the lattice strain in the 2Y-TZP was observed at the second stage of annealing. At the third stage of annealing, almost all of the tetragonal phase with a certain amount of the lattice strain was transformed to the monoclinic phase and several percent of the tetragonal phase remained. The tetragonal particles with 0% lattice strain cannot be transformed to the monoclinic phase as is observed in the 2Y-TZP powder after being calcined at 1400°C.

Thus, further phase transition was not observed at the third stage of annealing. The reaction between the adsorbed water and 2Y-TZP powder will be the rate-determining step in the t-m phase transition, and the storing of a large quantity of lattice strain may assist the diffusion of OH^- ions into the 2Y-TZP lattice. The amount of adsorbed water and also the water supplied from the annealing atmosphere determine the amount of transformed monoclinic phase during the annealing [7]. The adsorbed water is released from the surface of the 2Y-TZP powder above 280°C. The gas-solid reaction between the water vapor and 2Y-TZP does not occur in the 2Y-TZP powder after being calcined below 1200°C. Thus, no t-m phase transition was observed during the annealing above 280°C in air. A small percent of the tetragonal phase is transformed to the monoclinic phase during the heating of 2Y-TZP powder up to 280°C.

Acknowledgement

The present study was supported in part by the Nippon Sheet Glass Foundation for Material Science and Engineering.

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Received 17 March
and accepted 17 August 1999