

# Influence of Temperature on Elastic Modulus and Strength of MgO-Partially Stabilized Zirconia (Mg-PSZ)

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## MgO 部分安定化ジルコニア (Mg-PSZ) の弾性率及び強度の温度変化

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The influence of temperature on elastic modulus and strength of 9 mol% MgO-containing partially stabilized zirconia (Mg-PSZ) aged around 1100°C was studied. Elastic moduli on heating increased with increasing temperature after showing minimum values around 600°C. Elastic moduli on cooling monotonously increased with decreasing temperature. The strength of as-received specimen A have a maximum value around 200°C. The strengths of aged specimens on heating increased with increasing temperature after showing a minimum value around 600°C. On cooling, the strength of specimen B aged for 2 h increased remarkably with decreasing temperature to a maximum value at 450°C, and then decreased remarkably. On the other hand, the strength of specimen C aged for 8 h showed a constant value between 1000 and 400°C and decreased slightly below 400°C.

**Key-words:** Mg-PSZ, PSZ, Partially stabilized zirconia, Elastic modulus, Young's modulus, Strength, Flexural strength, Monoclinic zirconia, Thermal hysteresis

### 1. Introduction

Because of high strength and high fracture toughness, zirconia alloys have received considerable attention for structural applications. Especially, the materials having high strength above 2000 MPa in yttria-containing tetragonal zirconia (Y-TZP) have already been developed.<sup>1)</sup> However, it was known that Y-TZP exhibited the degradation of strength by thermal aging for long period or applying stress from 200 to 300°C.<sup>2)-4)</sup> On the other hand, MgO-containing partially stabilized zirconia (Mg-PSZ) have the possibility used as engineering materials in higher temperature than Y-TZP because there is no degradation of strength from 200 to 300°C, and it has been tried to apply as engine components, or extrusion and wire-drawing dies. There are many reports about observation of microstructure, and mechanical and thermal properties of Mg-PSZ. It has been already appeared

that their properties were affected by the condition of thermal treatment.<sup>5)-8)</sup> However, the thermal hysteresis of elastic modulus and strength has not been reported as far as we know. In this paper, the flexural strength and Young's modulus of Mg-PSZ on heating and cooling were reported and the relation between their properties and the tetragonal to monoclinic phase transformation of zirconia estimated from thermal expansion-contraction curves were considered.

### 2. Experimental procedure

The specimens used in this paper are 9 mol% MgO-containing partially stabilized zirconia manufactured by normal sintering. The mixed powder of ZrO<sub>2</sub> and MgO (TZ-9MG, Tosoh Co., Ltd.) was pressed uniaxially at 20 MPa and then was compacted isostatically at 200 MPa. The compacted specimens were sintered at 1700°C for 2 h, cooled at 200°C/h to 1000°C, and then the electric source of furnace has been off. Specimen A is as-fired, and specimens B and C are aged for 2 and 8 h around 1100°C, respectively. Differences in grain sizes were scarcely recognized among their specimens and the average grain size was 25 μm. The sintered bodies were ground and polished into rectangular bars of 3×4×20 mm for measuring a thermal expansion-contraction curve, 6×1×70 mm for an elastic modulus and 3×4×40 mm for a flexural strength. The elastic modulus was measured by a flexural resonant vibration method<sup>9)</sup> and the flexural strength was measured by a three-point bending method with a span of 30 mm and a crosshead speed of 0.5 mm/min.<sup>10)</sup> The thermal expansion coefficient was measured on a continuous recording dilatometer. In all cases, the heating and cooling rates were 5°C/min, and the elastic modulus and flexural strength were measured after holding for 10 min at the measuring temperature. The mirror-polished surface of specimens were etched for 2-10 min in aqueous solution

saturated by ammonium fluoride ( $\text{NH}_4\text{F}$ ) and the microstructures were characterized by scanning electron microscopy (SEM). Lattice parameters and monoclinic zirconia contents were measured by an X-ray powder diffraction method.<sup>11),12)</sup> The whole-powder-pattern-fitting method developed by Toraya was used for analysis of diffraction patterns.<sup>11)</sup>

### 3. Results

#### 3.1 Microstructure

Table 1 shows the lattice parameters and monoclinic zirconia contents obtained by X-ray powder diffraction. Cubic, tetragonal and monoclinic zirconia for specimen A, and cubic and monoclinic zirconia for specimens B and C were detected. The

monoclinic zirconia contents of specimens A, B and C were 13, 48 and 66%, respectively.

Figure 1 shows the microstructures of three specimens with the different aging time. Number 1 in the photographs of specimens A, B and C show the macroscopic structure, and numbers 2 and 3 show the microstructures of grain boundary and inner part of grain, respectively. In the case of specimen A, precipitation phases in grain boundary were little and uncontinuous. The cubic zirconia was decomposed into tetragonal zirconia and MgO on cooling, and a part of the tetragonal zirconia transformed to monoclinic zirconia below about 1200°C.<sup>5)</sup> It is estimated that the precipitates such as oblate ellipsoids in grains were tetragonal zirconia and the

Table 1. Lattice Parameters and Monoclinic Zirconia Contents

	Cubic $\text{ZrO}_2$		Tetragonal $\text{ZrO}_2$			Monoclinic $\text{ZrO}_2$					
	a (Å)	V (Å <sup>3</sup> )	a (Å)	c (Å)	V (Å <sup>3</sup> )	a (Å)	b (Å)	c (Å)	$\beta$ (deg)	V (Å <sup>3</sup> )	Xm (%)
A	5.0775	130.9	3.5919	5.194	134.0	5.231	5.080	5.348	98.89	140.4	13
B	5.0840	131.4	-	-	-	5.154	5.161	5.335	98.85	140.2	48
C	5.0800	131.1	-	-	-	5.151	5.195	5.324	99.05	140.7	66

a, b, c : lattice parameter (Å),  $\beta$  : axial angle, V : cell volume (Å<sup>3</sup>)

Xm : monoclinic zirconia (wt%)

Specimen A is as fired. Specimen B and C are aged for 2 and 8 h.

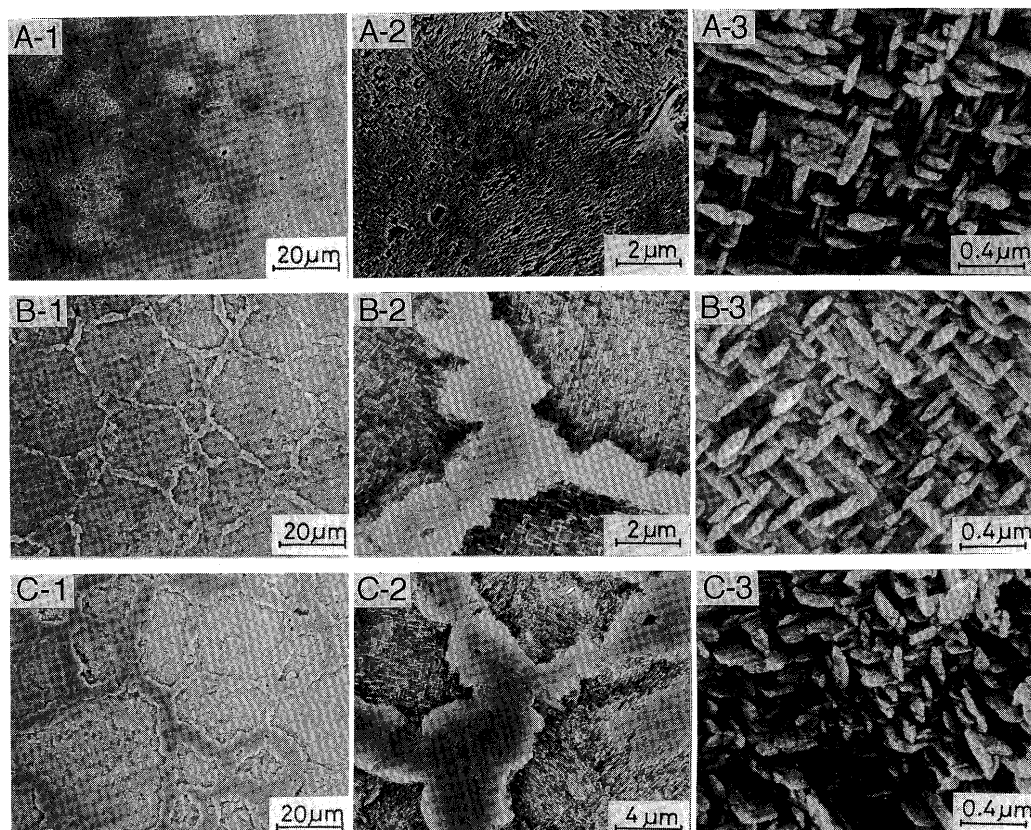


Fig. 1. Microstructures of MgO-partially stabilized zirconia (Mg-PSZ). Specimen A is as-fired. Specimens B and C are aged for 2 and 8 h, respectively.

precipitates in grain boundary consist of monoclinic zirconia mixed with MgO.<sup>13)</sup> The amount of precipitates in the grain boundary became large by aging time for long periods. It is considered that the tetragonal zirconia such as oblate ellipsoidal transformed to monoclinic zirconia on cooling to room temperature because tetragonal zirconia was not recognized in specimens B and C as shown in Table 1. It was estimated that the cracks in specimens B and C were more than that in the specimen A, because most of the cracks to affect to the strength were in precipitation phases<sup>5),13)</sup> and the amount of precipitation phases in specimens B and C were more than that in specimen A.

### 3.2 Thermal expansion-contraction curves

Figure 2 shows the thermal expansion-contraction curves in the range of room temperature and 1000°C. In the specimen A, there were slight changes in the thermal expansion coefficient in the range of 600 and 700°C on heating and 650 and 550°C on cooling. It was estimated that their changes corresponded to the phase transformation between monoclinic and tetragonal zirconia, but their changes were slight because the monoclinic zirconia content in specimen A was less than those in specimens B and C. On the other hand, the thermal expansion-contraction curves for specimens B and C showed the remarkable hysteresis and inflection points cor-

responding to the phase transformation was also clear. If monoclinic to tetragonal phase transformation and tetragonal to monoclinic phase transformation were defined as  $A_s$  and  $M_s$  points, the  $A_s$  point and the end point of phase transformation for the specimen B on heating were 580 and 770°C, and the  $M_s$  point and the end point on cooling were 420 and 270°C, respectively. After slightly increasing of the thermal expansion coefficient in the range of 415 and 470°C, the thermal expansion curve of the specimen C showed the tendency of slight decreases above 470°C and remarkable decrease in the range of 750 and 950°C, but the  $A_s$  point was ambiguous unlike that of the specimen B. On the other hand, the inflection point on cooling was clear and it was estimated that the  $M_s$  point and the end point of phase transformation were 580 and 335°C.

### 3.3 Elastic modulus

Figures 3, 4 and 5 show the influence of temperature on Young's moduli of specimens A, B and C on heating and cooling. The Young's modulus of specimen A was 192 GPa at the room temperature and decreased with increasing temperature to a minimum value of 133 GPa at 600°C. The elastic modulus increased with increasing temperature above 600°C and showed a constant value around 140 GPa in the range of 800 and 1000°C. On the other hand, the Young's modulus on cooling increased monotonously with decreasing temperature and coincided with the curve on heating at 200°C.

The Young's modulus of specimen B was 197 GPa at the room temperature and decreased with increasing temperature to a minimum value of 141 GPa at 600°C. After increasing with increasing temperature above 600°C, that showed a constant value around 164 GPa in the range of 800 and 1000°C. However, the tendency of increasing above 600°C was remarkable rather than that of specimen A and the Young's modulus at 1000°C was larger than that of specimen A. On the other hand, the Young's modulus increased monotonously with decreasing temperature on cooling and coincided with the curve on heating at 200°C.

The change of Young's modulus of specimen C on

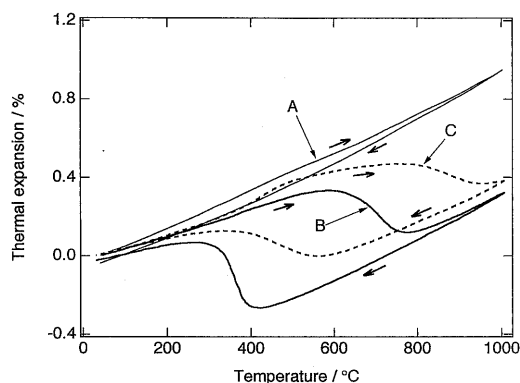


Fig. 2. Thermal expansion-contraction curves of MgO-partially stabilized zirconia.

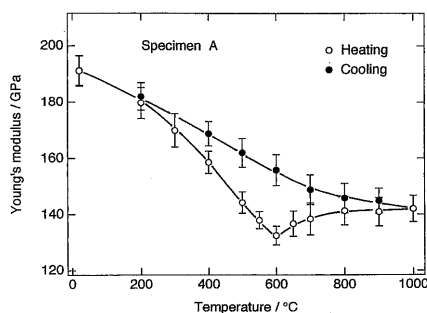


Fig. 3

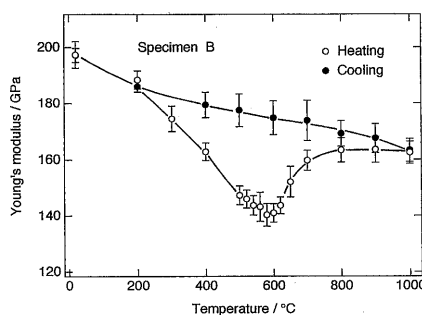


Fig. 4

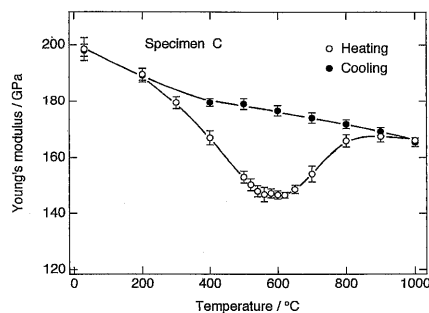


Fig. 5

Fig. 3. Young's modulus of MgO-partially stabilized zirconia (specimen A) on heating and cooling.

Fig. 4. Young's modulus of MgO-partially stabilized zirconia (specimen B) on heating and cooling.

Fig. 5. Young's modulus of MgO-partially stabilized zirconia (specimen C) on heating and cooling.

heating and cooling were similar to those of specimen B except that the minimum value of specimen C at 600°C was slightly higher than that of specimen B. But the Young's modulus of specimen C shows a broad minimum when compared with that of specimen B.

### 3.4 Flexural strength

Figures 6, 7 and 8 show the flexural strengths of specimens A, B and C on heating and cooling. Data points and error bars in their figures were average strengths for 5 specimens and standard deviations, respectively. The flexural strength of specimen A was 537 MPa and it is about twice of specimens B and C. The strength decreased monotonously with increasing temperature after reaching a maximum value of 578 MPa at 200°C and became 426 MPa at 1000°C. The strength on cooling coincided with that on heating unlike the elastic modulus.

The flexural strength of specimen B was 285 MPa at the room temperature and slightly decreased with increasing temperature to a minimum value of 270 MPa at 600°C. The strength above 600°C increased with increasing temperature and showed the unchanged value from 321 to 330 MPa in the range of 900 and 1000°C. The strength on cooling was a constant value in the range of 1000 to 750°C and remarkably increased with decreasing temperature to a maximum value of 514 MPa at 450°C in the range of 750 and 450°C. The strength decreased remarkably in the range of 450 and 400°C and reached a value near that on heating at 200°C.

The flexural strength of specimen C was 293 MPa and the relation between strength and temperature on heating was similar to that of specimen B. The strength of specimen C in the range of 900 and 1000°C showed the unchanged value from 298 to 303 MPa being lower than that of specimen B. The strength on cooling was from 296 to 307 MPa being almost unchanged in the range of 1000 and 400°C, and did not show a remarkable increase of strength unlike that in specimen B. The strength below 400°C decreased with decreasing temperature and reached a value near that on heating at 200°C.

## 4. Discussion

There are chemical bonding, crystal structure, and the length and the number of microcracks<sup>14)</sup> as the factors interacting to mechanical properties such as elastic modulus and strength. The effect of chemical bonding is negligible because the chemical composition is a constant value of 9 mol% MgO.

Although it was estimated that the amount of microcracks in specimen A was less than those of specimens B and C as described in a previous section, the Young's modulus of specimen A was slightly lower than those of specimens B and C. Therefore, it is considered that the influence of microcracks on Young's modulus was little for the specimens used in this study.

In general, the tetragonal to monoclinic phase transformation in zirconia is reflected by the change of thermal expansion coefficients.<sup>15)</sup> That is, it was considered by comparing with the temperature dependence of thermal expansion that Young's moduli of three specimens above 600°C increased with increasing temperature, because monoclinic zirconia transformed to tetragonal zirconia above that temperature. But the magnitude of Young's modulus in specimen A increased by the phase transformation was less than those in specimens B and C because the monoclinic zirconia content of specimen A was less than those of specimens B and C, that is, the amount of tetragonal zirconia increased by the phase transformation was less than those of specimens B and C. On the other hand, it was estimated that the tendency of change of Young's modulus with temperature became broad because the tendency of change of thermal expansion with temperature became little in the range of 470 to 770°C.

The monoclinic zirconia contents on the fracture surface after measuring the strength increased from 13 to 40% in specimen A, but did not change in specimens B and C. That is, it was estimated that the strength of specimen A at room temperature became about twice of specimens B and C, because of occurring of the phase transformation in specimen A and not in specimens B and C. Furthermore, it was considered that the strengths of specimens B and C

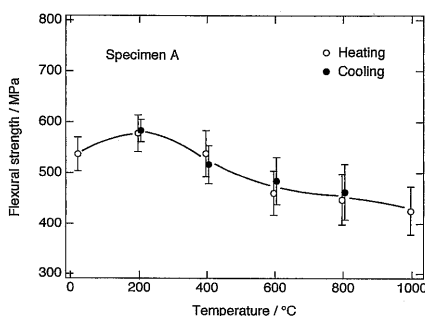


Fig. 6

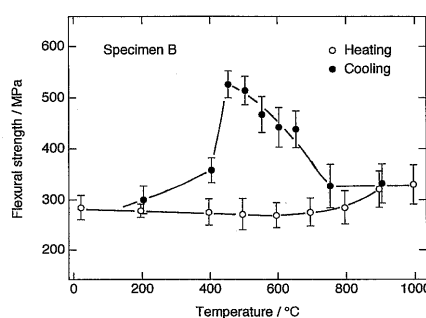


Fig. 7

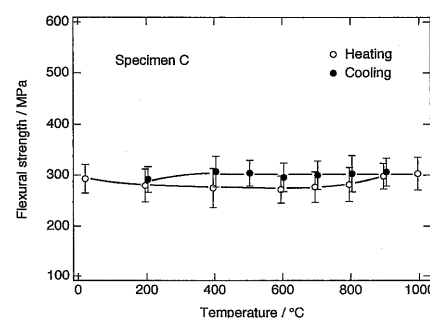


Fig. 8

Fig. 6. Flexural strength of MgO-partially stabilized zirconia (specimen A) on heating and cooling.

Fig. 7. Flexural strength of MgO-partially stabilized zirconia (specimen B) on heating and cooling.

Fig. 8. Flexural strength of MgO-partially stabilized zirconia (specimen C) on heating and cooling.

became weaker than that of specimen A, because the precipitating phases in specimens B and C were thicker than that in specimen A and the lengths of cracks in the grain boundary to affect the strength corresponded to the thicknesses of precipitating phases. However, as shown in Fig. 1, the strength of specimen C on heating was similar to that of specimen B, although the grain boundary layer in specimen C was thicker than that in specimen B, that is, the number of cracks in specimen C was more than that in specimen B. The similar strengths may suggest that the lengths of their cracks were nearly similar in both specimens. The increase of strength in specimens B and C in the range of 900 and 1000°C are attributed to increase of the elastic modulus relating to the phase transformation from monoclinic to tetragonal zirconia.

The strength of specimen B on cooling reached a maximum value at 450°C after beginning to increase at 750°C and decreased abruptly with decreasing temperature below 450°C. The temperature range showing abrupt decrease of strength corresponded to the temperature range showing abrupt change in thermal expansion-contraction curve, that is, showing the phase transformation from tetragonal to monoclinic zirconia. If there is no external constraint,  $M_s$  point being temperature of phase transformation from tetragonal to monoclinic zirconia rises to higher temperature.<sup>15)</sup> However, the  $M_s$  point lowers because there is volume expansion of about 4.5% in the phase transformation and the volume expansion is suppressed in solid. The suppressed volume expansion is converted into internal stress in their specimens and the accumulated internal stress increases with a lowering of temperature. If the accumulated internal stress becomes beyond the fracture stress of materials, microcracks evolve and phase transformation happens. The increase of strength of specimen B below 750°C on cooling corresponds to the accumulation of internal stress. It is considered that the fracture stress became a maximum at 450°C because the accumulation of internal stress became a maximum at 450°C. On the other hand, it is difficult to accumulate internal stress in specimen C because the number of microcracks in specimen C is more than that in specimen B. Therefore, the abrupt increase of strength in specimen C on cooling did not happen unlike specimen B. The slight increase of strength in specimen C on cooling was more than that on heating and it is attributed to increase of elastic modulus.

### 5. Conclusion

The influence of temperature on elastic moduli and strengths of 9 mol% MgO-containing partially stabilized zirconia (Mg-PSZ) aged around 1100°C was studied. Specimen A was not aged and consisted of cubic, tetragonal and monoclinic zirconia with a monoclinic zirconia content of 13%. Specimens B and C were aged for 2 and 8 h, and consisted of cubic

and monoclinic zirconia with monoclinic zirconia contents of 48 and 66%, respectively. Results obtained are as follows:

(1) Elastic moduli of specimens A, B and C on heating showed minimum values around 600°C and increased with increasing temperature above 600°C. Their increasing elastic moduli were associated with the phase transformation of zirconia from monoclinic to tetragonal.

(2) The strength of specimen A decreased with increasing temperature after having a maximum value around 200°C. The relation between strength and temperature on cooling was similar to that on heating.

(3) On heating, the strength of specimens B and C were increased with increasing temperature after reaching the minimum values around 600°C and showed the unchanged values in the range of 900 to 1000°C. On cooling, the strength of specimen B increased remarkably with decreasing temperature till a maximum value at 450°C after showing a constant value at 1000 to 750°C, and decreased abruptly below 450°C. The strength of specimen C on cooling showed the unchanged value in the range of 1000 and 400°C and decreased slightly below 400°C.

(4) It was estimated that the increasing strength of specimen B in the range of 750 and 450°C on cooling was attributed to accumulation of internal stress associating with the phase transformation from tetragonal to monoclinic zirconia.

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