Effects of Transition Metal Oxides on Mechanical Properties of Y-TZP

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Mechanical properties of Y_2O_3 -containing tetragonal ZrO_2 polycrystals (Y-TZP) were investigated. Several additives were used to modify the hardness and fracture toughness of Y-TZP. The effects of these individual additives were discussed and their interactions were also analyzed. Each additive, such as CoO, Fe_2O_3 . MnO_2 was found to deteriorate the mechanical properties of Y-TZP when it was used singly. But the fracture toughness of Y-TZP was significantly improved when these additives and Al_2O_3 were added in combination at a certain ratio.

Key words: Zirconia, Y-TZP, Hardness, Fracture toughness, Additive

I. Introduction

A number of researches on stabilized zirconia have been performed and their main concerns were focussed on stabilization of zirconia and toughening mechanism. [-3] Recently, as the usage of zirconia expands some other properties have been required and Y-TZP needs to be modified by adding some additives. [4-7] As the selection and way of addition of these additives change, new properties appear in the Y-TZP matrix or they may improve fracture toughness and other characteristics.

In this study, Al_2O_3 and several transition metal oxides such as CoO, Fe_2O_3 , MnO_2 were selected as additives. The effects of these materials are not known precisely, although they have been used mainly for coloring Y-TZP or for other purposes. These additives were used singly or in combination for enhancement of mechanical properties and their effects were discussed.

II. Experimental procedure

Specimens were prepared by normal ceramic processing techniques. The Y-TZP powder used was manufactured by Kyoritsu Yogyo Genryo, Ltd., Japan, and contained 5.35 wt% Y_2O_3 as stabilizer. Al_2O_3 was manufactured by Sumitomo Chemicals, Ltd., Japan and other transition metal oxides were purchased from Yakuri Ltd., Japan. Organic additives for granulation were Ceraperse-5468CF and HS-LUB1445, manufactured by San Nopco, as defloculant and binder, respectively.

Each additive may change the phase stability and mechanical properties of Y-TZP. The effect of the additives on the properties was investigated for the cases that the additives were used singly and used in combinations. For the case of single addition, the amount of additive

was varied from 0 to 8 wt%. The powders were granulated and compacted under the pressure of 1 ton/cm², sintered at 1450°C for 2 h. Phase change was investigated by X-ray diffractometer and hardness and fracture toughness were measured by a Vickers hardness tester. Microstructure was investigated by observing fracture surfaces with SEM.

These additives were added in combination to investigate the interactions of them. The amount of each additive was varied from 0 to 3 wt% and their combinations were referred from the experimental table by Taguchi method. Phase change and mechanical properties of the specimens were analyzed by using the same method.

III. Results and Discussion

1. Single additives

Y-TZP raw materials were sintered to almost tetragonal $\rm ZrO_2$ phase. But when transition metal oxides were added to Y-TZP, monoclinic $\rm ZrO_2$ phase appeared and the mechanical properties were also affected. These results were summarized in Fig. 1, Fig. 2 and Fig. 3. In Fig. 1, the ratio of monoclinic to tetragonal phase was calculated from the height of monoclinic (111) peak divided by the summation of the heights of tetragonal (111) peak and monoclinic (111) peak.

As shown in these figures, Al_2O_3 was found not to change phase and mechanical properties. The same results have been reported in many studies. But monoclinic phase increased as the amount of additive in cases of transition metal oxides and deteriorated hardness and fracture toughness. These trends depended on the ratio of monoclinic ZrO_2 phase. Fracture toughness of Y-TZP increased as monoclinic ZrO_2 phase increases up to about 18%, over which fracture toughness and hardness showed

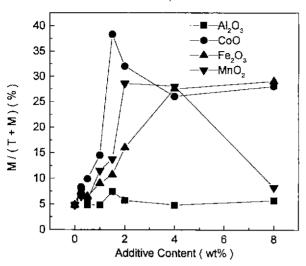


Fig. 1. The ratio of monoclinic phase in the various Y-TZP as a function of additive content.

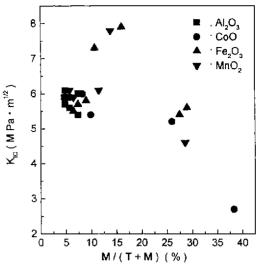
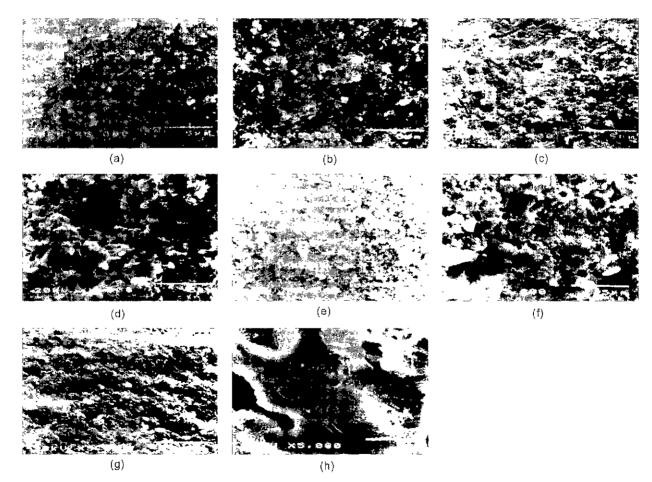


Fig. 2. Dependency of fracture toughness on the ratio of monoclinic phase.



 $\begin{tabular}{ll} \textbf{Fig. 3.} Scanning electron micrographs of fracture surface of various specimens sintered at 1450°C for 2 h. \\ (a) Y-TZP+0.25 wt%Al_2O_3, (b) Y-TZP+8.00 wt%Al_2O_3, (c) Y-TZP+0.25 wt%Fe_2O_3, (d) Y-TZP+8.00 wt%Fe_2O_3, (e) Y-TZP+0.25 wt%CoO, (f) Y-TZP+8.00 wt%CoO, (g) Y-TZP+0.25 wt%MnO_2, (h) Y-TZP+8.00 wt%MnO_2 \\ \end{tabular}$

very low values. Small addition of these materials made Y-TZP unstable and monoclinic phase appeared. The ratio

of monoclinic phase decreased again when additives were more than certain amounts which seem like solid solu-

Table 1. Mechanical Properties and the Ratio of Monoclinic Phase of Sintered Specimens for Combinational Addition

No.	Fe ₂ O ₃ (wt%)	Al ₂ O ₃ (wt%)	MnO ₂ (wt%)	CoO(wt%)	M/(T+M)(%)	Hv(kgf/mm²)	$K_{IC}(MPa \cdot m^{1/2})$
1	0.0	0.0	0.0	0.0	4.8	1229	5.9
$\overset{-}{2}$	0.0	0.0	1.5	1.5	32.0	1007	3.9
3	0.0	0.0	3.0	3.0	19.4	980	5.5
4	0.0	1.5	0.0	1.5	16.0	1209	8.4
5	0.0	1.5	1.5	3.0	30.6	1055	3.6
6	0.0	1.5	3.0	0.0	30.6	991	3.8
7	0.0	3.0	0.0	3.0	18.7	1122	5.9
8	0.0	3.0	1.5	0.0	17.4	1197	8.6
9	0.0	3.0	3.0	1.5	24.8	1075	5.9
10	1.5	0.0	0.0	3.0	30.1	1037	5.9
11	1.5	0.0	15	0.0	30.1	926	3.6
12	1.5	0.0	3 0	1.5	27.5	654	5.0
13	1.5	1.5	0.0	0.0	12.3	1120	7.5
14	1.5	1.5	1.5	1.5	31.5	1075	4.7
15	1.5	1.5	3.0	3.0	27.5	970	4.4
16	1.5	3.0	0.0	1.5	18.0	1201	10.8
17	1.5	3.0	1.5	3.0	31.5	1055	4.3
18	1.5	3.0	3.0	0.0	29.6	1004	4.8
19	3.0	0.0	0.0	1.5	28.1	1013	5.5
20	3.0	0.0	1.5	3.0	27.5	681	5.2
21	3.0	0.0	3.0	0.0	32.0	839	6 0
22	3.0	1.5	0.0	3.0	28.1	1033	5.0
23	3.0	1.5	1.5	0.0	31.5	886	4.4
24	3.0	1.5	3.0	1.5	32.4	989	4.6
25	3.0	3.0	0.0	0.0	27.0	915	6.5
26	3.0	3.0	1.5	15	26.5	1031	6.5
27	3.0	3.0	3.0	3.0	30.1	1038	4.7

tion limits.

Microstructures of some specimens are shown in Fig. 3. In case of $\mathrm{Al_2O_3}$, fine structure is maintained even though 8 wt% of $\mathrm{Al_2O_3}$ was added. But in case of transition metal oxides, very big grains appear as the amount of additive increases. As a result mechanical properties were deteriorated and several specimens were fractured during the sintering process. Transition metal oxides were found to be improper additives when they were added alone to Y-TZP.

2. Combinational additives

As shown above, single addition of transition metal oxides was improper for developing a high fracture toughness $\rm ZrO_2$. They made tetragonal $\rm ZrO_2$ unstable and decreased hardness. If these additives are used simultaneously, they would interact each other and their effects on phase stability and mechanical properties may show more complex behavior.

In this study, four additives were mixed as shown in Table 1. Phase stability and mechanical properties were investigated and the results are summarized in Table 1. In Fig. 4 and Fig. 5, fracture toughness and hardness are displayed as a function of the ratio of monoclinic phase. Similar to the case of single addition, fracture toughness of Y-TZP increased as monoclinic ${\rm ZrO_2}$ phase increases up to about 18%, over which fracture toughness and hard-

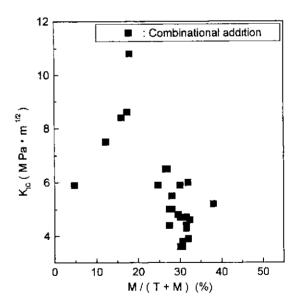


Fig. 4. Dependency of fracture toughness on the ratio of monoclinic phase.

ness showed very low values. In case of No. 16 specimen, the value of fracture toughness was up to about 11 MPa m^{1/2} while hardness keeps high value.

Sintered specimens were investigated with an optical microscope and many specimens had macrocracks at as-

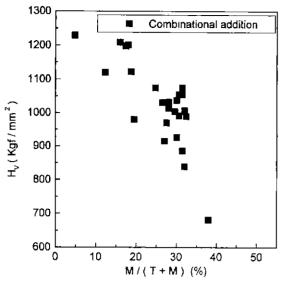


Fig. 5. Dependency of hardness on the ratio of monoclinic phase.

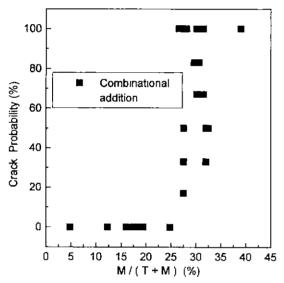


Fig. 6. Dependency of crack probability on the ratio of monoclinic phase.

sintered state. The number of cracked specimens were converted crack probability and plotted in Fig. 6. Crack probability was found to depend strongly on the ratio of monoclinic ZrO_2 .

In Fig. 7, fracture surfaces of some specimens are compared with each other. When 1.5 wt% CoO was singly added to Y-TZP, sintered specimens had macrocracks and very low values of mechanical properties. But in No. 16 specimen, 1.5 wt% CoO was added to Y-TZP with other additives such as ${\rm Al_2O_3}$ and ${\rm Fe_2O_3}$ and its mechanical properties was excellent. This seems to be due to the interactions of additives and resulted in high fracture toughness, high hardness and fine microstructure, however the exact reason is not known at present.

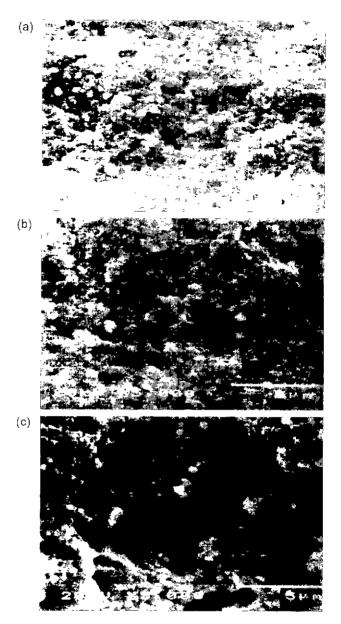


Fig. 7. Scanning electron micrographs of fracture surface of various specimens sintered at 1450° C for 2 h. (a) Y-TZP, (b) Y-TZP+1.5 wt% Fe₂O₃+3.0 wt% Al₂O₃+1.2 wt% CoO, (c) Y-TZP+3.0 wt% Fe₂O₃+3.0 wt% Al₂O₃+3.0 wt% MnO₂+2 4 wt% CoO

IV. Summary

Y-TZP was modified by additives such as Al₂O₃, CoO, Fe₂O₃ and MnO₂. Phase change, microstructure and mechanical properties were investigated and analyzed.

When transition metal oxides were added singly, monoclinic phase increased and mechanical properties were deteriorated. The fracture toughness was increased with the ratio of monoclinic phase and was maximum at the ratio of 18%. However these additives and ${\rm Al_2O_3}$ were added in certain combination, the sintered specimens showed fine microstructure and very high fracture toughness without degradation of hardness.

About 18% of the ratio of the monoclinic phase was a boundary, under which fracture toughness increased as monoclinic phase increased and over which fracture toughness decreased. Hardness was greatly decreased over this boundary.

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