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Effect of Transition Metal Oxides Addition on Yttria－stabilized Zirconia for improving Physical and Mechanical Properties

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<Abstract>

Mechanical properties of Y2O3-containing tetragonal ZrO2 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 analysed. Each additive, such as CoO, Fe2O3, MnO2 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 Al2O3 were added in combination at a certain ratio. The addition of CoO, Fe2O3 and MnO2 into Y-TZP resulted in the more complex behavior of fracture toughness and hardness. The specimen with 1.5 wt%-Fe2O3, 3.0 wt% -Al2O3 and 1.5 wt%-CoO showed the monoclinic to tetragonal phase ratio of 18% and the highest toughness of 10.8 MPa · m1/2 with Vickers hardness of 1201 kgf/mm2. However, the toughness decreased as the ratio increased and macrocracks developed beyond the ratio of 25%. Sample No. 16 is improved high Physical and Mechanical Properties.

Key Words : Tetragonal, Polycrystals, Hardness, Fracture Toughness, Transition Metal Oxides, Monoclinic

Ⅰ. Introduction

A number of researches on stabilized zirconia have been done and their main concerns were focussed on stabilization of zirconia and toughening mechanism[1-3]. 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 appears in Y-TZP matrix or they may improve fracture toughness and other characteristics.

TZP is attracting interest because of its high fracture stress and fracture toughness. Its fracture stress is now being improved by refinements in the production process and by addition of some oxides. TZP is applied in catalytic-converter-system oxygen sensors for automobile exhaust-gas cleaning and in

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steel making. Its application to dies for cold-drawing soft metal, nonmagnetic tools for cutting magnetic recording tape, and so on is being attempted. It is expected to become a more important ceramic material in the future[8-9].

In this study, Al2O3 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 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 procedures

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

Each additive may change the phase stability and mechanical properties of Y-TZP and its effect was investigated when not only they were used singly but also used in combinations.

In case of single additions, the amount of additives was from 0wt% to 8wt%. These powders were granulated and compacted under the pressure of 1 ton/cm2, sintered at 1450℃ for 2h. Phase changes were investigated by X-ray diffractometer and hardness and fracture toughness were measured by a Vickers hardness tester. Microstructures were investigated by observing fracture surfaces with SEM.

These additives were added in combination to investigate the interaction of these additives. The amount of each additives was 0wt% to 3wt% and their combinations were referred from the experimental table by Taguchi method. Phase changes and mechanical properties for these specimens were also analysed by the same method.

Ⅲ. Results and Discussion

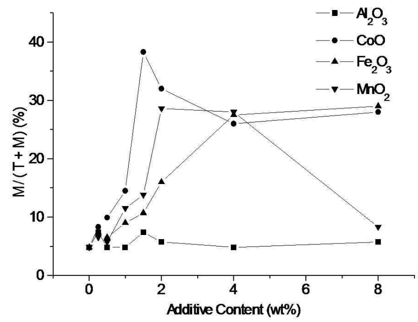
3-1. Single additives

Y-TZP raw materials were sintered to almost tetragonal ZrO_2 phase. But when transition metal oxides were added to Y-TZP, monoclinic ZrO_2 phase appeared and the mechanical properties were also affected. These results were summarized in <Figure 1>, <Figure 2> and <Figure 3>.

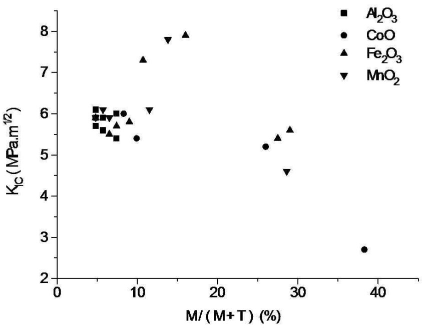
In <Figure 1>, the ratio of monoclinic phase was calculated from the height of monoclinic (111) peak divided by the summation of the heights of tetragonal (111) peak and monoclinic (111) peak.

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[10, 11]. 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



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

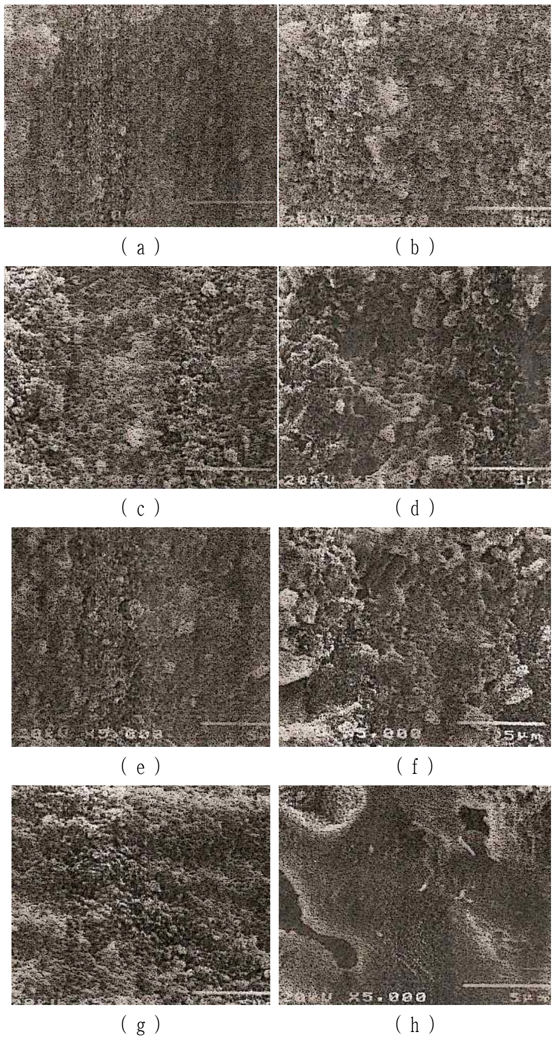


<Figure 2> Dependency of fracture toughness on the ratio of monoclinic phase

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 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 solution limits.

Microstructures of some specimens are shown in <Figure 3>. In case of Al2O3, fine structures are maintained even though 8wt% of Al2O3 was added.



<Figure 3> Scanning electron micrographs of fracture surface of specimens sintered at 1450℃ for 2h.
a) Y-TZP+0.25wt%Al2O3 b) Y-TZP+8.00wt%Al2O3
c) Y-TZP+0.25wt%Fe2O3 d) Y-TZP+8.00wt%Fe2O3
e) Y-TZP+0.25wt%CoO f) Y-TZP+8.00wt%CoO
g) Y-TZP+0.25wt%MnO2 h) Y-TZP+8.00wt%MnO2

But in case of transition metal oxides, very big grains appears as the amount of additives 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 added singly to Y-TZP.

3-2. Combinational additives

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

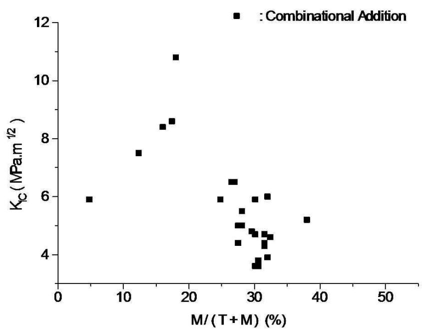
In this study, four additives were mixed as shown in Table 1. Phase stability and mechanical properties were investigated and the results are summarized in Table 1.

In <Figure 4> and <Figure 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 ZrO_2 phase increases up to about 18%, over which fracture toughness and hardness showed very low values. In case of No. 16 specimen, the value of fracture toughness was up to about 11MPa.m$^{1/2}$ while hardness keeps high value.

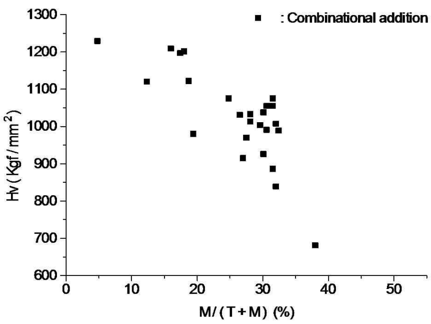
Sintered specimens were investigated with an optical microscope and many specimens had macrocracks at as-sintered states. The number of cracked specimens were converted crack probability and plotted in <Figure 6>. Crack probability was found to depend strongly on the ratio of monoclinic ZrO_2.

<Table 1> Mechanical properties and the ratio of monoclinic phase of sintered pecimens for combinational addition

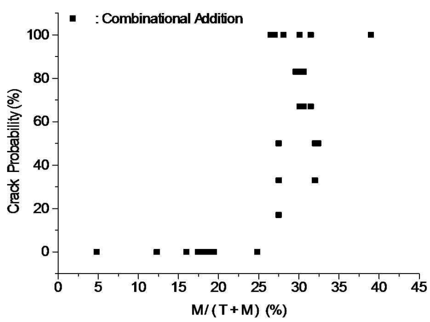
No.	Fe_2O_3 (wt%)	Al_2O_3 (wt%)	MnO_2 (wt%)	CoO (wt%)	m/(t+m.) (%)	Hv (kgf/mm^2)	K_{IC} (MPam$^{1/2}$)
1	0.0	0.0	0.0	0.0	4.8	1229	5.9
2	0.0	0.0	1.5	1.5	32.0	1007	3.9
3	0.0	0.0	3.0	3.0	19.4	980	5.5
4	0.0	1.5	0.0	1.5	16.0	1209	8.4
5	0.0	1.5	1.5	3.0	30.6	1055	3.6
6	0.0	1.5	3.0	0.0	30.6	991	3.8
7	0.0	3.0	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	1.5	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	1.5	26.5	1031	6.5
27	3.0	3.0	3.0	3.0	30.1	1038	4.7



<Figure 4> Dependency of fracture toughness on the ratio of monoclinic phase



<Figure 5> Dependency of hardness on the ratio of monoclinic phase



<Figure 6> Dependency of crack probability on the ratio of monoclinic phase

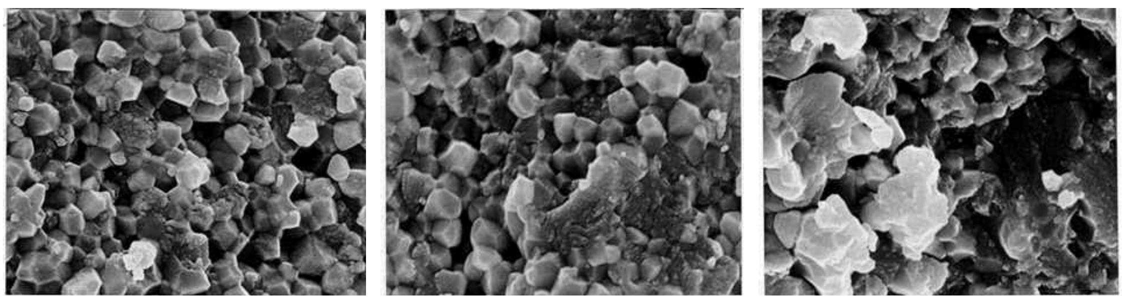
In <Figure 7>, fracture surfaces of some specimens are compared with each other. When 1.5wt%CoO was singly added to Y-TZP, sintered specimens had macrocracks and very low values of mechanical properties. But in No. 16 specimen, 1.5wt%CoO was added to Y-TZP with other additives such as Al_2O_3 and Fe_2O_3 and its mechanical properties was excellent.

This seems due to the interactions of additives and resulted in high fracture toughness, high hardness and fine microstructures.

Ⅳ. Summary

Y-TZP was modified by additives such as Al_2O_3, CoO, Fe_2O_3 and MnO_2. Phase changes, microstructures and mechanical properties were investigated and analysed.

When transition metal oxides were added singly, the ratio of monoclinic phase to tetragonal phase was changed by the addition of CoO, Fe_2O_3 and MnO_2 up to 8.00 wt%, monoclinic phase increased and mechanical properties were deteriorated. The



(a) (b) (c)

<Figure 7> Scanning electron micrographs of fracture surface of various specimens sintered at 1450℃ for 2h.
a) Y-TZP
b) Y-TZP+1.5wt%Fe_2O_3+3.0wt%Al_2O_3+1.2wt%CoO
c) Y-TZP+3.0wt%Fe_2O_3+3.0wt%Al_2O_3+3.0wt%MnO_2+2.4wt%CoO

toughness was increased with the ratio of monoclinic phase and was maximum at the ratio of 18%.

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.

However these additives and Al_2O_3 were added in certain combination, the sintered specimens showed fine microstructure and very high fracture toughness without degradation of hardness.

On the other hand, Al_2O_3 hardly affected the electrical conductivity of Y-TZP. The addition of CoO, Fe_2O_3 and MnO_2 into Y-TZP resulted in the more complex behavior of fracture toughness and hardness.

The addition of CoO, Fe_2O_3 and MnO_2 into Y-TZP resulted in the more complex behavior of fracture toughness and hardness. The specimen with 1.5 wt%-Fe_2O_3, 3.0 wt%-Al_2O_3 and 1.5 wt%-CoO showed the monoclinic to tetragonal phase ratio of 18% and the highest toughness of 10.8 MPa·$m^{1/2}$ with Vickers hardness of 1201 kgf/mm^2. However, the toughness decreased as the ratio increased and macrocracks developed beyond the ratio of 25%.

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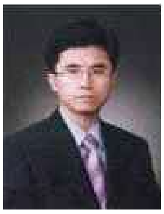

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