Calcination Condition of Magnesia Doped Zirconia Powder

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Abstract

Magnesia doped zirconia powder calcined under the temperature below 1400℃ shows X-ray peak pattern of monoclinic ZrO_2 crystals. Its lattice parameters and ununiform crystal strain influence the density of magnesia stabilized zirconia ceramics (Mg-PSZ), and are controlled by calcination temperature. The powder whose monoclinic lattice parameter $a \geqq 5.148A$ calcined under the temperature 1170～1400℃ is sintered to the high density Mg-PSZ.

1. Introduction

Magnesia stabilized zirconia ceramics (Mg-PSZ) shows excellent mechanical performance under high temperature. For this reason, Mg-PSZ is hoped especially as the material of hot exclusion dice, and its various use is tried such as the material of tools or molds.

By the characterization of Mg-PSZ, we found the variation of Mg-PSZ density sintered under the identical condition, and found degraded qualities in the relatively low dense Mg-PSZ.

Therefore, we studied systematically the relations between calcination temperature of magnesia doped zirconia powder and the density of sintered Mg-PSZ as one approach to trace the origin of degraded qualities.

Consequently, it became clear that the calcination temperature influences the lattice parameters and the ununiform crystal strain in the powder and that these crystallographic parameters decisively influence the density of sintered Mg-PSZ.

2. Experimental methods

Pure ZrO_2 powder was synthesized by hydrolysis method and calcined at 900℃. MgO powder was mixed with ZrO_2 powder to the content of 8～11mole%. This mixed powder was ball-mill ground in ethanol or water, and was calcined at 900 ～1400℃, and then was ball-mill ground again. Thus obtained powder was used as the starting material of Mg-PSZ.

X-ray diffraction patterns of the powder mixed with Si powder as the internal standard were measured by Rigaku RAD-RB diffractometer. From these X-ray patterns, crystal data was calculated by WPPD programed by Toraya[1]. Lattice parameters were determined from diffraction angles corrected by the standard peaks from Si whose lattice parameter was known. The ununiform crystal strain was determined by Hall method[2] from the distribution of peak widths against diffraction angles. MgO contents in the powder were analysed by ICP method.

This powder as the starting material characterized crystallographically was molded by pressure and sintered in the identical condition to Mg-PSZ. Density of the sintered Mg-PSZ was measured by picnometric method.

3. Results and discussion

Table 1 summarizes the calcination condition, crystal data of powder, and density of sintered Mg-PSZ obtained from the identical condition. The identical alphabet written in the items of powder indicates the powder synthesized in the identical process except calcination temperature.

Magnesia-doped zirconia powder calcined in the temperature range of 900～1400℃ has the monoclinic crystal structure. Its unit cell volume was almost identical to that of pure ZrO_2. From the X-ray diffraction pattern of non-calcined powder(G) containing 8.8mole% MgO, no diffraction peak of MgO was detected in the sensitiveness of X-ray diffractometer. These phenomena suggest that X-ray diffraction pattern of magnesia doped zirconia powder obtained in the temperature range of 900～1400℃ exhibits the diffraction pattern of monoclinic ZrO_2.

Table 1 also shows that high density material of Mg-PSZ can be obtained by sintering the powder calcined at the temperature ≧1200℃ (see A and B). Calcination temperature and density of sintered body are clearly related to the monoclinic a-axis lattice parameter and the ununiform crystal strain. Namely, the powder calcined at higher temperature, which can be sintered to the high density Mg-PSZ, has the monoclinic a-axis of lattice parameter of $a \geqq 5.148$A and relatively larger ununiform crystal strain. Especially, the turning point of a 5.148A decisively influences the density of sintered Mg-PSZ. By heating the powder of $a < 5.148A$ at the temperature beyond 1200℃, its monoclinic lattice parameter varies to $a \geqq 5.148A$, and this varied powder can be sintered to the higher density Mg-PSZ (see D and E).

In order to clarify the relation between calcination temperature and lattice parameters, powder F and G were calcined at 1100℃, 1150℃ and 1200℃, and then crystal data was determined. Consequently it became clear that the powder varies from $a < 5.148A$ to $a \geqq 5.148A$ beyond one temperature in the range of 1150 ~1200℃. This temperature range includes the monoclinic-tetragonal transition temperature 1170℃ of pure ZrO_2 [3]. This suggests that the systematic variation of lattice parameters and the increase of the ununiform crystal strain are relative to M→T transition of pure ZrO_2 crystals.

Thus, pure ZrO_2 powder was heated at 1250℃ after calcined at 900℃. Its crystal parameters were determined and compared with those of pure ZrO_2 powder only calcined at 900℃. Pure ZrO_2 powder heated at 1250℃ showed the lattice parameter $a \geqq 5.148A$ and larger ununiform crystal strain, while pure ZrO_2 powder only calcined at 900℃ showed the lattice parameter $a < 5.148A$, and smaller crystal strain. But after ball-mill grinding, this 1250℃ heated pure ZrO_2 powder showed the lattice parameter $a < 5.148A$ again, and its ununiform crystal strain was decreased. These phenomena give a proof of direct relation between the crystal parameter and M→T transition of pure ZrO_2 crystals.

Pure ZrO_2 crystal transforms into tetragonal from monoclinic by heating at temperature beyond 1170℃, and returns to monoclinic by cooling. By this process, the trace of tetragonal phase as crystal strain would be introduced to monoclinic ZrO_2. This crystal strain which is infered to be the effect of MgO-ZrO_2 solution appears as the increase of the ununiform crystal strain in one side, and appears as the variation of a-axis lattice parameter as the uniform crystal strain in another side. We call these phenomena the crystallographic thermal irreversibility of monoclinic ZrO_2.

Powder of $a < 5.148A$ not only gives insufficient density but also shows extremely instable sintering property, that is, they are sintered to different density by different condition of molding or sintering, and in the extreme case, the crack or expansion appears on the sintered body. On the other hand, powder of $a \geqq 5.148A$ shows stable sintering property, and gives small variation of Mg-PSZ density by different condition of molding or sintering.

In order to elucidate the origin of sintering instability, identical powder was molded in various pressure, and then sintered in the identical condition, and Mg-PSZ density was measured. Table 2 shows the result. Powder of $a < 5.148A$ showed the large variation of sintered Mg-PSZ density by the differense of molding pressure, and Mg-PSZ density tends to decrease by the increase of molding pressure. This phenomenon is inferred to be the influence of internal destruction caused by the change of crystal volume characteristic to the monoclinic-tetragonal transition when heating. Powder of a≧5.148A showed small variation of sintered Mg-PSZ density by the differense of molding pressure, and Mg-PSZ density becomes rather small when the molding pressure is relatively small. This is the reasonable character of ceramic powder as the starting material.

By the calcination in the tetragonal stable temperature range, monoclinic zirconia powder tends to retain the trace of tetragonal phase as crystal strain caused by the crystallographic irreversibility as clarified in this study. Such a trace contributes to the sintering performance because it lightens the shock of monoclinic-tetragonal transition when heat the moldings.

4. Conclusion

(1) Magnesia doped zirconia powder has the monoclinic structure regardless of calcination temperature.

(2) Magnesia doped zirconia powder calcined in the tetragonal stable temperature range (beyond 1170℃) shows the lattice parameter a ≧5.148A of monoclinic ZrO_2 and increased ununiform crystal strain. This phenomenon is infered to be the effect of MgO-ZrO_2 solution.

(3) This phenomenon contributes to the sintering performance of magnesia-doped zirconia powder.

References

1) H.Toraya:J.Appl.Cryst., 19, 440-447, (1986).
2) W.H.Hall:Proc.Phys.Soc., A62, 741-743, (1949).
3) E.C.Subbarao:Science and Technology of Zirconia, Advances in Ceramics, Vol.3, A.H.Heuer and L.W.Hobbs(eds.), The American Ceramic Society (1981), pp.1-24.

powder	a (A)	b (A)	c (A)	β (°)	V_M (A^3)	strain (10^{-3})	MgO-content (mole%)	density
A, 1200℃ cal.	5.1501	5.2069	5.3128	99.216	140.63	4.75	8.8	○ 5.845
A, 900℃ cal.	5.1465	5.2085	5.3135	99.201	140.60	2.58	8.6	× 5.579
B, 1200℃ cal.	5.1500	5.2071	5.3134	99.229	140.64	3.31	8.8	○ 5.817
B, 900℃ cal.	5.1464	5.2087	5.3133	99.206	140.59	1.93	8.6	× 5.393
C	5.1501	5.2072	5.3133	99.220	140.65	3.66	8.8	○ 5.844
D	5.1466	5.2088	5.3140	99.212	140.62	2.79	10.4	× 5.64
D, 1400℃ heat.	5.1505	5.2050	5.3126	99.171	140.60	6.08	10.4	○ 5.72
E, 900℃ cal.	5.1468	5.2103	5.3131	99.211	140.64	1.49	8.6	× 5.768
E, 1200℃ heat.	5.1507	5.2047	5.3147	99.214	140.64	2.79	8.6	○ 5.849
F, 1100℃ cal.	5.1463	5.2100	5.3132	99.203	140.62	1.29	10.0	× 5.547
F, 1150℃ cal.	5.1465	5.2099	5.3128	99.204	140.62	1.56	10.0	× 5.757
F, 1200℃ cal.	5.1493	5.2082	5.3128	99.234	140.64	3.19	10.0	○ 5.789
G, 1100℃ cal.	5.1462	5.2097	5.3124	99.206	140.59	1.45	8.8	× 5.572
G, 1150℃ cal.	5.1466	5.2103	5.3130	99.210	140.63	1.49	8.8	× 5.694
G, 1200℃ cal.	5.1493	5.2084	5.3129	99.225	140.65	3.88	8.8	○ 5.808
G, non-cal.	5.1461	5.2104	5.3119	99.227	140.59	1.84	8.8	
ZrO_2 *	5.1472	5.2070	5.3163	99.182	140.66	2.38	0.0	
ZrO_2 **	5.1512	5.2004	5.3177	99.228	140.61	4.78	0.0	
ZrO_2 ***	5.1470	5.2110	5.3124	99.218	140.64	2.05	0.0	

(* 900℃ calcined, ** 1250℃ heated, *** 1250℃ heated and ground)

Table 1. Crystal data of magnesia doped zirconia powder and density of sintered bodies

powder	pressure (Kgf/cm^2)	density (g/cm^3)
E, 900℃ cal. ill-sintered a < 5.148A	500	5.838
	700	5.818
	1000	5.810
	1500	5.788
	2000	5.768
E, 1200℃ heat. well-sintered a ≧ 5.148A	500	5.837
	700	5.843
	1000	5.845
	1500	5.849
	2000	5.849

Table 2. Relation between molding pressure and density of sintered bodies about powder E: 900℃ calcined and 1200℃ heated.