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Preparation of zirconia-alumina powder by co-precipitation①

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Abstract: A zirconia-alumina powder with a near spherical shape and an average size of 0.1 ~ 0.2 μm was prepared by co-precipitation. XRD analysis shows that α-Al_2O_3 phase may be directly transformed from amorphous in calcining the hydroxide composite. The ZrO_2-Al_2O_3 composite ceramics manufactured from this powder has the maximum fracture toughness of 9 MPa·$m^{-1/2}$ at 15 % ZrO_2 and 740 MPa fracture strength at 5 % ZrO_2. Zirconia grains about 1 μm in diameter are dispersed uniformly in the alumina ceramic matrix.

Key words: zirconia-alumina powder; coprecipitation; composite ceramics **Document code:** A

1 INTRODUCTION

Because of excellent mechanical properties, in particular, high fracture toughness, high strength, high hardness and wear resistance, zirconia toughened alumina (ZTA) is a desirable material for engineering applications. Since Clausen reported ZTA with high fracture toughness[1] in 1976, ZTA has received many researchers' attention. Many studies have been concentrated on the understanding of its toughening mechanism and a number of processes for preparing such powder have been proposed yet.

Zirconia has different stable phases at various temperatures[2]. At room temperature, its stable phase is monoclinic, while its stable phase is tetragonal when the temperature is higher than 1 150 ℃. During cooling down if not constrained, the zirconia will transform from tetragonal to monoclinic, i.e. martensitic transformation, accompanying volume expansion and shear strain. When being constrained the tetragonal can exist to room temperature and the transformation takes place under an applied stress leading to toughening. Some causes, including stress-induced transformation toughening[3], crack deflection and compressive surface stress[3], microcracking toughening[4], etc, attribute to toughening mechanism.

Manufacturing route and condition influence significantly the physico-chemical characteristics and crystallization behaviour of ZTA powder[5~7]. The methods for preparing ZTA powder can be divided into mechanical method and chemical method. Wet mixing or dry mixing alumina and zirconia powders and wear of zirconia media (extensively milling alumina powder by using zirconia media), belong to mechanical method. The chemical method includes CVD process[8], sol-gel process[9~11] and co-precipitation process which is to mix aluminium sulphate solution with suspending sol, obtained by adding ammonia to the zirconium oxychloride solution and then stirring for 5 h a zirconia suspending to form a mixing solution. NH_4OH was added to obtain a mixture of hydroxide powder of zirconium and aluminium. The mixture was then heat treated at temperature between 500 ~ 1 300 ℃ to decompose the hydroxide. All of the methods mentioned above have their own disadvantages due to its cost or the characteristics. So it is necessary to develop other new routes for the preparation of ZTA powder.

2 EXPERIMENTAL

Following equations were used to obtain alumina-zirconia powder by co-precipitation.

$$ZrCl_4 + 4NH_4OH = Zr(OH)_4(s) + 4NH_4Cl \quad K_{sp} = 6.3 \times 10^{-49} \tag{1}$$

$$Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3(s) + 3(NH_4)_2SO_4 \quad K_{sp} = 1.3 \times 10^{-33} \tag{2}$$

From the equations above, it can be calculated that the minimum pH values for precipitating hydroxide of aluminium and zirconium are respectively $pH_1 \approx 3.41$ and $pH_2 \approx 2.02$ when the concentrations of both Al^{3+} and Zr^{4+} are equal to 0.5 mol/L. So aluminium sulphate, zirconium chloride and ammonia can be used as starting materials to produce zirconia-alumina powder, neutralising the salt solutions of Al^{3+} and Zr^{4+} with NH_4OH solution.

ZTA powder was synthesized by neutralising 0.5 mol/L $ZrCl_4$ solution, its slurry was mixed with solu-

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tion containing 0.5 mol/L Al^{3+} aluminium sulphate and then was neutralised with 1 mol/L NH_4OH, followed by filtration, washing, drying and calcining for 60 min at 1 000 ℃. The volume of $ZrCl_4$ corresponds to the zirconia content in the ZTA powder. Very small amount of DBS (dodecycle benzenesulfonic acid sodium) was added to the co-precipitation process in order to accelerate the resultant slurry filtration. The calcined powder was then pressed in a steel die of 15 mm in diameter under pressure of 250 MPa. The thickness of samples was about 3 mm. After the sample was sintered for 90 min at 1 550 ℃, its mechanical properties were measured.

3 RESULT AND DISCUSSION

3.1 Characterization of powder

The SEM micrograph shows that the powder synthesized from aqueous solution by co-precipitation is near spherical with an average size of 0.1 ~ 0.2 μm and the particle distribution seems to be narrow. It can also be seen from the back scattered micrograph of ceramic specimen prepared by such powder that zirconia is well dispersed in the alumina matrix (see Fig.1).

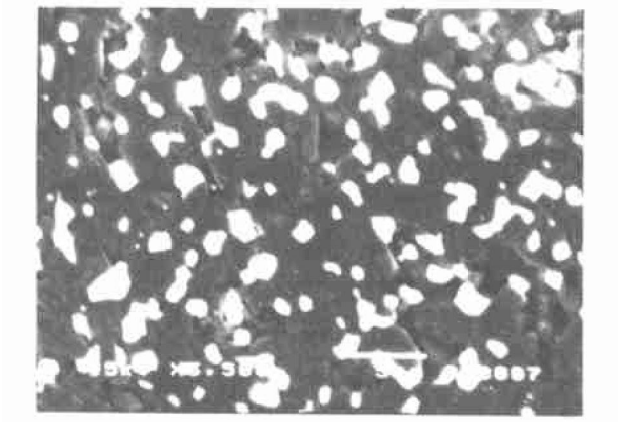

Fig.1 Back scattered micrograph of ZTA specimen

DTA analysis indicates that the hydroxide composite of zirconium and aluminium will transform from amorphous to crystalline at above 900 ℃ (see Fig.2). XRD analysis verifies the result from DTA. XRD reveals that the hydroxide composite obtained from the aqueous solution is amorphous and does not give good evidence for crystallization when the sample is calcined at temperature lower than 850 ℃. The XRD analysis result is listed in Table 1.

It can be known also from XRD analysis that the sample calcined at 1 400 ℃ contains some monoclinic zirconia. This is due to the $t \rightarrow m$ zirconia transformation during cooling. The contents of tetragonal and monoclinic zirconia, calculated according to the

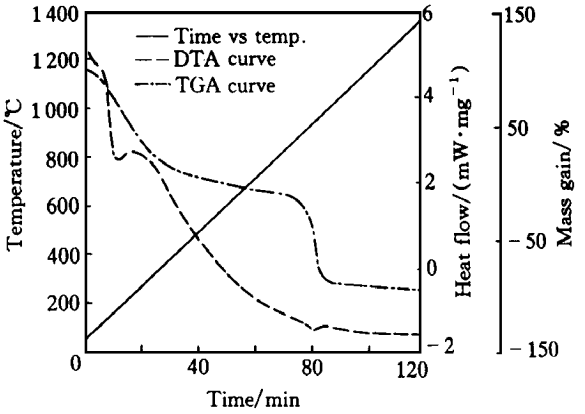

Fig.2 DTA and TGA curves of compound derived by co-precipitation

Table 1 XRD analysis results of samples calcined at various temperature

Temperature/℃	Phase	
	Alumina	Zirconia
Uncalcined	Amorphous	Amorphous
850	Amorphous	Amorphous
1 150	Amorphous	t-ZrO_2
1 400	α-Al_2O_3	t-ZrO_2, m-ZrO_2

following equations[12], are respectively about 96.87 % and 3.13 % of the total zirconia:

$$X_m = \frac{I_{m(111)} + I_{m(11\bar{1})}}{I_{t(111)} + I_{m(111)} + I_{m(11\bar{1})}} \quad (3)$$

$$V_t = \frac{1 - X_m}{1 + 0.311\ X_m} \times 100\ \% \quad (4)$$

where I_t and I_m denote the X-ray diffraction intensities corresponding to (111) and $(11\bar{1})$ planes of the t-ZrO_2 and m-ZrO_2 phases respectively. Since the t-ZrO_2 is an unstable phase at room temperature, parameter V_t, the volume fraction of t-ZrO_2 in the total amount of ZrO_2, represents the stability of t-ZrO_2 in the ZrO_2-Al_2O_3 ceramics.

3.2 Sintering behaviour and microstructure of ZTA ceramic

The sinterability of ZTA is demonstrated in Fig. 3. It indicates that the relative density does not vary as the zirconia content changes. This phenomenon differs from what Hideyuki and his colleagues had reported[13]. Their work showed the relative density decreases with increasing zirconia content. This may be attributed to the different routes adopted. From this figure and the SEM micrograph of the ceramic (see Fig.4), it can be seen that the densification of the specimen is not complete. This may be due to the poorer compaction of the very fine but agglomerated powders.

The SEM micrograph for the ZTA polished ceramic surface shows that the grain size of Al_2O_3 is

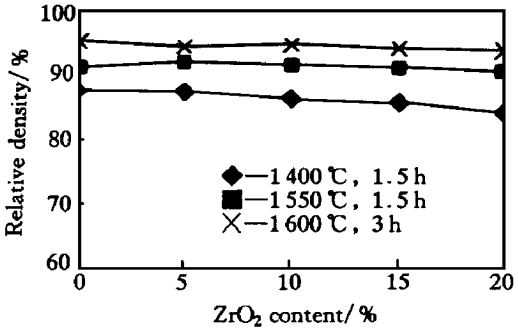

Fig .3 Relationship between relative density and zirconia content

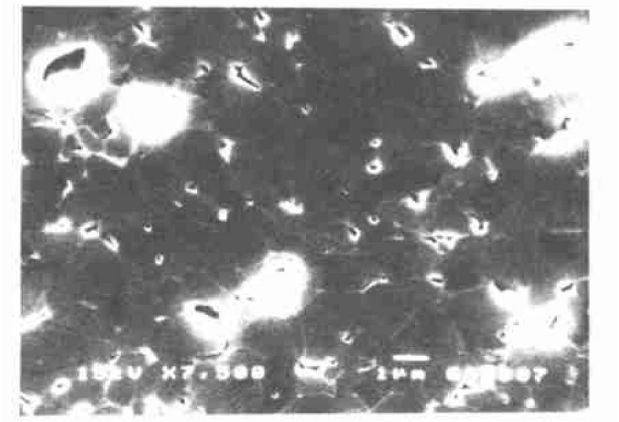

Fig .4 Scanning electronic micrograph of etched surface of ZrO_2-Al_2O_3 ceramic

1 .5 μm, as shown in Fig .4. It can also be seen from Fig .1 that the ZrO_2 grain about 1 μm is dispersed homogeneously in the matrix. It should be noted that the zirconia particle size might be improved by controlling the $ZrCl_4$ concentration.

3 .3 Mechanical properties of ZTA ceramic

Fig .5 illustrates the fracture toughness K_{IC} as a function of zirconia content for the ceramic sintered at 1 550 ℃ for 90 min. The fracture toughness K_{IC} was measured with indentation micro-fracture method at different loads under Vickers Hardness Test, K_{IC} can be calculated by using three different equations shown as below.

1) Liang's Equation[14]

$$\left(\frac{K_{IC}\phi}{Ha^{1/2}}\right)\left(\frac{H}{E\phi}\right)^{0.4}\alpha = \left(\frac{c}{a}\right)^{\left(\frac{c}{18a}-1.51\right)} \quad (5)$$

$$\alpha = 14\left[1 - 8\left(\frac{4\upsilon - 0.5}{1+\upsilon}\right)^4\right]$$

where c and a are the radical crack length and indentation diagonal half length respectively, μm; E is elastic modulus; H is hardness and ϕ is constant, being equal to 3; α is a non-dimensional constant as a function of Poisson ratio υ of the material.

2) Blendell Equation

$$\left(\frac{K_{IC}\phi}{Ha^{1/2}}\right)\left(\frac{H}{E\phi}\right)^{0.4} = 0.055\lg\left(\frac{8.4a}{c}\right) \quad (6)$$

3) Niihara Equation[15]

$$\left.\begin{aligned}\left(\frac{K_{IC}}{Ha^{1/2}}\right)\left(\frac{H}{E}\right)^{0.4} &= 0.018\left(\frac{c-a}{a}\right)^{-0.5} \\ (c/a < 2.5)& \\ \frac{K_{IC}}{Ha^{1/2}} &= 0.203\left(\frac{c}{a}\right)^{-1.5} \\ (c/a \geqslant 2.5)&\end{aligned}\right\} \quad (7)$$

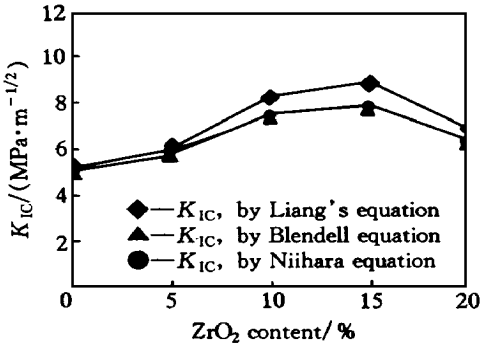

Fig .5 Curves of fracture toughness K_{IC} vs zirconia content

The elastic modulus in Eqn.(5) varies with the zirconia content according to Liang's work[13], while in Eqns.(6) and (7), the elastic modulus are treated as a constant, 380 GPa[15]. The value of Poisson ratio in Eqn.(5) was taken to be 0 .27.

The Ball-on-Ring Test was introduced to evaluate the fracture strength for the disc sample. The experimental data was treated with the following equation to calculate the stress value:

$$\text{Stress/ MPa} = \left[\frac{19.77L}{t^2} \times 0.606\ln\left(\frac{S}{t}\right) + 1.13\right] \times 10^{-6} \quad (8)$$

where L represents loads, N; t is the sample thickness, m; S is the radius of knife-edge of the Ball-on Ring Test, m.

From Figs .5 and 6, it can be seen that the fracture strength reaches the maximum value of about 740 MPa at 5 % zirconia content, while the fracture toughness maximum of 9 MPa·m$^{-1/2}$ is at 15 % zirconia content. The great difference in the zirconia contents for both strength and toughness maximum values implies the mechanisms for the enforcement of the two items are different, i.e. it is difficult to obtain best fracture toughness and fracture strength simultaneously. It is probable that too much zirconia will produce too many cracks when ceramic cools due to volume expansion and thus decrease its fracture strength.

4 CONCLUSIONS

1) A uniformly dispersed ZTA powder, with

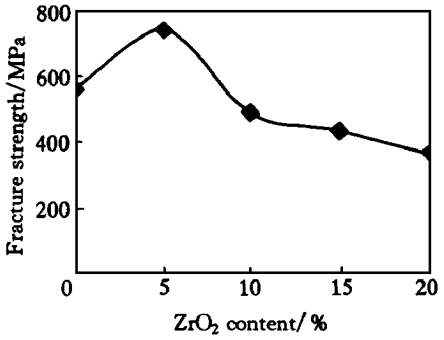

Fig.6 Curve of fracture strength vs zirconia content

a near spherical shape and an average size of 0.1 ~ 0.2 μm, has been prepared by co-precipitation. XRD analysis shows that α-Al_2O_3 phase may be directly transformed from amorphous in calcining the hydroxide composite.

2) The fracture toughness of the ZTA ceramic manufactured with the co-precipitated powder achieves the maximum value at 15% zirconia content, while the fracture strength reaches its best at 5% zirconia content.

3) The grain size of Al_2O_3 in the ZTA ceramic is about 1.5 μm and ZrO_2 is about 1 μm. The ZrO_2 grain is dispersed uniformly in the ceramic matrix.

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