

Process study on alumina-zirconia nanocomposite *via* ammonolysis route

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Wet-chemical process using ammonia to precipitate aluminum ions dissolved in a zirconia sol solution is examined. Formation of crystalline bayerite is unfavorable for fine dispersion of zirconia nanoparticles in alumina matrix after heat treatment. To avoid the bayerite formation, it was preferred to make a precipitation with a diluted ammonia or with an ammonia gas flow at high temperature. By optimizing the precipitation process and the calcination temperature, we successfully prepared the uniform microstructure in which tetragonal zirconia particles of ~30 nm is finely dispersed within the alumina grains.

Key words: Zirconia-toughened alumina, Ammonia precipitation, Microstructure.

Introduction

As the most promising oxide ceramics for engineering use, Al₂O₃-ZrO₂ composite (or zirconia toughened alumina) has been studied for a quarter of century [1]. In order to achieve fine and uniform dispersion of t-ZrO₂ (tetragonal zirconia) particles in Al₂O₃ matrix on nanometer level, a wet-chemical powder preparation is advantageous [2]. This paper proposes to use cheaper starting materials such as inorganic salts in the wet-chemical route, where neutralization with ammonia is a key process to produce a desirable powder.

In the early study [3], we examined the neutralization methods using ammonia to precipitate Al(OH)₃ in a solution containing ZrO₂ nanoparticles, which were previously prepared by the hydrolysis of ZrOCl₂. It was concluded from the experimental results that gradual precipitation using ammonia (+nitrogen) gas flow is superior to conventional precipitation using ammonia water. This paper further examines the neutralization process to achieve high t-ZrO₂ content, which means the fine dispersion of ZrO₂, and homogeneous microstructure of Al₂O₃-ZrO₂ nanocomposite.

Experimental

ZrOCl₂ aqueous solution of 0.02 mol/dm³ was previously boiled at ~100°C and hydrolyzed for 3 days to synthesize ZrO₂ sol. Then, Al(NO₃)₃ aqueous solution of 0.2 mol/dm³ was added to the sol, aiming at the composition of Al₂O₃-10 mol% ZrO₂. The following four routes were employed to precipitate the Al³⁺/ZrO₂

containing solution which was vigorously stirred by a magnetic stirrer.

Process A: Gas mixture of NH₃(54%)+N₂ flowed over the solution at 50°C.

Process B: Conc. NH₃ water (25%) was titrated into the solution at 50°C.

Process C: Gas mixture of NH₃(54%)+N₂ flowed over the solution at 70°C.

Process D: Diluted NH₃ water (2.5%) was poured into the solution at 50°C.

The final pH's are adjusted at 7 in all processes. Precipitates thus obtained were washed, freeze-dried, calcined in air at 1100-1500°C, and hot-pressed (HP) in Ar at 1500°C and 50MPa. Microstructure in the calcined powders and the HP specimens was examined by scanning electron microscopy (SEM). Tetragonal phase content of ZrO₂ was determined by X-Ray Diffractometry (XRD).

Results and Discussion

Precipitation Process

In the prepared ZrO₂ sol, nanoparticles of ~30 nm were stably dispersed in a high acid solution of pH~2. These particles, after they dried, were found to be amorphous by XRD.

Ammonolysis of Al(NO₃)₃ dissolved in the sol solution proceeded gradually at the solution surface in the processes A and C. According to the pH measurements, the precipitation occurred at pH 3.5~4.0, and it took about 1 hour to complete the processes at pH~7. In the processes B and D, on the other hand, white precipitate was formed immediately after the addition of ammonia water.

XRD indicated that crystalline bayerite appeared in

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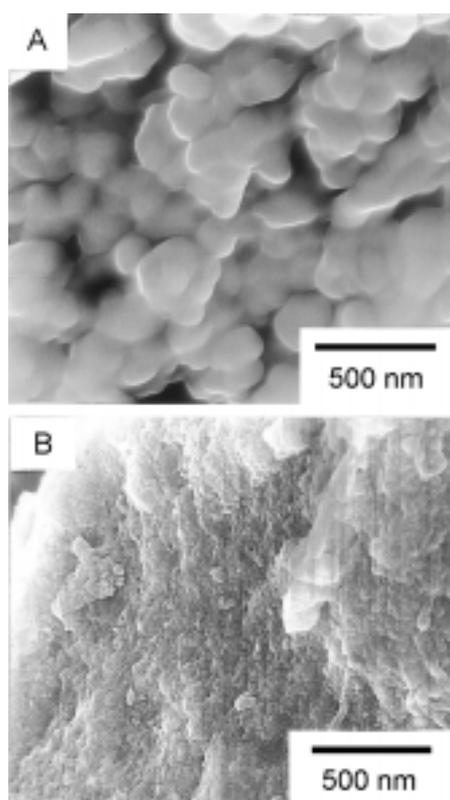


Fig. 1. Morphology of the Freeze-dried Precipitates from Processes A and C.

the precipitates from A and B and that only halo pattern was found in those from C and D. Since the following results and discussion are generally similar in these two groups, we would proceed mainly by comparing the processes A and C.

When the crystalline phase is found, round-shaped particles of ~100 nm were observed by SEM, as shown in Fig. 1(A). Primary particles of the precipitate C are much finer than A. Considering that the size of hydrous ZrO₂ particles is ~30 nm, the mixing of ZrO₂ and Al(OH)₃ is more homogeneous in the process C than in A. We consider that the processes C and D are the improved ones for the processes A and B, respectively, in that C and D are free from the bayerite formation.

Calcination Process

Calcination in this study means not only a decomposition of the hydroxide or a mere crystallization but also the microstructural tailoring to let the ZrO₂ nanoparticles be involved within the Al₂O₃ grains during the formation of α -Al₂O₃.

The XRD-identified phases after calcination are summarized in Table 1. Phase evolution was quite similar between A and B, and between C and D, respectively. Precipitates with amorphous Al(OH)₃ reached the stable phase of α -Al₂O₃ at lower temperature than those with bayerite.

Table 1. XRD-identified Phases after Calcination

Calcination Temp.	Process A, B		Process C, D	
	ZrO ₂	Al ₂ O ₃	ZrO ₂	Al ₂ O ₃
before calcined	Amor.	bayerite	Amor.	Amor.
1100°C	t, m	θ, γ	t, m	θ
1200°C	t, m	α, θ, γ	t	α
1300°C	t, m	α	t	α
1500°C	t, m	α	t, m	α

Amor: amorphous, t: tetragonal, m: monoclinic

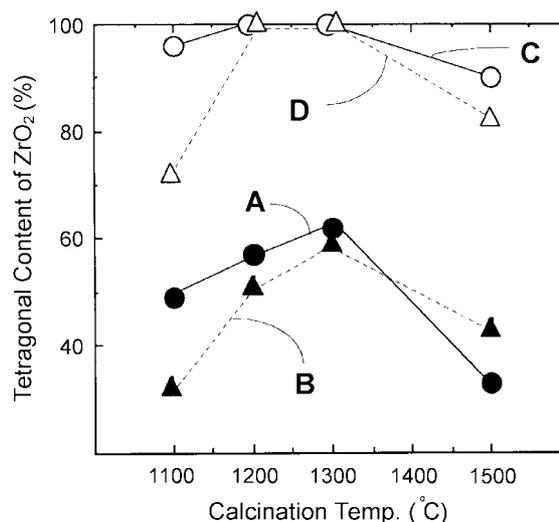


Fig. 2. Tetragonal Phase Content of ZrO₂ in the Various Precipitated Powders after Calcined at Various Temperatures.

Regarding the ZrO₂ component, on the other hand, the tetragonal phase content as a function of the calcination temperature is shown in Fig. 2. Although the transformation temperature of pure ZrO₂ is known to be ~1170°C, ZrO₂ nanoparticles in this study obviously transformed at 1100°C. Assuming that the finer particles are more transformable from monoclinic to tetragonal, distinct difference in the phase content at 1100 °C suggests that the dispersion state of ZrO₂ particles is superior in the order of C > D > A > B. After all m-ZrO₂ particles transformed to tetragonal at higher temperatures, t-ZrO₂ particles must transform again to monoclinic if they are cooled down to room temperature. Preservation of tetragonal phase upon cooling is also interpreted as a criterion of the particles dispersion at high temperature. If they are finely dispersed and constrained in the Al₂O₃ matrix, they are stable in the tetragonal form. If their dispersion is poor, oppositely, they are coarsened at high temperature and transformed to monoclinic during the cooling process.

Figure 3 shows SEM photographs of the calcined powder. The agglomerates in the process A were irregular-shaped and consisted of wormy Al₂O₃ particles at 1100°C, and then after, significant coarsening occurred

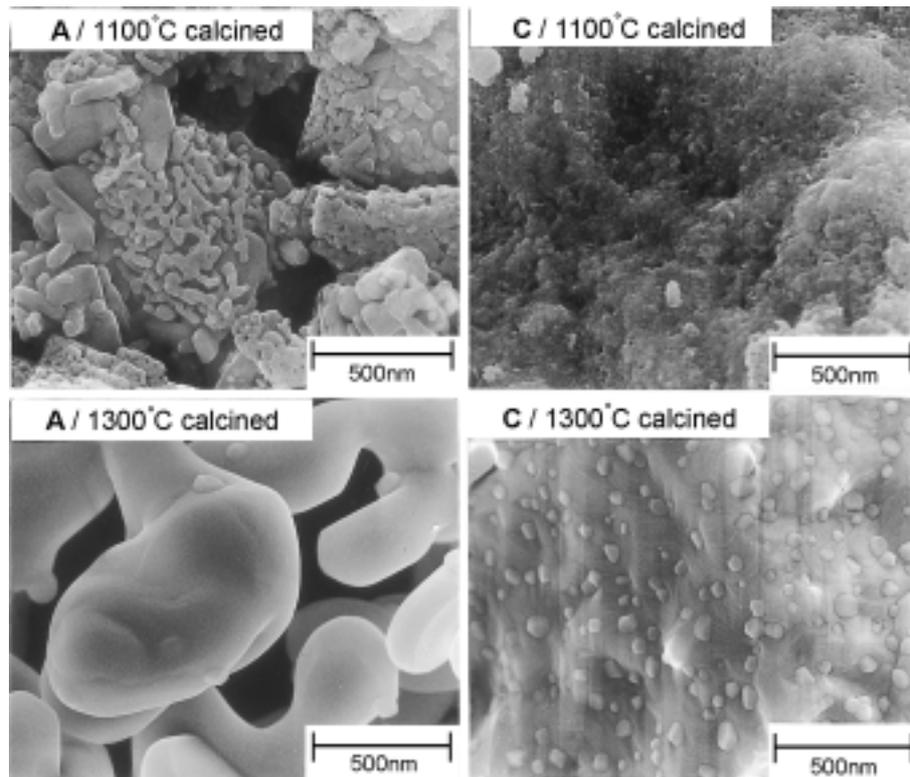


Fig. 3. Morphology of the Calcined Powders from the Processes A and C.

Table 2. Relative Densities of the HP Specimens from Different Processes

Process	A	B	C	D
Calcined at 1100°C	98.0%	97.2%	95.2%	95.6%
Calcined at 1300°C	97.4%	95.8%	94.4%	95.1%

(Hot Pressed at 1500°C)

at 1300°C, together with the α - Al_2O_3 formation. ZrO_2 particles of ~ 100 nm are found beside Al_2O_3 grains. Whereas in the process C, the agglomerates are still bulky and composed of fine particles at 1100°C. Then, ZrO_2 particles of 30~40 nm appeared on the surface of the bulk at 1300°C. They are well dispersed and free from coagulation.

Microstructure in the Hot Pressed Bodies

The ZrO_2 content in the HP specimens was determined by EDX (Energy Dispersive X-ray Spectroscopy) analysis. Since the analyzed values of 5~9 mol% were smaller than the aimed composition of Al_2O_3 -10 mol% ZrO_2 , the determined composition was used to normalize the densities of the specimen. As shown in Table 2, relative densities of the HP specimens all exceeded 94%. The increase of calcination temperature resulted in the decrease of the powder sinterability.

Although the ZrO_2 dispersion in the calcined powders

was superior in the processes C and D, the densification is inferior to the other group. Sinterability of the calcined powder should be improved in the future work.

Figure 4 compares the microstructure of the HP specimens from the processes C and D. It should be noted that fine dispersion in the process C is preserved in the densified body. ZrO_2 particles of ~ 100 nm are sometimes found at the grain boundaries of the Al_2O_3 matrix. Nanoparticles of 30~40 nm, which are usually involved in the Al_2O_3 grains, were observed at higher magnification of SEM. Whereas in the D-derived specimen, ~ 300 nm particles are frequently located at the grain boundaries.

Conclusion

Al_2O_3 - ZrO_2 composite powders were prepared by precipitating $\text{Al}(\text{OH})_3$ in ZrO_2 sol solution and subsequent calcination. By comparing various precipitation methods using ammonia, it was concluded that gradual precipitation using ammonia gas flow at high temperature is preferred for avoiding the formation of crystalline bayerite and for dispersing the ZrO_2 nanoparticles in the Al_2O_3 precursor. As for the calcination temperature, 1100°C was found to be the best one to avoid the coarsening of ZrO_2 and to achieve uniform microstructure of the Al_2O_3 - ZrO_2 nanocomposite with higher density.

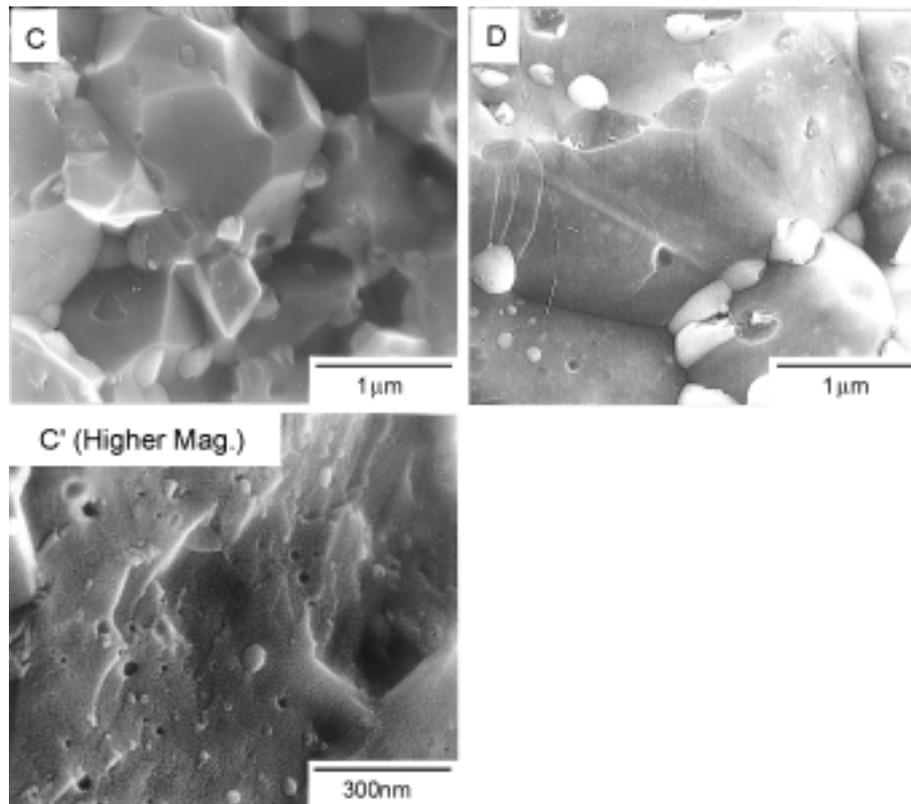


Fig. 4. Fractured Surface of the **C**- and the **D**-derived Specimens. (Calcined at 1100°C and Hot-Pressed at 1500°C, 50 MPa)

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