Fabrication of Duplex Ceramic Composites by Organic-Inorganic Solution Process

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ABSTRACT

Duplex microstructure of zirconia and alumina has been achieved via an organic-inorganic solution technique. Zirconium 2,4-pentanedionate, aluminum nitrate and polyethylene glycol were dissolved in ethyl alcohol without any precipitation. The organic-inorganic precursor gels were turned to porous powders having volume expansion through explosive, exothermic reaction during drying process. The volume expansion was caused by abrupt decomposition of the organic groups in the gels during the vigorous exothermic reaction. The volume expanded, porous powders were crystallized and densified at 1500°C for 1 h. At the optimum amount of the PEG polymer, the metal cations were well dispersed in the solution and a homogeneous polymeric network was formed. The polymer content also affected on the specific surface area of the synthesized powder and the grain size of the sintered composite.

Key words : Duplex composites, Polyethylene glycol, Porous powders, Organic-inorganic solution technique

1. Introduction

C hemical processing routes based on organic/inorganic complexation in solution have recently been used to produce pure and homogeneous ceramic powders.[1-4] In the process, the polymeric long chain in the mixture ensures the homogeneous distribution of the metal ions in its polymeric network structure and inhibits their segregation and/or precipitation from the solution. Polyethylene Glycol (PEG) is one of the polymeric carriers for the polymer complexation process. The polymer surrounds and covers the cations or sol particles, which decreases their mobility and constrains the system to reduce premature agglomeration. In the PEG organic-inorganic solution process, the properties of precursor and final powder are dependent upon the molecular weight and amount of PEG used.[5] The process also produces porous and carbonaceous materials that give heat through its combustion, so that soft, fine and single-phase powders can be formed at a relatively low external temperature.[3-9]

Zirconia-Toughened Alumina (ZTA) ceramics have been studied because of their excellent mechanical properties. However, the fabrication and mechanical properties of pure zirconia-alumina composites which have the same volume percentage have not been widely studied. By mixing ZrO_2 and Al_2O_3 phases in 1 : 1 volume ratio, which have limited solid solubility, the growth of each phase is inhibited and the fine microstructure will have excellent mechanical properties. In particular, dual interpenetrating microstructure can be expected in the system.[10] In the microstructure, the final grain size strongly depends on the homogeneity of precursor in the soft solution process. A homogeneous zirconia-alumina composite system can be prepared by the organic-inorganic solution process. Previous studies[11-14] have shown that aqueous mixtures of zirconia or alumina sources pyrolyze and crystallize to metastable phases at low temperatures. In all cases, an amorphous solid was first produced during pyrolysis, and subsequently crystallized to the metastable phases having 20-100 nm grain size. After sintering at high temperatures (≥ 1500°C), densification occurred with the formation of crystalline phases, viz., monoclinic (m-ZrO_2), tetragonal (t-ZrO_2) zirconia and alpha alumina (α-Al_2O_3).

In the present study, dense ZrO_2 and Al_2O_3 composites in 1 : 1 volume ratio have been made at low temperature from porous precursor powders prepared by a modified PEG process. For making homogeneous zirconia-alumina composite having small grain size, the effects of polymer content on the specific surface area of the synthesized powder and the grain size of sintered composite are examined. In addition, the distinct calcination behavior involving an explosive reaction are also studied.

2. Experimental Procedure

A transparent sol was prepared from zirconium 2,4-pentanedionate ($Zr(C_5H_7O_2)_4$), which is a water-insoluble chem-

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ical, and aluminum nitrate $(Al(NO_3)_3 \cdot 9H_2O)$ in proportions of 50 : 50 vol%. After dissolving these reagents in ethyl alcohol, the organic carrier, PEG (M.W.: 2000) was added, and the mixture was stirred and heated on elevating temperature. The amount of PEG was calculated using a ratio of total weight of metal ions from cation sources to weight of PEG. Ratios ranging from 1 : 1 to 5 : 1 were used. As the viscosity increased by evaporation of ethyl alcohol, the sol turned to a syrup-like gel. Subsequently, a vigorous exothermic reaction occurred, which converted the gel into an expanded, porous solid. Finally, the precursor powders were calcined at 800°C for 2 h. The calcined, porous powders were ball milled with zirconia ball media for 12 h on wet milling condition using isopropyl alcohol. The ultra-fine powders were uniaxially pressed at 10 MPa followed by cold iso-static pressing at 80 MPa for 10 min. The pellet-shaped green compacts were sintered in an air atmosphere, at 1500°C for 1 h.

The pyrolysis and decomposition behavior of organic/inorganic precursors were monitored by differential scanning calorimetry (DSC, Model STA 409, Netzsch GmbH, Selb, Germany) up to 500°C at various heating rate, in an air atmosphere. Fourier Transform Infrared Spectroscopy (FTIR, Model Bomen MB 102, Hartmann & Brown) was used to examine the distinct calcination behavior accompanying explosive expansion reaction. The specific surface areas of the precursors and calcined powders at each PEG content were studied by the nitrogen gas adsorption (Model ASAP 2400, Micromeritics, Norcross, GA) method. The final phases present after densification were determined with an X-ray diffractometer (Dmax automated powder diffractometer, Rigaku/USA, Danvers, MA) using CuKα radiation (40 kV, 40 mA). The measurements were made with a scanning speed of 10°C/min and a sampling interval of 0.02°C at room temperature. The average grain sizes of sintered samples were analyzed according to the Jeffries-Saltykov method.[15] The powder morphology and polished microstructure of the sintered pellet were examined by Scanning Electron Microscopy (SEM) (Hitachi S530, Hitachi, Japan). The specimens were mounted on an aluminum stub and Au-Pd sputtered on 15 mA for 40 sec.

3. Results and Discussion

3.1. Study of Explosive, Exothermic Reaction

The syrup-like, precursor gel was quite flammable and had a vigorous explosion reaction on continuous heating. After the reaction, the gel changed to a sooty, porous solid having about a 20-fold volume expansion. Fig. 1 displays the precursor gel before the reaction and the sooty, porous powder after the reaction. The explosive reaction occurred in quite short time exhaling black-color smoke. Thermal analysis behavior for the syrup-like, precursor gel were examined and the DSC results according to heating rate are shown in Fig. 2. As heating rate increase, the temperature of exothermic reaction increased. In the case of the heating
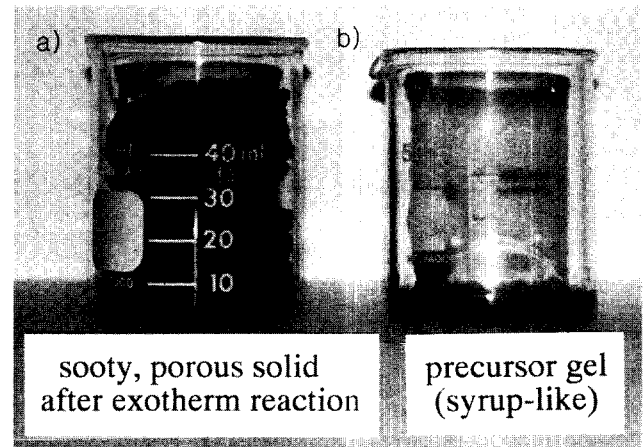

Fig. 1. Photographs of organic-inorganic precursors pre and after explosive, exothermic reaction. (a) sooty, porous powder after exothermic reaction and (b) syrup-like precursor gel before the reaction.
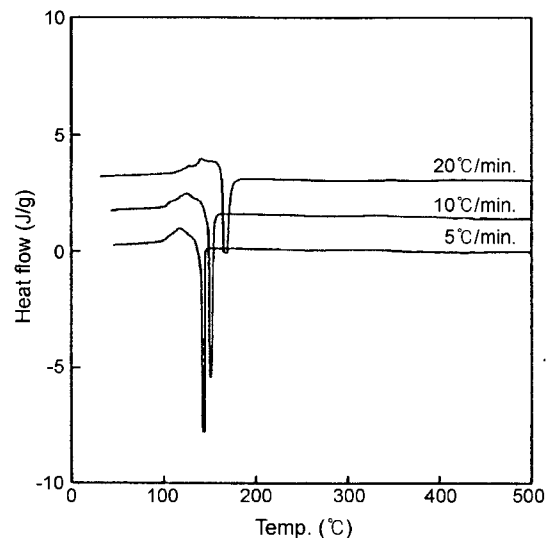

Fig. 2. DSC curves of precursor gel as a function of heating rate.

rate of 20°C, exothermic reaction was started at 120°C and finished at 160°C. This means the explosive reaction occurs at around 150°C during the heating process for dry of the precursor gel. The large endothermic peaks just after exothermic reactions may be due to the volume expansion in a moment by gas formation and evaporation in the precursor powders.

To examine the cause of the explosive reaction involving volume expansion, the changes of chemical structure of the precursors pre and after the explosive reaction were studied. Fig. 3 shows the FTIR spectra for the volume expanded powder sample and syrup-like gel sample which is obtained just before the explosive reaction. In the expanded powder after reaction, decrease of O-H bond groups at 3500 cm^{-1} was observed in comparison with the result of the gel sample. It means that evaporation of structural water in the aluminum nitrate and some chemical bonding between
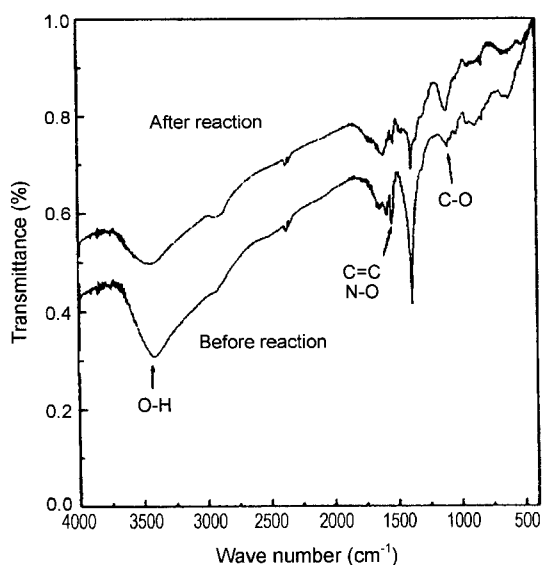
Fig. 3. FTIR spectra of volume expanded powder sample (after reaction) and syrup-like gel sample (before reaction).
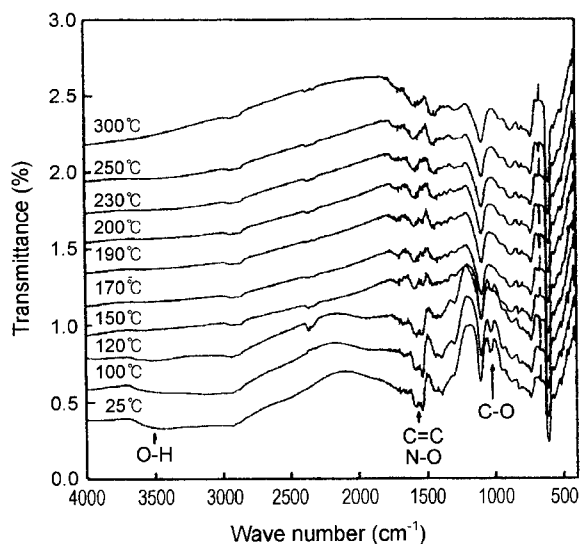
Fig. 4. FTIR spectra of precursor gel sample at each temperature on continuous heating condition.

PEG and metal ions occurred during the explosive reaction. And the decrease of the peaks at 1600 cm^{-1} in the powder after reaction explains that the decomposition of N-O and C=C groups in aluminum nitrate and zirconium 2,4-pentanedionate occurred during the exothermic reaction. The spectra for C-O bond groups, which are shown at 1100 cm^{-1}, were also changed after the reaction. This means that metal cations formed to M-O bonding by oxidation reaction as a result of the pyrolysis of C-O bond in the PEG.[16] These chemical structure changes on continuous heating condition were also examined with FTIR spectroscopy attaching heating equipment. Fig. 4 represents the results of FTIR in-situ analysis for the precursor gel sample as a function of heating temperature. The spectrum was changed at about 150°C
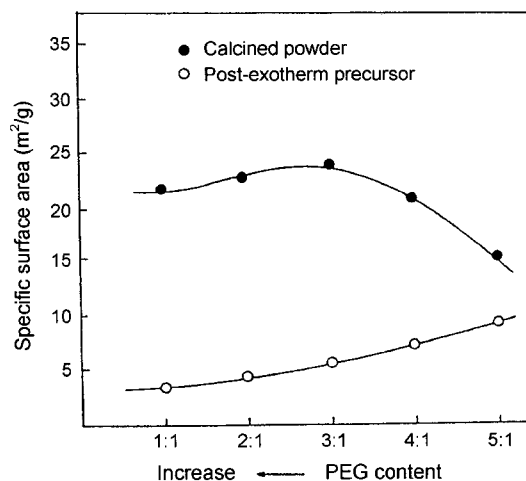
Fig. 5. The change of BET specific surface areas of the volume expanded precursor powders and calcined powders as a function of PEG content.

showing almost similar behavior to the results of Fig. 3. The O-H bond groups, N-O and C=C groups, and C-O bond groups gradually decreased as the temperature increase up to 300°C. It suggests that PEG and organic groups from metal salts were slowly burned out after the explosive reaction.

Finally, it may be speculated that the reason of the explosive reaction is the residual, flammable alcohol solvent in the precursor gel. The alcohol ignited at about 150°C, and the abrupt decomposition of the organic groups during the vigorous exothermic reaction resulted in the volume expansion of the precursor powder with forming extensive voids in the powder structure.

3.2. Effect of PEG Content

The change of BET specific surface areas of the volume expanded precursor powders and calcined powders as a function of PEG content are presented in Fig. 5. The precursors had higher specific surface areas as the PEG content decreased. After calcination, however, the powder derived from the 3 : 1 ratio (metal ions to PEG content ratio) had the highest specific surface area. In the drying process, the predecomposed organic compounds formed after the vigorous exothermic reaction covered the microporous channels in the porous precursors. Hence, the precursors which had the lowest PEG content showed the highest specific surface area. After removal of all organics, the calcined powders were still porous, showing lower specific surface area in the powder derived from low content PVA. The calcined powders prepared from 1 : 1 to 3 : 1 ratio resulted in a slight decrease in specific surface area as the PEG content increased. This was caused by the excess polymer in the precursor which resulted in entanglements of the polymer chains and incomplete polymer burn out. In the 1 : 1 ratio, the calcined powder was a bright grey color because of residual carbons, in comparison with the white-color powder in the 3 : 1 ratio.

Table 1. Phases Present and Grain Size Ranges of Duplex Zirconia-alumina Composites (1:1 vol%) Sintered at 1500°C for 1 h from Different PEG Content

PEG content (wt% cations : wt% PEG)	Phase present	Grain size range (μm)
1 : 1	m-, t-ZrO_2, α-Al_2O_3	~0.5–0.3
3 : 1	m-, t-ZrO_2, α-Al_2O_3	~0.4–0.3
5 : 1	m-, t-ZrO_2, α-Al_2O_3	~0.7–0.3

The crystalline phases present and grain sizes of the composites, which were pressureless sintered at 1500°C for 1 h, were compared in the metal ions to PEG content ratios of 1 : 1, 3 : 1, and 5 : 1. Table 1 lists the results. In all cases, m-ZrO_2 and t-ZrO_2 coexisted with α-Al_2O_3 phase. However, the m- and t-ZrO_2 peaks were different in their intensities in each case. In the 5 : 1 ratio composition, the grain size range was wider than that of the 3 : 1 ratio. This may be caused by agglomeration of the metal cations due to insufficient polymer content. The calcined powder derived from the 5:1 ratio showed the lowest specific surface area (Fig. 5). It may be speculated that the PEG content of 5 : 1 ratio was not enough to prevent segregation and/or agglomeration of the metal ions. It means some agglomeration occurred during the powder fabrication process. Hence, this resulted in an un-uniform grain size distribution in the sintered microstructure. In the examination of phase present, the composite derived from 5:1 ratio showed higher relative volume fraction of m-ZrO_2 to t-ZrO_2 than that of the composite in 3 : 1 ratio. This implies that the 5 : 1 ratio composite has more extent of larger grain size than the critical grain size for transformation[17] in comparison with the 3 : 1 ratio composite.

3.3. Microstructures

The powder morphology of the volume expanded precursor derived from 5 : 1 ratio is shown in Fig. 6. The precursor powder showed the highest specific surface area (Fig. 5). The SEM micrograph revealed quite porous structure. A lot of cavities in the powder structure explain that the decom-
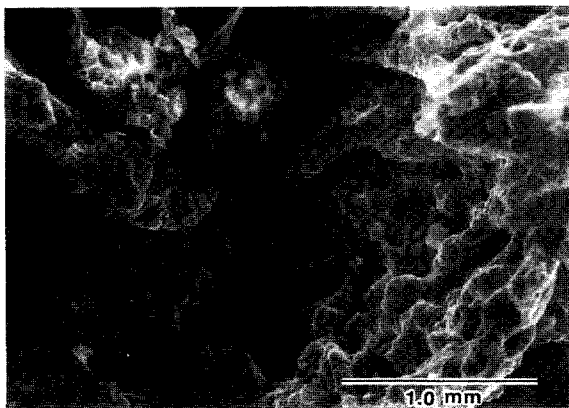
Fig. 6. SEM micrograph of the volume expanded precursor powder derived from the metal ions to PEG content ratio of 5:1.
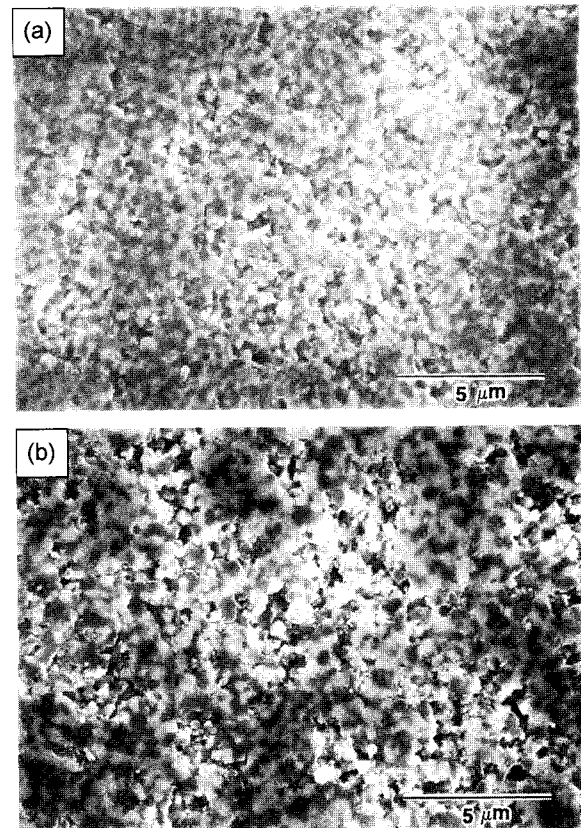
Fig. 7. SEM micrographs of surface microstructures of sintered composites derived from the metal ions to PEG content ratios of (a) 3 : 1 and (b) 5 : 1.

posed gases made the porous structure during the vigorous, explosive reaction.

The surface microstructures of the sintered composites derived from 3 : 1 and 5 : 1 ratios are shown in Fig. 7. As explained in Table 1, the sintered composite derived from 3 : 1 ratio showed more homogeneous microstructure having smaller grain size than the composite of 5 : 1 ratio.

4. Conclusions

The duplex, alumina-zirconia composites were successfully fabricated by a polyethylene glycol complexation process. In particular, an explosive exothermic reaction in drying process resulted in a formation of volume expanded, porous precursor powders. Polymer decomposition in a moment by the vigorous exothermic reaction made the volume-expanded powders having porous microstructure. The porous powders were ground easily by ball milling and the milled, fine powders were densified at 1500°C.

In the polymer complexation process, the PEG content affected on the specific surface area of the calcined powder and microstructure of sintered composite. Dispersion of the metal cations in the organic-inorganic sol depended on the PEG content and affected on the homogeneity of precursor gel. In case of the composite prepared from the metal ions to PEG content ratio of 3 : 1, the microstructure was relatively

homogeneous and the grain size was smaller than the other cases. This means homogeneous distribution of the metal ions in polymeric network structure can be achieved in the optimum PEG content.

Acknowledgements

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