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Fabrication of ceramic composites consisting of powders with different specific gravity by the slip-casting technique

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For composites, it is of great importance to fabricate well-dispersed green compacts, in order to improve their mechanical properties and reliability. In the present study, the slip-casting technique was applied to the fabrication of ZrO_2–WC–Al_2O_3 composites. The specific gravity of each composition in this material was very different, that is, 6.07 for ZrO_2, 15.6 for WC and 3.94 for Al_2O_3. The compositions in the green compacts were afraid to separate from each other owing to the difference in their specific gravities, leading to heterogeneity in the microstructure. The relative density of the obtained compacts was approximately 60%. WC and Al_2O_3 were well-dispersed in the ZrO_2 matrix. The separation and/or heterogeneity due to difference could not be recognized by energy-dispersive X-ray analysis. The slip-casting technique was found to be applicable to the fabrication of ceramic composites consisting of raw powders with different specific gravities.

1. Introduction

In recent years, ceramic composites with particles or whiskers have been extensively studied in order to improve the mechanical properties, such as fracture toughness and strength [1–3]. For processing of these composites, most of the materials were prepared using a hot-pressing technique. This technique is very convenient for preparing dense and fine-grained ceramic composites. However, in this technique the shape of the final products is limited to a disc or plate. Thus, this technique is not practically suitable for products with complicated shape and large products.

Slip-casting is one of the promising techniques to fabricate ceramics and ceramic composites with a complicated shape, or large products [4, 5]. In this technique, more intimate mixing could be possible with a well-dispersed slurry [6]. This is an advantage for forming ceramic composites through the suspension route, to improve their reliability. However, some problems exist in applying this technique to the fabrication of ceramic composites, for example, differences in specific gravity, dispersibility, and particle size between the particles for the matrix and the particles for the dispersion, etc. In the present study, the slip-casting technique was used to fabricate ZrO_2–Al_2O_3–WC composites. The possibility of using slip-casting to fabricate well-dispersed compacts consisting of powders with very different specific gravities, was also studied.

2. Experimental procedure

2.1. Raw materials

ZrO_2(OZC-2YC, Sumitomo Osaka Cement Co. Ltd, Tokyo, Japan), Al_2O_3 (AKP-20, Sumitomo Chemical Industries Co. Ltd, Tokyo, Japan) and WC (WC-F, Japan New Metals Co. Ltd, Osaka, Japan) were used as starting materials. All powders were of high-purity and commercially available. Table I shows the characteristics of these raw powders. The specific gravity of WC was 15.6, approximately four times as heavy as that of Al_2O_3. ZrO_2 contained 2 mol % Y_2O_3 and the average particle size was 0.094 μm. The diameters of Al_2O_3 and WC were also very fine, 0.54 and 0.69 μm, respectively. Particles of ZrO_2 and Al_2O_3 were relatively round and the particle-size distribution was narrow, as shown in Fig. 1. For WC, however, the primary particles were very fine, but they mutually sintered to form polycrystals with porosity. Then, the particle size became larger and the distribution became wider.

2.2. Preparation of slurry

In order to determine optimum conditions for preparing slurry, flow point [7, 8] and viscosity were examined. Polyacrylate (C-72: Nippon Kayaku Co. Ltd, Tokyo, Japan) and deionized water were used as a dispersant and a solvent, respectively. The flow point is the least amount of water required to give the slurry fluidity. Rheological characteristics of slurry

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TABLE I Characteristics of the starting powders

	Average particle size (μm)	Specific surface area ($m^2\ g^{-1}$)	Specific gravity	Porosity %	Purity %
ZrO_2	0.094	9.5	6.07	–	99.6
Al_2O_3	0.54	4.4	3.94	–	99.99
WC	0.69	2.5	15.6	0.72	99.98

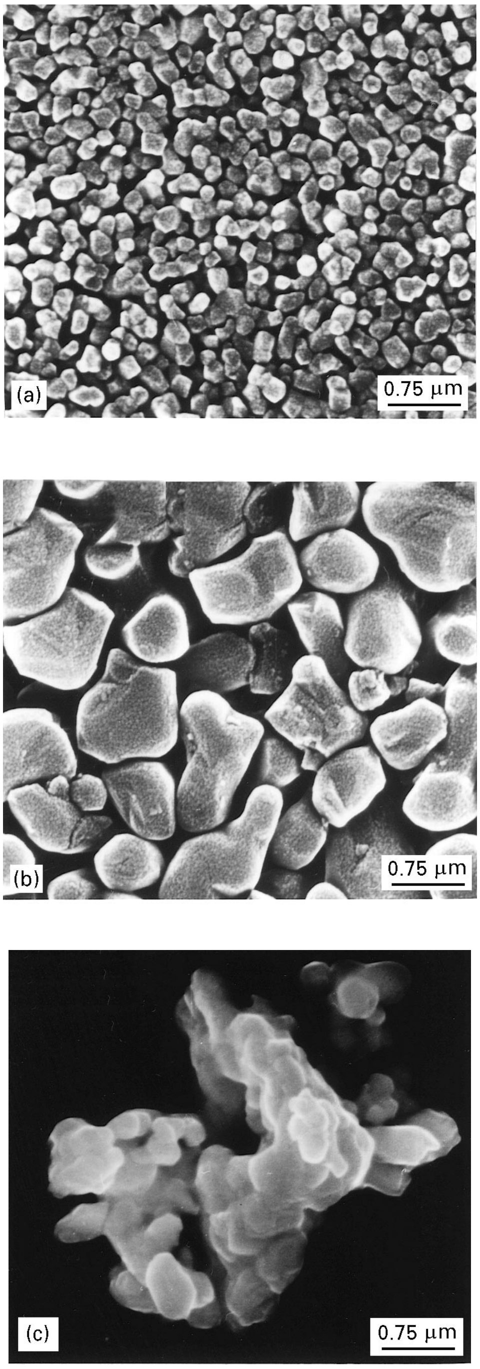

Figure 1 Scanning electron micrographs of the starting powders: (a) ZrO_2, (b) Al_2O_3, (c) WC.

were estimated with a viscometer (Type E Viscometer: Tokyoseiki Co. Ltd, Tokyo, Japan).

2.3. Fabrication of green compacts

Fig. 2 shows a schematic diagram of the fabrication of green compacts of ZrO_2–Al_2O_3–WC composites.

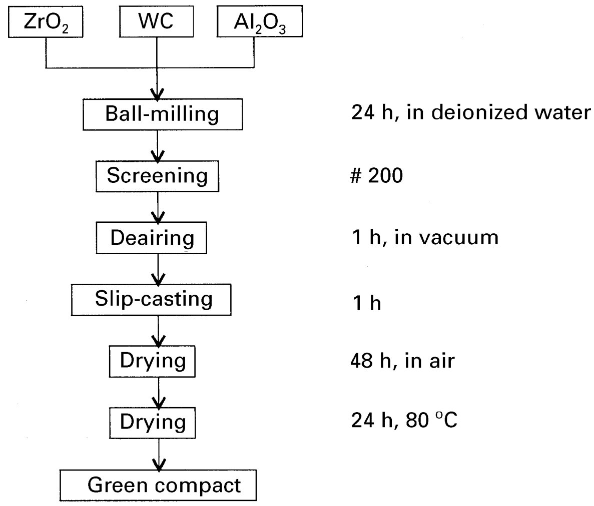

Figure 2 Schematic diagram of the fabrication of a green compact of ZrO_2–WC–Al_2O_3 composites by the slip-casting technique.

TABLE II Batch composition (vol %) of the slurry

	2Y-TZP	WC	Al_2O_3
TW0A30	70	0	30
TW10A20	70	10	20
TW20A10	70	20	10
TW30A0	70	30	0

The batch composition used is shown in Table II. The fraction of ZrO_2 as matrix phase was fixed at 70 vol %. Each fraction of Al_2O_3 and WC as dispersion phase was changed from 0–30 vol %. These raw powders were ball-milled for 24 h, with deionized water and a dispersant, on the basis of the optimum conditions determined by measurement of the flow point and viscosity. The obtained slurry was passed through a sieve of #200. Slurry was then placed in a vacuum desiccator under magnetic stirring for 1h to remove small air bubbles, and then cast into a conventional gypsum mould. Green compacts could be obtained in an hour after casting. The compacts were kept in air for 48 h and then dried in an oven at 80 °C for 24 h. The size of each compact was 100 mm × 50 mm × 5 mm.

2.4. Evaluation of green compacts

The density of green compacts was calculated from their dimensions and weight. In order to evaluate the dispersibility of Al_2O_3 and WC, quantitatively, their contents were analysed at various points of a compact using energy-dispersive X-ray analysis (EDX). Fig. 3 shows the 9 points at which the analysis was carried out, that is, at three parts of the compact, top, centre and bottom in length corresponding to the gravitational

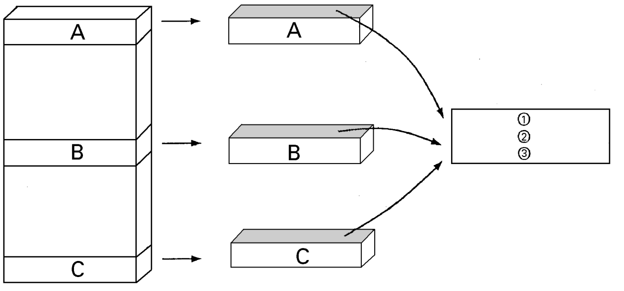

Figure 3 The nine points of a green compact analysed by EDX.

direction, and at three points along the thickness direction in each part. The analysed area was 1.5 mm × 1.5 mm.

3. Results and discussion

Fig. 4 shows the effect of dispersant on the flow point of each starting material. The amount of dispersant and the flow point are expressed as weight percentage to solids and volume fraction of water in the slurry, respectively. The amount of dispersant that minimizes the flow point is defined as the optimum amount to prepare a thick slurry with fluidity. The behaviour of the flow point is known to reflect the dispersibility of a slurry. Without a dispersant, for each powder an addition of more than 75–80 vol % water was needed for the slurry to exhibit fluidity. For ZrO_2 and Al_2O_3, in particular, similar behaviour was observed. A small addition of dispersant caused the flow point to increase, but more than 0.1 wt % dispersant decreased the flow point remarkably. Such behaviour of the flow point was discussed from the viewpoint of electric charge on the particle surface [7]. The optimum amount of dispersant was different for each raw powder. For ZrO_2, Al_2O_3 and WC, the values were 0.35, 0.3 and 0.1 wt %, respectively. These values would be effective to prepare each monolithic green compact. In the case of composites, however, it is very difficult to determine which value is effective. In the present study, the optimum amount of dispersant was assumed to be the least amount that was required for each powder to disperse simultaneously. The amount was determined to be 0.35 wt % and the following operation was carried out.

The optimum amount of water would be defined as the least amount of water that could make slip-casting possible. The amount is a very important parameter for the preparation of a slurry. Extra water would have a deleterious effect on green compacts and the subsequent sintering process. For example, it decreases the density and strength of the compacts, leading to the deterioration of some properties of the sintered bodies. The specific gravity of each ceramic powder used in the present study was very different, as shown in Table I, and so the sedimentation rates were supposed to differ resulting in heterogeneous separation in the green compacts. Therefore, preparation of a thicker slurry is preferable because an increase in viscosity is expected to restrain the separation of each composition owing to the difference of the sedimentation rate.

The viscosity of each slurry is shown in Fig. 5. Although a smaller amount of water is desirable in preparing a slurry, as mentioned above, an amount less than 50 vol % was insufficient to prepare a fluid slurry in every batch composition. Slurries could be prepared with water amounts of 55 and 60 vol % and were examined. In the case of a composition rich in WC (TW30A0), a fluid slurry could not be obtained, even with 55 vol % water. Consequently, the amount of water used for every composition was kept constant at 60 vol %.

In spite of the amount of water being constant, the viscosity was found to change depending on the batch composition. Slurries with 10 vol % WC gave the minimum value of viscosity for both water contents.

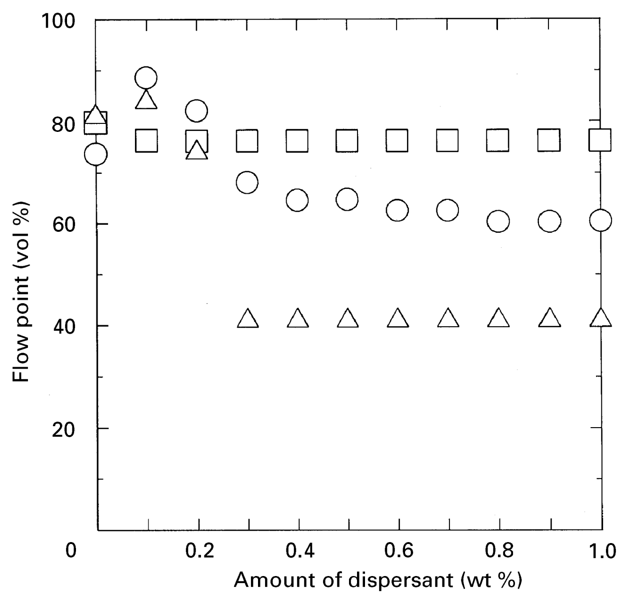

Figure 4 The effect of dispersant on flow point of (○) ZrO_2, (□) WC and (△) Al_2O_3.

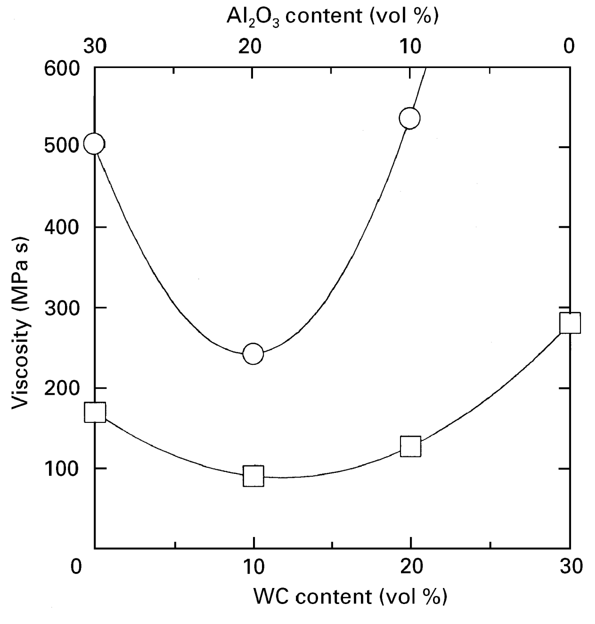

Figure 5 The effect of batch composition on the viscosity of a slurry at water contents of (○) 55% and (□) 60 vol %.

Such a dependence was supposed to be influenced by interactions between the polymer (dispersant) and the ceramic particles and/or between ZrO_2 and Al_2O_3 and WC particles. In order to apply the slip-casting technique to the fabrication of a variety of composites, it is very important to clarify these interactions. However, the interaction is not clear in detail.

A deairing operation was carried out in vacuum under magnetic stirring. During this operation, blackish powders appeared on the surface of the slurry. These powders were inferred to be WC, because the only blackish powder used as a starting material was WC, and such floating powders could not be observed when preparing ZrO_2–Al_2O_3 composites. In fact, this matter was identified as WC by X-ray diffraction analysis. This behaviour was supposed to be caused by wettability of WC and/or porosity in WC. Green compacts prepared from such a slurry were found to be hollow inside. The blackish matter was observed selectively on the surface around the hollow. That is, this matter is inferred to restrain the slurry from settling uniformly, resulting in the hollow. Elimination of the floating WC during casting would be significant for fabricating compacts without the hollow. In order to prevent the floating WC powders from slipping into a gypsum mould, a stop cock was attached at the side of the container of slurry and casting was carried out from the stop cock. Consequently, green compacts with no hollows could be obtained by using this container.

It was easy to remove a compact from a gypsum mould in 1 h after casting. It was strong enough to handle. Fig. 6 shows the relative densities of the compacts. The densities were approximately 60%, regardless of the batch composition. A slurry with a lower viscosity seemed to have a tendency towards higher density.

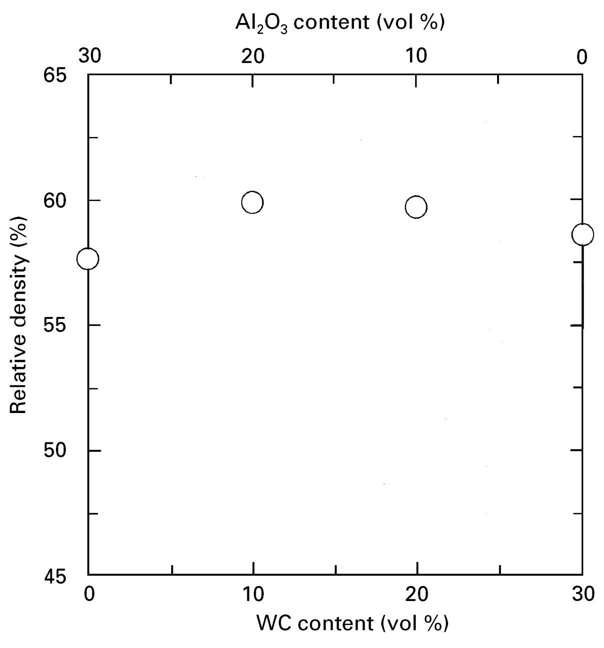

Figure 6 The relative density of green compacts prepared by the slip-casting technique.

TABLE III WC content (vol %) analysed by EDX at various points on a green compact

	1	2	3
A	17.95	17.69	18.19
B	18.02	18.09	18.20
C	17.25	17.28	17.17

TABLE IV Al_2O_3 content (vol %) analysed by EDX at various points on a green compact

	1	2	3
A	11.42	11.17	11.23
B	11.52	11.07	11.31
C	11.90	11.75	11.87

Tables III and IV show the results of EDX analysis for a green compact with 20 vol % WC and 10 vol % Al_2O_3 (TW20A10) in order to examine their dispersibility. The sedimentation rate of particles in a slurry would depend upon their size and specific gravity. The rate for WC was supposed to be faster than the others, resulting in separation and/or heterogeneity of the composition in the compacts, because the specific gravity was much larger than that of ZrO_2 and Al_2O_3, as shown in Table I. In the gravitational direction (A–C), in particular, more WC was supposed to be detected at the bottom (C) and less at the top (A). However, no remarkable heterogeneity could be recognized on WC. The variation in composition was very small. Al_2O_3 was also found to be dispersed in this direction as well as WC. In the thickness direction (1–3), on the other hand, the variation was also small for both WC and Al_2O_3. The observed amount of WC was slightly smaller than the prepared amount at every point. This decrease was inferred to be due to the removal of floating WC during the deairing operation. In compacts with 30 vol % WC (TW30A0), furthermore, WC and Al_2O_3 were uniformly dispersed and their variation was as small as that of TW20A10.

4. Conclusion

In order to fabricate composites consisting of powders with different specific gravities by the slip-casting technique, in the present study, slurries were prepared using polyacrylate as a dispersant. The viscosity of the obtained slurries was from 100–300 MPa s depending on the composition. Homogeneous green compacts, without the separation of composition due to differences of specific gravity, could be prepared from thick slurries. The relative density of the obtained compacts was dense and approximately 60%. The slip-casting technique was found to be applicable to the fabrication of ceramic composites consisting of powders with different specific gravities.

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