Journal of the European Ceramic Society 18 (1998) 1281–1285

PII: S0955-2219(98)00054-5
0955-2219/98/$—see front matter

Zirconia–Stainless Steel Functionally Graded Material by Tape Casting

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Abstract

Ceramic/metal functionally graded material (FGM) was fabricated by tape casting. Zirconia (ZrO_2) and stainless steel (SUS) were stably dispersed in deionized water (DI-water). An optimal dispersion condition of ZrO_2 was obtained from electrokinetic sonic amplitude (ESA) data, and ZrO_2 particles could be dispersed by electrostatic repulsion. Conversely, a stable SUS slurry was prepared by increasing solution viscosity and using steric hindrance. Monophase and binary slurries were cast at uniform thickness through a doctor blade. ZrO_2/SUS FGM was sintered at 1350°C in Ar/H_2 atmosphere. The sintering defects could be controlled by the adjustment of the particle size and phase-type of ZrO_2. As a consequence, the microstructure and interface showed a compositional gradient continuously.

1 Introduction

In recent years, further developments in science and technology will depend upon the development of new materials that can withstand severe conditions. There are two approaches: (a) to create a new material that differs completely from any present materials and (b) to develop an advanced material with new functions. Composites can fulfill these requirements, especially composites which have various different functions. Because of that reason, many special composites have been designed to eliminate the macroscopic boundary in laminated-type materials.[1] These are the motivations for the development of functionally graded materials (FGM).

In order to avoid defects in FGMs, we should control the shrinkage and sintering behaviors over the entire compositional range as follows: (1) control the particle size of starting materials, (2) adjust the mixing condition for homogeneity, (3) pressure sintering, (4) inclusion additions, and (5) temperature gradient.[2–5] In this work, we tried to minimize the sintering defects using monoclinic zirconia polycrystals (MZP), which have a larger particle size than tetragonal zirconia polycrystals (TZP).

Preparation of ceramic bodies by tape casting has been thought to be one of the most favorable and feasible routes for FGM, with which a large thin sheet of uniform thickness can be processed along with complex shape-forming capability. Generally, this process has been performed for non-aqueous systems.[6,7] In this work, we manufactured FGMs using tape casting in an aqueous system. The stable dispersion of the slurry is indispensable for the tape casting process. Ceramic powders are of high surface area and relatively low solubility, and surface chemistry tends to control their charging behavior. There are three possible mechanisms:[8,9]

(a) non-stoichiometric dissociation/adsorption (i.e. clay);
(b) adsorption/dissociation of hydroxyl and hydrogen ions (i.e. oxide);
(c) preferential adsorption of specific additive or impurity ions (i.e. dispersant).

Ceramic particles such as zirconia's can be charged primarily by the second mechanism. Dispersion of TZP and MZP is stabilized using the surface charge, that is, electrostatic repulsion. So, for the optimized condition of dispersion, we investigated the interaction between starting materials and organic additives with electrokinetic sonic amplitude (ESA, MBS-8000, Matec Applied Science, USA) and the rheology of each composition using a viscometer (Brookfield, DV-II). The green sheets prepared with various compositions were sintered and then characterized in terms of sintering properties and compositional continuity of FGM. As a result, we can describe in this work the dispersion of starting materials in an aqueous system and the control of sintering defects.

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2 Experimental Procedure

The starting materials were 3 mol% Y_2O_3-doped TZP (99.9%; Tosho Co., Japan) and MZP (SC30, 99%; Imperial Poly-chemicals Co., USA) as ceramics, and stainless steel 316L (SUS316L; Anval Co., Sweden) as the metal. TMP is arbitrarily denoted as the mixed powder for various ratios of TZP and MZP. The properties of the starting materials are shown in Table 1. We used several organics for dispersion and casting, and the properties of organic additives are shown in Table 2.

ZrO_2/SUS316 FGM was fabricated by tape casting, as shown in the experimental procedure of Fig. 1. We evacuated in the vacuum chamber for 2 hours to remove foams. To prevent inter-particle agglomeration, 1 h sonifing (Sonifier 450; Branson Ultrasonics, USA) and sieving were performed. The dispersed slurry was cast onto a flat mylar film and dried slowly in a humid room in order to avoid cracks due to the difference of drying rates. Then the stacked sheets were pressed at 20 MPa and burned-out below 500°C. The compacted green body was sintered in an Ar/H_2 atmosphere at 1350°C for 2 h. The microstructure of the prepared FGM was examined with an optical microscope (Reichert Metaplan 2; Leica, Austria) and scanning electron microscope (SEM, JSM-5200; Jeol, Japan). Also, the continuity of the interface was identified with SEM and a wavelength dispersive spectrometer (WDS, JAX-8600; Jeol, Japan).

3 Results and Discussion

3.1 Dispersion of ZrO_2 and SUS316

All powders were dispersed in DI-water. Figure 2 shows the zeta-potential (ζ) of TZP, MZP and SUS316 versus pH plots, respectively. The dispersant of TZP and MZP is DAXAD-34 solution, which has been used frequently as a dispersant for ceramic powders.[10–13] The DAXAD-34 solution is almost entirely composed of PMAA. PMAA has a compressed coil polymer at acidity, but a long extended one at basicity. Therefore, the isoelectric point (IEP) of TZP and MZP is shifted toward 3·4 (IEP of PMAA) as PMAA is added. PMAA is the anionic polymer, and carboxy acid in PMAA solution is to desorb carboxyl group above pH 3·5. IEP of TZP and MZP is shifted toward acidity as the weight per cent of the PMAA is increased. So, we have determined the optimized dispersion condition as TZP +0·5 wt% PMAA and MZP +0·3 wt% PMAA at pH 8·0.

In the case of SUS powder, electrostatic repulsion may not be used, resulting from smooth change with pH-variation. SUS powder could be suspended by means of raising a dispersing medium's viscosity.[14] Therefore it was effective by means of steric hindrance rather than electrostatic repulsion. Sediment weight varied with time. 0·1 wt% Na–CMC solution was almost sedimented after 2 h, 0·1~0·7 wt% Na–CMC solution after 2 days, and all slurry after 4 days, and thus we decided on 0·7 wt% Na–CMC. We have determined the optimized dispersion condition as

Table 1. Properties of starting materials

Properties ▶ *Materials* ▽	*Melting point (°C)*	*Density (g/cm³)*	*Thermal expansion coefficient (10^{-6}/°C)*	*Modulus of elasticity (GPa)*	*Poisson's ratio*	*Mean particle size (μm)*	*Specific surface (m²/g)*
TZP[a]	2719	6·05	9·6 (20~400°C) 11·8 (20~1000)°C	186 (20°C)	0·31	0·15	13·46
MZP[b]	2677	5·56	6·5 (20°C)	210 (20°C)	0·3	0·36	4·90
SUS316L[c]	1375~1400	8·06	15·9 (0~100°C) 16·2 (0~315°C) 17·5 (0~558°C)	260 (20°C)	0·3	6·83	0·11

[a] 3 mol% Y_2O_3-doped tetragonal zirconia polycrystal.
[b] Monoclinic zirconia polycrystal.
[c] Stainless steel 316L.

Table 2. Properties of organic additives

Materials	*Company*	*Chemical analysis (wt%)*	*Average molecular weight*	*Function*
Na–CMC[a]	Yakuri Chemical Co.	Na–CMC 98·5% Water < 1·5%	—	Suspending agent
PEG[b]	Aldrich Chermical Co.	PEG 100%	400	Plasticizer
PVA[c]	Yankuri Chemical Co.	99% hydrolysed	66,000	Binder
DAXAD-34	Hampshire Chemical Co.	PMAA 25% Water 75%	10,000	Dispersant
D-SK	Dongnam Synthesis Co.	—	—	Antifoaming agent

[a] Carboxymethylcellulose sodium salt.
[b] Poly(ethylene glycol).
[c] Poly(vinyl alcohol).

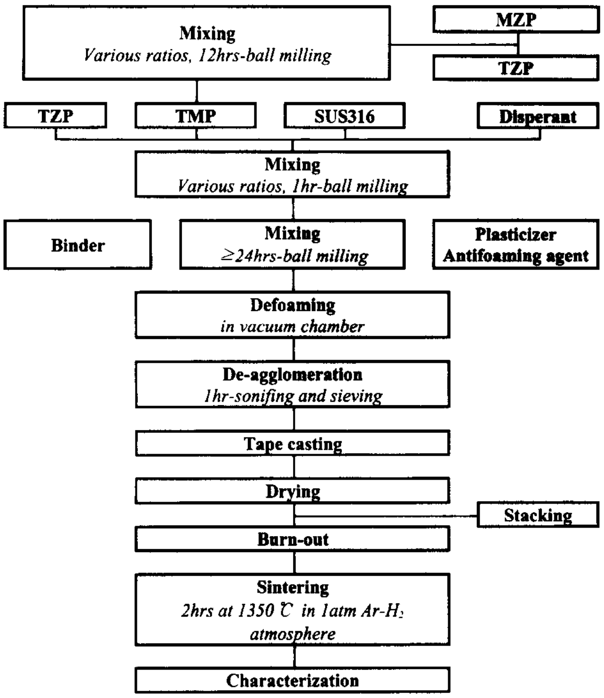


Fig. 1. Schematic diagram of experimental procedure.

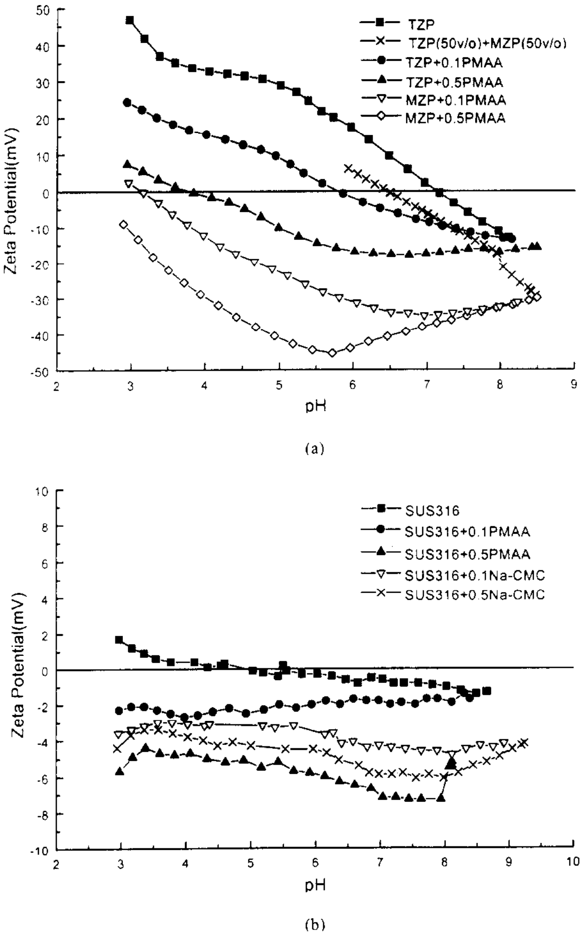


Fig. 2. Zeta-potential of (a) TZP and MZP, (b) SUS316 with pH variation.

SUS316 + 0·7 wt% carboxymethylcellulose sodium salt (Na–CMC) + 0·015 wt% PMAA at pH 8·0.

TZP slurry and SUS slurry under optimal dispersion conditions were homogeneously mixed for 1 h. By this route we could obtain a stable binary slurry. If two powders are charged with different polarity, electrostatic attraction takes place so that dispersion is unstable and agglomeration occurs.[15]

When all the additives are added, the viscosity of the slurry was found to be about 4000∼5000 cps. At that time, solid loading of TZP, MZP and SUS is 25, 40 and 80 vol%, respectively. The heating schedule was determined by the TG-DTA data,[16] at which most of the binders are burned-out below 500°C.

3.2 Control of the sintering defects and microstructure

When joining dissimilar materials, there will be a discontinuity in material properties. FGM, a kind of joining material, was also, and therefore it was necessary to minimize the presence of sintering defects and the internal stress. Sintering defects, which resulted from the different shrinkage rate, was usual, so that the adjustment of particle size and phase-type of ZrO_2, that is, TMP/SUS FGM (rather than TZP/SUS FGM) could prevent sintering defects in this work. As shown in Fig. 3, no crack or delamination occurred. This fact is due to: (a) the larger particle size of MZP and (b) the 35 vol% expansion which takes place in MZP on cooling.[17] The use of an interlayer material (MZP) can reduce mismatch stress, thereby preventing joint failure.[18] Intervening MZP powder could reduce the shrinkage rate between TZP and SUS. Warping was seen in Fig. 3. Warping occurred in a specimen stacked with thin sheets, which originated from the large thermal expansion coefficient of the metal side. This is appreciably relieved by pressing the specimen and increasing the number of layers. At this time, pressure sintering just means that sintering is performed under some load to the specimen. In pressureless sintering, warping appears toward the ceramic-rich region, although we control the difference of shrinkage rate and the sintering behavior between the ceramic and the metal. It has been thought to be the effect of the difference of solid loading.

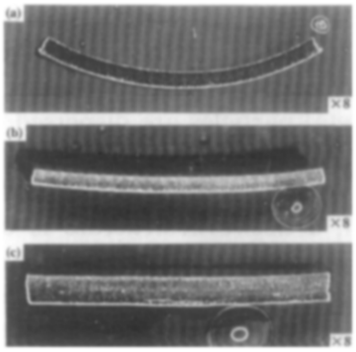


Fig. 3. Photograph of FGM samples (16 layers); (a) 200 μm thick, pressureless sintering; (b) 200 μm thick, pressure sintering; (c) 400 μm thick, pressure sintering.

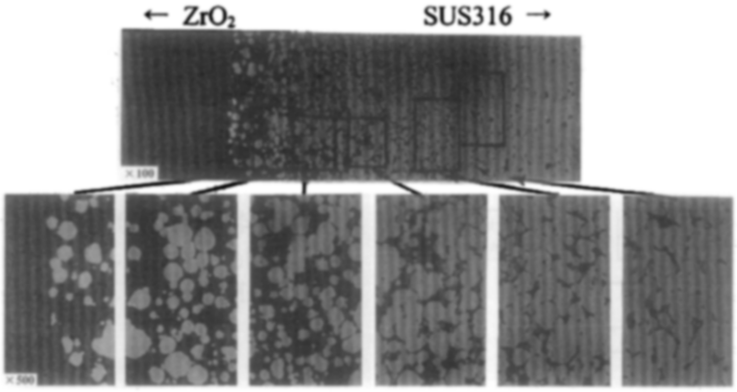
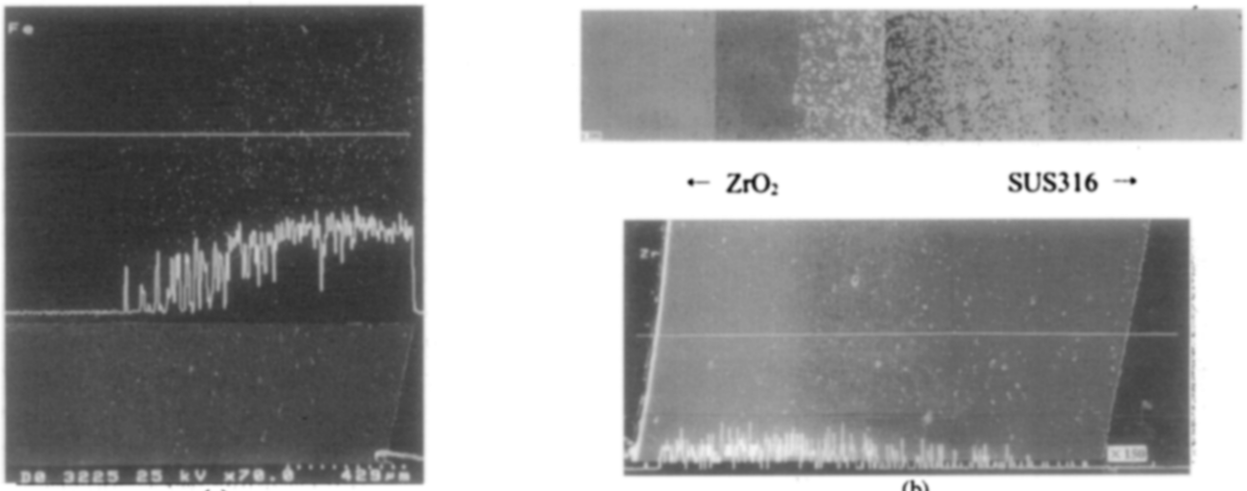


Fig. 4. Multilayer and interface structure.



(a) (b)

Fig. 5. Element distribution in ZrO_2/SUS FGM with WDS; (a) Fe distribution and (b) Zr distribution.

From the data concerning the influence of metal volume fraction and sintering temperature on shrinkage,[7] we established the optimized number of stacking layers and compositional gradient. The number of stacking layers is 16 and the compositional difference between each layer is 10 vol%.

The continuous compositional change throughout FGM was observed with an optical microscope as shown in Fig. 4. The composition gradually changes from the ZrO_2-rich region to the SUS316-rich region. We observe the dispersive structure in the metal side, in which ceramic particles are dispersed in the metal matrix. Also, the dispersive structure can be shown in the ceramic side to the contrary, metal particles are dispersed in the ceramic matrix, as if the dispersing particles and matrix are woven with each other. For the intermediate composition, a network structure is observed, in which two phases are linked as the volume fraction of each phase is increased. These microstructures are consistent with the model designed theoretically and proposed by Watanabe *et al.*[1,3,19]

Figure 5 shows the distribution of Zr and Fe obtained in the ZrO_2/SUS FGM without any defect as a consequence of the optimum adjustment of starting particles size and layers composition.

4 Conclusions

For the tape casting of ZrO_2/SUS FGM, monophase and binary slurries could be stably prepared by the ESA data and sediment weight with time. The dispersion of ZrO_2 depended upon electrostatic repulsion; however, that of SUS depended upon steric hindrance. Well-dispersed slurries were cast onto a mylar film at uniform thickness according to optimal compositional gradient and 16 layers. The optimized amount of each powder is TZP + 0·5 wt% PMAA, MZP + 0·3 wt% PMAA, and SUS316 + 0·7 wt% Na–CMC + 0·015 wt% PMAA at pH 8·0. The sintering defects due to the different sintering shrinkages of the starting components could be controlled by the adjustment of the particle size and phase-type of ZrO_2. Also, the warping could be reduced or eliminated by pressing the specimen or increasing the number of layers. The continuity of microstructure and composition of ZrO_2/SUS FGM was investigated and the structural change at the interface and microstucture of FGM were analogous to the theoretical design.

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