

Microstructure control of Ce-TZP/Ba ferrite composites using an amorphous precursor of the second phase

Takashi KOJIMA,[†] Shinya OORI, Takuya WATANABE, Yuya SHIMADA, Syunpei NORO, Naofumi UEKAWA and Kazuyuki KAKEGAWA

Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522

Composites consisting of Ce-TZP matrix and in situ-grown particles of barium ferrite (BaM) were prepared using various starting materials. For the starting material for the second phase, an amorphous precursor powder of BaM was prepared by coprecipitation and calcination. Uniform hematite particles were also prepared using liquid-phase synthesis under hydrothermal conditions. The Ce-TZP/20 wt % BaM composites were prepared by sintering the mixed powders of Ce-TZP, barium carbonate, hematite, and amorphous precursor of BaM. The aspect ratio of the in situ-grown BaM particles increased concomitantly with an increase in the mixing ratio of the amorphous precursor powder. The exaggerated grain growth of the BaM in the Ce-TZP matrix was efficiently suppressed by the addition of a small amount of barium carbonate and hematite to the amorphous precursor of BaM.

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In situ formation of a plate-like second phase, such as hexaaluminate^{1)–13)} or hexaferrite^{14)–21)} particles in yttria or ceria-stabilized tetragonal zirconia polycrystals (Y-TZP or Ce-TZP) was reportedly effective for improving the mechanical properties of zirconia ceramics. Composites consisting of TZP matrix and in situ-grown plate-like particles, of ferromagnetic hexaferrite such as barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$, Ba M-type ferrite: BaM),^{14)–16)} and lanthanum ferrite ($\text{LaFe}_{12}\text{O}_{19}$, La M-type ferrite: LaM),^{17)–21)} have already been reported. Composites with hexagonal ferrite phase exhibited ferromagnetism as well as improved mechanical properties. Generally, these TZP/hexaferrite composites were prepared by simply sintering a mixed powder of matrix phase and starting materials for the second phase. Microstructure control of these composites has been tried by changing the sintering temperature and composition of the second phase. In addition, only commercial powders, such as hematite ($\alpha\text{-Fe}_2\text{O}_3$),^{17)–21)} or maghemite ($\gamma\text{-Fe}_2\text{O}_3$),^{14)–16)} were used as the iron source for the second phase; other starting materials have not been examined. Therefore, in this study, the effect of the starting materials on the microstructure of Ce-TZP/hexaferrite composites were examined. Prior to undertaking this study, the authors selected LaM as the second phase.^{17)–21)} In fact, LaM is suitable for improving the mechanical properties of the composites because it readily forms plate-like particles with a high aspect ratio.^{17)–22)} However, additives were necessary to stabilize the LaM phase because its stable temperature range is very narrow.^{17)–21),23)–25)} In this study, to exclude the effect of additives on the composite microstructure, BaM was selected for the second phase. Actually, BaM is the most typical hexagonal ferrite phase; it is more stable than LaM.^{26),27)} To evaluate the effect of the starting materials for the second phase on the microstructure of the composite, an amorphous precursor powder

of BaM with a composition of Ba:Fe = 1:12 was prepared by coprecipitation.²⁸⁾ Using an amorphous precursor powder with high reactivity and small primary particles, an increase in the size and aspect ratio of the in situ-grown BaM particles was expected. A mixed powder of BaCO_3 and $\alpha\text{-Fe}_2\text{O}_3$, conventional starting materials for BaM, was also used. However, if particles with a wide size distribution and which are significantly aggregated are used as the starting materials, then microstructure control of the in situ-grown particles becomes extremely difficult. Consequently, uniform $\alpha\text{-Fe}_2\text{O}_3$ particles were also synthesized using the gel-sol method.^{29),30)} For BaCO_3 , a commercial powder was used because the amount of BaCO_3 in the starting materials is small (3.5 wt %), and this will decompose at the first stage of BaM formation.^{14),31)}

The reagents used for this study were iron (III) chloride, barium chloride, sodium hydroxide, sodium carbonate (Wako Pure Chemical Industries Ltd., Japan), and 12 mol % CeO_2 -doped ZrO_2 powder (CEZ-12SD (binder added type), Daiichi Kigenso Kagaku Kogyo Co. Ltd., Japan). The amorphous precursor of BaM was prepared through coprecipitation and calcination.²⁸⁾ First, $[3.1 \text{ M NaOH} - 3.0 \times 10^{-1} \text{ M Na}_2\text{CO}_3]$ mixed aqueous solution was added slowly to $[6.3 \times 10^{-2} \text{ M BaCl}_2 - 7.5 \times 10^{-1} \text{ M FeCl}_3]$ mixed aqueous solution until the pH value became 12 under magnetic stirring at room temperature. The stirring was continued for 5 min after adding the solution. After stirring, the obtained precipitate was washed three times with water by centrifugation and then freeze-dried. The dried powder was calcined at 500°C for 1 h to obtain the amorphous precursor of BaM. The $\alpha\text{-Fe}_2\text{O}_3$ particles were prepared using the gel-sol method.^{29),30)} First, 5.4 M NaOH aqueous solution was added to the same volume of 2.0 M FeCl_3 aqueous solution over 2.5 min under magnetic stirring at 80°C. The resulting gel was stirred for a further 5 min. Immediately after stirring, the sample was treated hydrothermally at 100°C for 6 days. The obtained particles were washed three times with water by centrifuging and then freeze-

[†] Corresponding author: T. Kojima; E-mail: tkojima@faculty.chiba-u.jp

Table 1. Mixing ratios of the starting materials for the second phase

	*BaCO ₃ + α -Fe ₂ O ₃ (wt %)	Amorphous Precursor (wt %)
AP0	100	0
AP20	80	20
AP50	50	50
AP80	20	80
AP90	10	90
AP95	5	95
AP100	0	100

*BaCO₃: α -Fe₂O₃ = 1:6 (molar ratio). The (BaCO₃ + α -Fe₂O₃) powder was weighed in consideration of the weight decrease due to decarbonation at the sintering stage.

dried. The Ce-TZP/20 wt % BaM composites were prepared as follows. First, starting powders of BaM and 12 mol % CeO₂-doped ZrO₂ powder were mixed using a mortar. The mixing ratios of the starting materials of the second phase (BaM) are presented in **Table 1**. The mixing ratio of Ce-TZP:BaM after sintering was set at 80:20 in weight. After mixing and sieving, the powder mixtures were cold isostatically pressed at 100 MPa to yield green compacts. The compacts were sintered at 1350°C for 12 h. The heating and cooling rates were set at 10°C/min.

Crystalline phases were identified using X-ray diffractometry (XRD, M18X-HF-SRA; Mac Science Ltd., Japan) with Cu K α radiation with a monochromator. The sample's morphology was observed using scanning electron microscopy (SEM, JSM-6330F; JEOL, Japan). The mean particle sizes and mean aspect ratios of the second phase in the composites were determined by measuring the size of about 100 particles in the SEM images of each sample. The thermal decomposition behavior of the coprecipitated powder was examined using thermogravimetry (TG8120; Rigaku Corp., Japan). The Vickers hardness of the composites was measured using a Vickers hardness tester (AVK-A2; Akashi Corp., Japan) at a load of 294 N. The fracture toughness of the composites was preliminarily evaluated using the indentation fracture method.³²⁾

Figure 1 shows a SEM image of the amorphous precursor of BaM prepared by coprecipitation and calcination at 500°C for 1 h. The calcination temperature was determined at the point that weight loss of the coprecipitated powder was almost finished in the TG curve. A powder with small primary particles (ca. 30 nm) was obtained. The XRD measurement confirmed that the coprecipitated powder retained the amorphous phase after the calcination. **Figure 2** shows a SEM image of the α -Fe₂O₃ particles prepared by hydrothermal treatment. Uniform α -Fe₂O₃ particles without aggregation were obtained. The XRD measurement confirmed that the particles were single-phase α -Fe₂O₃.

Using starting materials with various mixing ratios for the second phase, Ce-TZP/20 wt % BaM composites were prepared. The XRD measurements revealed that all the prepared composites consisted solely of tetragonal zirconia and in situ-formed BaM phase. When the composites were prepared using the AP0 and AP80–AP100 powder as the starting material for the second phase, dense sintered bodies with no cracks were obtained. On the other hand, the composites prepared using AP20 and AP50 powder were often cracked. For that reason, the mechanical properties of these samples could not be measured. This sample cracking might arise from the thermal stress caused by the mismatch of the formation timing of BaM particles that occurs using starting materials of two different types. **Figure 3** shows SEM images of the Ce-TZP/20 wt % BaM composites prepared

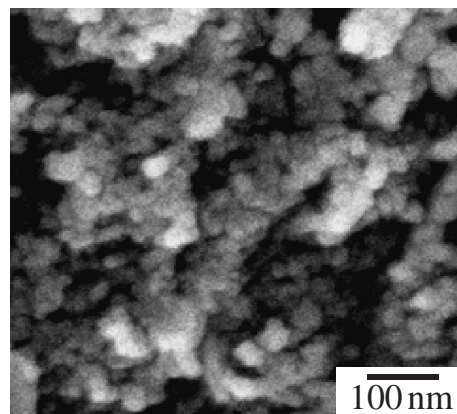
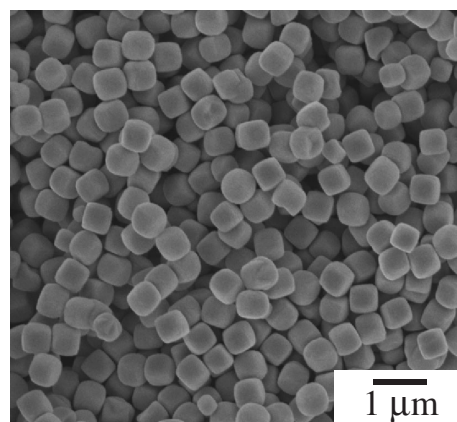


Fig. 1. SEM image of the prepared amorphous precursor of BaM.

Fig. 2. SEM image of the prepared α -Fe₂O₃ particles.

using the starting materials for the second phase with various mixing ratios. **Table 2** summarizes the mean particles sizes (length) and mean aspect ratios (length/thickness) of the second phase (BaM) in the composites. BaM particles with plate-like hexagonal shapes were formed in situ in all samples between sintering. When the composite was prepared using only the mixed powder of BaCO₃ and α -Fe₂O₃ (AP0, Fig. 3(a)), the BaM particles were small and seemed to be ineffective for increasing the effect of crack deflection.²²⁾ On the other hand, exaggerated grain growth of BaM was observed in the composite prepared using only amorphous precursor (AP100, Fig. 3(e)). Because of the small size of the amorphous precursor particles, the distance between them became very short in the green compact of the composite. Therefore, BaM crystals may grow exaggeratedly through absorbing the surrounding high reactive precursors. To suppress this exaggerated grain growth, a mixed powder of BaCO₃, α -Fe₂O₃, and amorphous precursor powder was used (AP80–AP95, Figs. 3(b)–3(d)). The aspect ratio and particle size of BaM particles in the composites increased concomitantly with an increase in the mixing ratio of amorphous precursor powder. Moreover, the exaggerated grain growth of BaM particles was efficiently suppressed by the addition of only 5 wt % of BaCO₃ and α -Fe₂O₃ (AP95, Fig. 3(d)). The existence of BaCO₃, α -Fe₂O₃ and intermediate phases such as BaFe₂O₄³¹⁾ formed by the reaction of BaCO₃ and α -Fe₂O₃ may inhibit the diffusion of Ba and Fe species from the high reactive amorphous precursors. **Figure 4** shows the Vickers hardness and fracture toughness of Ce-TZP/20 wt % BaM composites prepared using starting

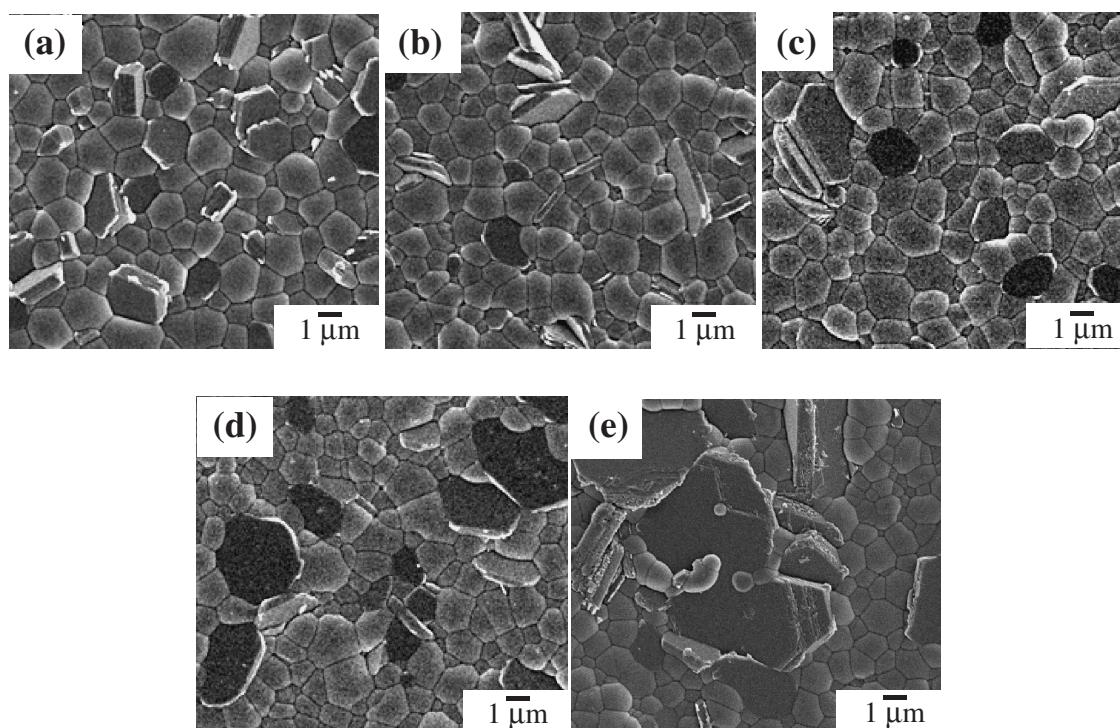
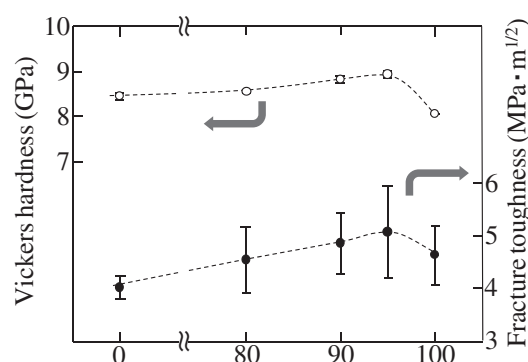


Fig. 3. SEM images of Ce-TZP/20 wt % BaM composites prepared using powders of (a) AP0, (b) AP80, (c) AP90, (d) AP95, and (e) AP100 as starting materials for the second phase.

Table 2. Mean particle sizes and mean aspect ratios for the second phase

	Mean particle size (length: μm)	Mean aspect ratio (length/thickness)
AP0	1.9	2.7
AP80	2.2	4.6
AP90	2.6	5.0
AP95	2.8	5.0
AP100	4.7	8.4



Mixing ratio of amorphous precursor in the starting materials for the second phase (wt%)

Fig. 4. Vickers hardness and fracture toughness of the Ce-TZP/20 wt % BaM composites prepared with various mixing ratios of the starting materials for the second phase.

materials with various mixing ratios. The values of the Vickers hardness of the composites were almost identical. The slightly lower value for the composite prepared using AP100 powder is

attributable to the formation of weak grain boundaries between large BaM particles and the Ce-TZP matrix. Although the values of fracture toughness measured using the indentation fracture method were themselves not accurate due to the unusual R-curve behavior associated with transformation toughening of tetragonal zirconia, they are meaningful as a comparison of samples belonging to the same system.³³⁾ The sample prepared using AP95 powder exhibited the maximum value for fracture toughness, which may result from the moderate grain size and aspect ratio of the second phase particles (Fig. 3(d)) for deflecting the cracks that develop in the composite.²²⁾

In summary, Ce-TZP/BaM composites were prepared using various starting materials for the second phase, BaCO_3 , uniform $\alpha\text{-Fe}_2\text{O}_3$, and amorphous precursor particles. The aspect ratio and the grain size of the in situ-formed BaM particles were controlled by adjusting the mixing ratio of the starting materials. This microstructure control procedure could be effective for improving the mechanical properties of structural ceramics.

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