Abnormal Grain Growth Mechanism of Calcium Hexaluminate Phase

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Abstract

Calcium-hexaluminate phase (CA_6) is known to be effective for the crack shielding due to the spinel block crystal structure. In this study, we focused to the control of CA_6 morphology for good damage tolerance behavior in alumina and zirconia/calcium-hexaluminate (CA_6) composites. Calcium-hexaluminate (CA_6) composites were prepared from zirconia, alumina and calcium carbornate powders. Calcium-hexaluminate (CA_6) phase was obtained by the solid reaction through the formation of intermediate phase (CA_2). CA_6 phase showed the column type abnormal grain grown behavior composed of small blocks. Due to the typical microstructure of CA_6, alumina and zirconia/calcium-hexaluminate composites provide a well controlled crack propagation behavior.

Keywords : Calcium-hexaluminate(CA_6), Abnormal Grain Growth, CA_6 composites

1. Introduction

Calcium hexaluminate(CA_6) is composed of spinel blocks and mirror planes stacked alternatively along the C-axis, and large alkali ions, such as Ca^{2+}, Nd^{2+}, Sr^{2+}, easily accommodated in the mirror plane known to be mechanically weak. Therefor this compound is expected to be used as good candidate material for a weak interface in the oxide laminate composites [1].

The morphology of CA_6 grains during the solid reaction sintering shows a plate like shape with preferential growth along their basal plane [2]. Also, such grain growth morphology can be observed in the abnomally grown alumina microstructure. Because most of abnormal grain growth was observed in the final growth stage, the origin of abnormal grain growth was the main concerns. However, Park et. al., reported that the abnormal grain growth was started from the nuclei formation composed of small grains [3]. After nuclei formation, abnormal grain growth will occur in the manner of typical abnormal grain shape, such as plate like shape or hexagonal shape.

In this study, we intend to observe the abnormal grain growth behavior of Ca-hexaluminate during the solid state reaction sintering of Al_2O_3/CA_6 and ZrO_2/CA_6 composites during the crack propagation.

2. Experimental and Results

Samples were prepared from commercial Al_2O_3 (AKP-50, <0.3μm average size, purity> 99.99%, Sumitomo Chemicals, Japan) and cubic-ZrO_2 (TZ-8Y, purity> 99.9%, Toyosoda, Japan) and cubic-$CaCO_3$ (purity>99.5%, Wako, Japan) powders. Ca-hexaluminate (CA_6) powder was prepared from the calcination of equimolar mixtures of Al_2O_3 and $CaCO_3$ at 1550°C for 2h in air. The proportioned powders were mixed by wet-milling using ZrO_2 balls as milling media for 6h. Raw powders were dried at 40 °C for 48h by dring oven. After drying, the powders were isostatically pressed under 200MPa, and then sintered at 1600°C for 2h in air. The sintered samples were polished to a 1m finish and thermally etched at 1400°C for 15min in air. The microstructure was observed using scanning electron microscopy (S-4700, Hitachi, Japan). Synthesis of Ca-hexaluminate was determined by XRD (MO3XHF, MAC Science, Japan) and Energy dispersive X-ray spectrometry (EDS, Horiba, Japan). Vicker's indentation (HM-124, Akashi, Japan) cracks were generated under a 10kg load on the polished surfacee of specimen to observe the crack propagation behavior.

Direct solid reaction of Ca hexaluminate phase was perfomed with the variation of reaction composition and reaction temperature, as shown in Fig. 1.

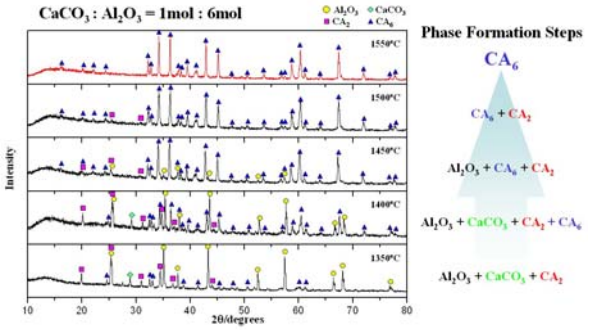

Fig. 1. X-ray diffraction patterns showing the phase formation steps of Ca-hexaluminate.

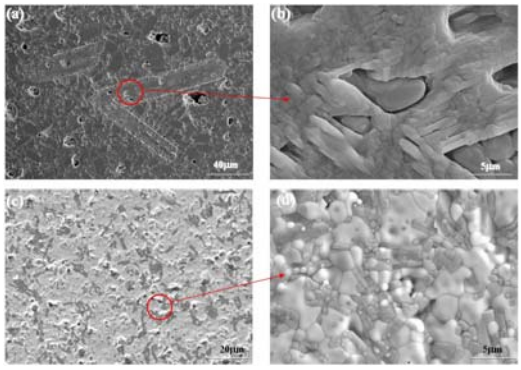

Fig. 2. Alumina and zirconia/Ca-hexaluminate Compo sites. ((a),(b) Al_2O_3- 20vol% CA_6, (c),(d) ZrO_2-20Vol% CA_6, specimen Sintered at 1600°C for 16h).

Fig. 2 shows a typical abnormal grain shape of CA_6 observed in alumina/CA_6 and zirconia/CA_6 composites. The difference in grain size and shape reflects the difference in grain growth between alumina and zirconia. Because of the fast diffusion rate of Ca^{2+} ions, a relatively high grain growth of alumina was observed due to the segregation of Ca^{2+} ions at the fast growth plane of alumina. Due to the solubility limit of alumina, excess Ca^{2+} ions located at the surface of alumina grain will provide an easy nucleation site of CA_6 phase. However, a relatively small grain size of zirconia and CA_6 was observed due to the low solubility of Ca^{2+} ions in zirconia compared to alumina. However, all of CA_6 grains were composed of small grains with preferential growth. This grain morphology of CA_6 will provide a clue for the abnormal growth steps such as nucleation and growth. This abnormal grain growth mode can be applied in the co-texturing of alumina and CA_6 phase as shown in fig. 3(a). Due to the different crystal structure, abnormal grain growth was not observed in zirconia with cubic crystal structure compared to alumina with hexagonal crystal structure. However, abnormal grain growth of CA_6 grain will be the same as shown in fig. 3. Fig. 4 shows the crack propagation behavior in Al_2O_3 and ZrO_2/20vol%CA_6 composites after Vickers indentation. Crack was deflected at the interface of alumina/Ca-hexaluminate and zirconia/ Ca-hexaluminate. Because the weak interface will be formed in the magnetoplumbite crystal structure such as Ca-hexaluminate, and then cracks will be easily deflected at the interface between alumina and Ca-hexaluminate [4]. Therefore, the enhancement of damage tolerance behavior is expected in Ca-hexaluminate dispersed oxide composites.

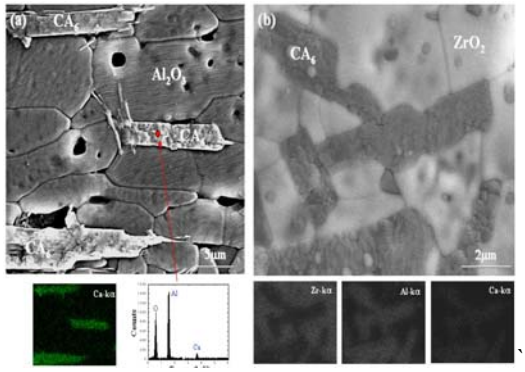

Fig. 3. EDS analysis of (a) alumina/CA_6 and (b) zirconia /CA_6 composites.

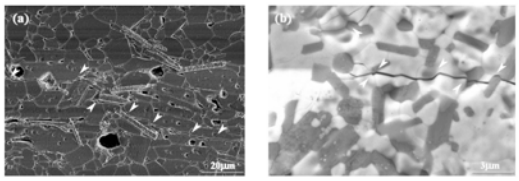

Fig. 4. SEM micrographs of crack deflection in (a) alumina/CA_6 and (b) zirconia/CA_6 composites specimen sintered at 1600°C for 2h.

3. Summary

In this study, the abnormal grain growth behavior of Ca-hexaluminate was observed during the sintering of Ca-hexaluminate composites based on alumina and zirconia. Abnormal grain growth behavior of Ca-hexaluminate showed a grain rearrangement with small grains during the phase formation reaction between alumina and Ca ions. Such grain growth mechanism was similar to the formation of abnormal nuclei before the abnormal grain growth in ceramic systems with hexagonal crystal lattice. Due to the magnetoplumbite crystal structure of Ca-hexaluminate, crack deflection behavior was observed at the interface of Ca-hexaluminate and oxide grains such as alumina amd zirconia.

4. References

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