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Fracture Behavior of Alumina-Titania-Monazite Composites

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ABSTRACT

Fracture behavior was investigated in the Al_2O_3-TiO_2(3 wt%)-$LaPO_4$(25 wt%) composite ceramics. To improve the fracture toughness of alumina ceramics, TiO_2 and $LaPO_4$ as a second phase were introduced. The samples were made by conventional powder processing method. Green compacts were sintered at 1600°C for 2 h in air. Fracture toughness was tested using Indentation Strength Bending(ISB) method. From the bending test, enhanced fracture toughness was found in the composite, compared to the pure and TiO_2-doped alumina. The main factor of the enhancement of fracture toughness seems to be attributed to the weak interphase role of the $LaPO_4$ as a particulate type.

Key words* : *Toughness, Fracture behavior, Alumina, Monazite

1. Introduction

Alumina is well known as a representative structural ceramics, because of its high hardness, high wear resistance, low friction coefficient, and high strength even at high temperature(~1500 - 1700°C). On the other hand, alumina has many detrimental properties such as low toughness, and large susceptibility to thermal and mechanical shock as an engineering application. Many researchers are thus focusing on overcoming these unfavorable properties in an engineering application. Especially, enhancing its low toughness has been extensively studied. Based on the linear fracture mechanics, toughness of a brittle material depends on the microstructure of the material. Conceptually, the fracture toughness of brittle ceramics can thus be improved by tailoring the microstructure.[1)]

Several toughening mechanisms in ceramics and ceramic composites are operating.[2-4)] These toughening mechanisms are depending on how crack paths are controlled by variant factors: (i) bulk toughness, (ii) grain boundary toughness, (iii) grain size, (iv) grain shape, (v) grain orientation, (vi) grain boundary energy, (vii) coefficient of friction between the grains, and (viii) the magnitude of the residual stress due to Thermal Expansion Anisotropy(TEA). In a brittle material, additional energy is required to propagate a crack by the above factors and thereby its toughness is enhanced.

Recently, $LaPO_4$(monazite) was known to improve the toughness of alumina ceramic composites. In placing monazite as an interphase between a reinforcement and alumina matrix, the monazite enhanced the toughness through an interfacial debonding. Monazite is thus considered as a new interphase that can replace current interphases of BN or carbon for oxide composites, because of the problems of high temperature oxidation and chemical stability.[5-9)]

TiO_2 is known as grain growth enhancer in alumina. Under a critical condition, anisotropic grains are produced by in-situ grain growth in TiO_2-doped alumina matrix and the anisotropic grains can be self-reinforcements to enhance the fracture toughness.[10)] Also, when the amount over the solubility limit at heat-treatment temperature is added to the alumina, aluminum titanate(Al_2TiO_5) is formed.[11)] The aluminum titanate has extremely anisotropic thermal expansion coefficient and its large mismatch with alumina.[3)] The increment of the toughness in alumina ceramics can therefore be expected due to the microstructural coarsening by TiO_2 and the residual stress caused by thermal expansion anisotropy or mismatch of the aluminum titanate, as described previously.

In this study, the effect of the addition of $LaPO_4$ and TiO_2 on the toughness of the alumina ceramics was thus investigated. In particular, the present work was focused on the toughening effect of $LaPO_4$ as a particulate type. To date, coated $LaPO_4$ on the reinforcement was mostly used as an interphase. From the bending test, the improvement in toughness of the Al_2O_3-TiO_2(3 wt%)-$LaPO_4$(25 wt%) composite was found, compared to the both pure and TiO_2 doped alumina. The Al_2O_3-TiO_2(3 wt%)-$LaPO_4$(25 wt%) composite may be thought of as a candidate material for an interlayer in ceramic hybrid laminates to improve K_{IC} without much degradation of strength, based on its microstructure and chemical compatibility of its constituents.

2. Experimental Procedure

To make an alumina-titania-monazite composite, conven-

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tional powder processing method was used. The powders for the composites were prepared by mixing high purity a-Al_2O_3 (AKP-50 Sumitomo Chemical Co. Ltd., Tokyo, Japan) adding a $LaPO_4$(25 wt%) and TiO_2(3 wt%: Merck, Germany) with an alcohol. The $LaPO_4$ was converted from a $LaPO_4 \cdot xH_2O$(Alfa Aesar, Ward Hill, MA01835) after calcination at 900°C for 2 h.

Approximately 4 g of the mixed powder was uniaxially pressed into rectangular bar under 0.5 MPa and then the bars were cold isostatically pressed under 200 MPa for 2 min. The powder compacts were sintered at 1600°C for 2 h in air. The heating and cooling rate was approximately 5°C/min, respectively. The sintered densities were measured using the Archimedes method with deionized water as the immersion medium. Sections of the samples were cut and polished to a 1 μm finish using standard ceramograhic techniques. The sections were thermally etched at 1500°C for 30 min in air, gold coated and examined by SEM. The identification of developed phases was made through the analysis of XRD patterns or EDS analysis.

To control flaw sizes on the polished surface of the specimens, a Vickers diamond indenter was used at 5 kg load. The flexural strength was determined by three-point bending method. Test bars with dimension of 2.0 × 1.5 × 25 mm were polished to 1 μm diamond slurry and long edges chamfered. Then, the bars were annealed at 1200°C for 30 min to remove machining stresses. Instantly after indentation, a drop of silicone oil was placed on the indentation to minimize environmentally assisted subcritical crack growth before strength test. Flexural strength measurement was carried out by universal test machine(Hounsfield, H10KS) with 20 mm span at room temperature. The crosshead speed was 5 mm/min. As a crack configuration, center crack on the sample was used. All the data of the strength were obtained from the samples with failure originated from the indentation.

Fracture toughness, K_{IC}, was calculated using the following equation:

$$K_{IC} = \xi (E/H)^{1/8} (\sigma_f P^{1/3})^{3/4} \quad (1)$$

where ξ is the geometrical constant of 0.59[1)]; E is Young's modulus; H hardness; σ_f fracture strength, and P the indentation load. For this calculation, we used $E_{alumina} = 400$ GPa,[7)] $E_{monazite} = 133$ GPa,[7)] $E_{titania} = 282$ GPa,[12)] $E_{composite} = 397$ GPa for Al_2O_3-TiO_2(A-T) composite, and $E_{composite} = 340$ GPa for Al_2O_3-TiO_2-$LaPO_4$(A-T-L) composite. For simplicity, the Young's modulus of these composites was estimated by the rule of mixture, because we are not concerned about the exact toughness value but relative comparison between pure and composite samples.

3. Results and Discussion

3.1. Microstructure

For monazite as an interphase to give damage tolerance to an oxide composite, the chemical stability between oxide and monazite is required. According to the previous researches,[5-9)] stoichiometric monazite is stable with alumina. As seen in Fig. 1, Al_2O_3, TiO_2, Al_2TiO_5, and $LaPO_4$ phases were observed from the three different samples through XRD analysis. Here, Al_2O_3, TiO_2, and $LaPO_4$ are starting materials and Al_2TiO_5 was formed by the reaction between excess TiO_2 above its solubility limit and Al_2O_3. In this study, much amount of TiO_2(3 wt%) above its solubility limit[13)] at 1600°C was added into alumina matrix. There seemed, therefore, to be no reactions between alumina and monazite as well as titania and monazite, as shown in Fig. 1(a). The result agrees well with the previous results.[5-9)] The result is also supported by the microstructure as is shown in Fig. 2.

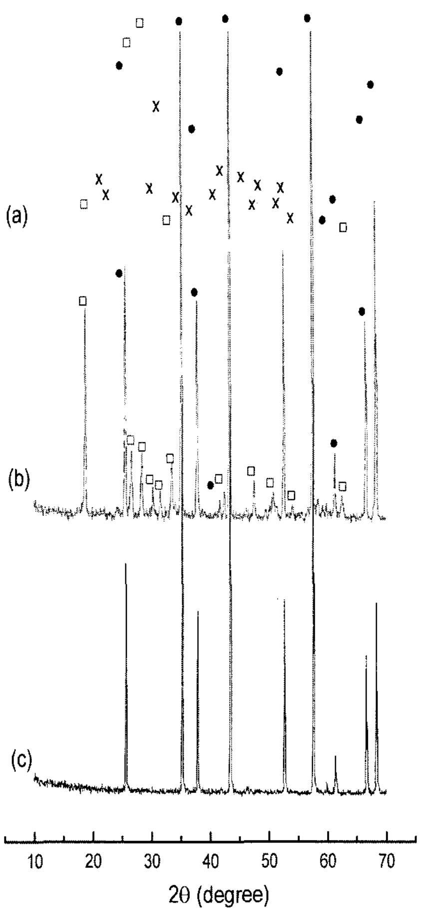
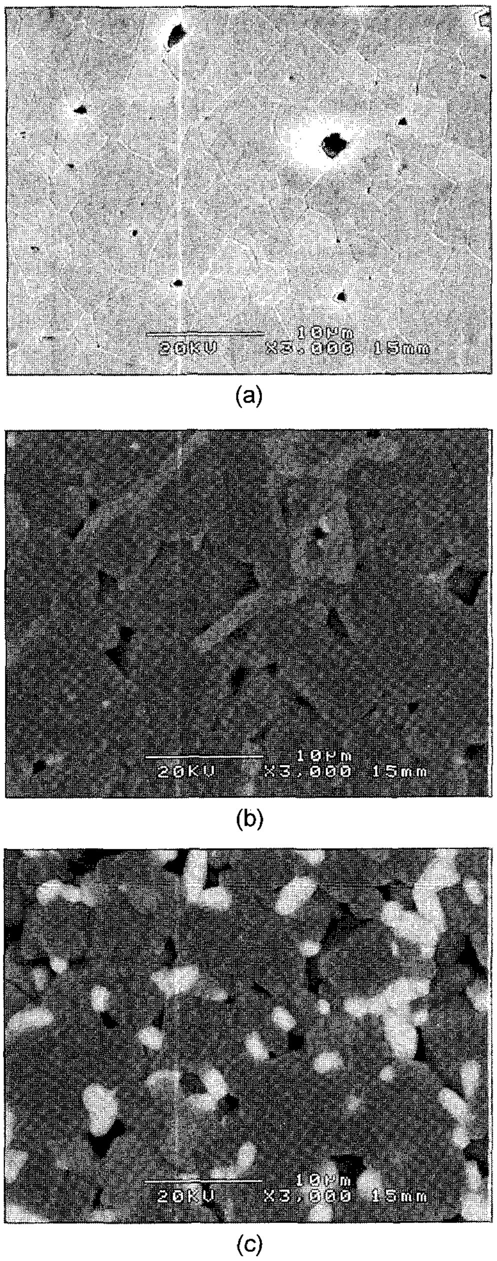


Fig. 1. XRD patterns obtained from (a) Al_2O_3-TiO_2(3 wt%)-$LaPO_4$(25 wt%) sample, (b) Al_2O_3-TiO_2(3 wt%) sample, and (c) pure alumina. ●: Al_2O_3; □: Al_2TiO_5; ×: $LaPO_4$. TiO_2 peaks cannot be distinctly discerned, because of their low intensities.

TiO_2 played a role of grain growth enhancer with increasing grain size of the alumina by the addition of TiO_2 into the alumina matrix(Fig. 2(a)), as shown in Fig. 2(b). But anisotropic alumina grains were not found. Aluminum titanate was formed due to the reaction of the excess titania over its solubility limit with the alumina matrix. Very small amount of unreacted titania particle was also found. The



(a)

(b)

(c)

Fig. 2. SEM microstructures of (a) pure alumina using secondary electrons, (b) Al_2O_3-TiO_2(3 wt%) sample using backscattered electrons(grayish phase with rod shape is aluminum titanate and white phase with particulate type is unreacted titania), and (c) Al_2O_3-TiO_2(3 wt%)-$LaPO_4$(25 wt%) sample using backscattered electrons(grayish phase with rectangular shape is aluminum titanate and white phase is monazite).

Table 1. Fracture Toughness(T), Strength(σ_f), and Density(ρ) Data of Test Materials

	T (MPa · $m^{1/2}$)	σ_f (MPa)	ρ (g/cm^3) [%theoretical]
A	2.52(±0.1)	107(±5)	3.88 [97%]
A-T	2.50(±0.3)	102(±15)	3.88 [≥97%]
A-T-L	2.72(±0.1)	104(±7)	3.79 [≥90%]

results were supported by the XRD or EDS analysis. Some aluminum titanates kept a shape of rod. Additional self-reinforcing effect by the aluminum titanates, therefore, may be expected, based on the linear fracture mechanics.

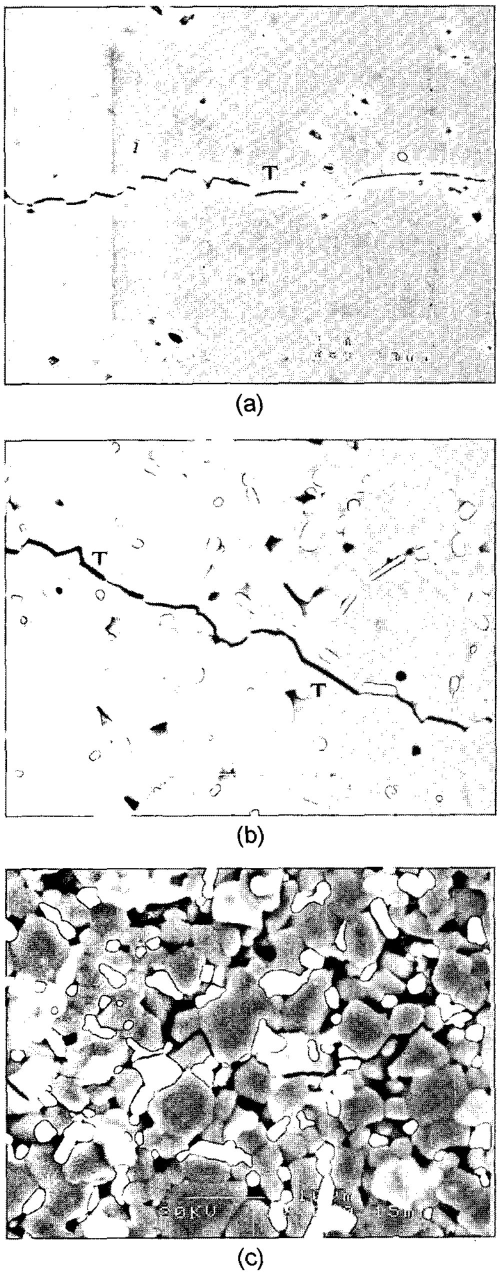
On the other hand, $LaPO_4$ seemed to suppress the grain growth of alumina grains, as seen in Fig. 2(c). In Fig. 2(c), white phase is $LaPO_4$, because of high elemental contrast of backscattered image. The rectangle or rod-shaped grains with grayish color are aluminum titanates. Compared with the microstructure in Fig. 2(b), alumina grain size decreased and aluminum titanate grains with the rod shape were not found. The shape change of aluminum titanate is interesting, but the reason is not well explained by the present study. The compatibility of the alumina/monazite and the aluminum titanate/monazite was also kept well, because there are no reactions at heat-treatment temperature, based on the XRD analysis. The results are well consistent with the previous investigations[5-9] on the stability of alumina/monazite or titania/monazite.

3.2. Fracture Toughness

The effect of the microstructural change on the fracture toughness was measured from the three point bending method, as shown in Table 1. The relative densities of the test samples were ~97% for both the pure and TiO_2-doped alumina, and ~90% for the Al_2O_3-TiO_2-$LaPO_4$ sample. The respective theoretical densities(except for the pure alumina) were theoretically calculated using the rule of mixture. For simplicity, the amount of Al_2TiO_5 was neglected. If the volume of Al_2TiO_5 is considered, the relative densities will be higher than the present values, because the theoretical density of Al_2TiO_5(ρ_{th} = 3.10 g/cm^3) is lower than that of Al_2O_3 (ρ_{th} = 3.98 g/cm^3).

In general, fracture toughness is enhanced at the cost of strength, based on the linear fracture mechanics. In the case of TiO_2-doped alumina (A-T) sample, the toughness value is the nearly same as that of the pure alumina, despite the decreased strength. Increasing grain size, the rod-shaped aluminum titanate, and the internal residual stresses derived from thermal expansion anisotropy of the aluminum titanate and its mismatch with alumina were expected to improve the toughness of alumina, as mentioned earlier. In view of the present result, the above factors, however, gave no significant effect on the toughness of the alumina.

According to the previous research,[14] the amount of anisotropic grains needed to increase fracture toughness is more than 10 vol% for rod-shaped grains. It is thus believed that the amount of aluminum titanate would be below the critical value needed to impart improved toughness to the alumina. Because of the small amount of aluminum titanate, therefore, microcrack density caused by the internal stress derived from the aluminum titanate would be low and thereby the aluminum titanate would be ineffective in improving the toughness. The strength decrement due to the formation of aluminum titanates could also be explained by the microcracking caused by the residual stress. That is why the thermal expansion anisotropy or mismatch might improve thermal shock resistance but the microcrack caused by these would be a failure origin to decrease the strength of the composite.[1] Grain size increment also seems not to be enough to induce crack deflection or crack bridging for toughness enhancement.



(a)

(b)

(c)

Fig. 3. SEM microstructures showing crack propagations in (a) pure sample, (b) Al_2O_3-TiO_2(3 wt%) sample, and (c) Al_2O_3-TiO_2(3 wt%)-$LaPO_4$(25 wt%) sample.

In case of Al_2O_3-TiO_2-$LaPO_4$(A-T-L) composite, fracture toughness increased without much decrement of its strength, despite the porosity increment(Table 1). Compared with the result in A-T composite, $LaPO_4$ seemed to make a great contribution to the toughness enhancement of A-T-L composite. As described previously, $LaPO_4$ inhibited the grain growth of alumina and controlled the shape of the aluminum titanate grains. In addition, $LaPO_4$ played a role of weak interphase(second phase) to prevent crack propagation into alumina matrix, as seen in Fig. 3. Among these facts, the role as a weak interphase seems to be dominant in the toughness enhancement in terms of crack paths.

Fig. 3 shows crack paths of the three samples at 5 kg indentation load. In case of pure sample, fracture was occurred through intergranular or transgranular mode (indicated by "T" on the microstructure). In case of A-T sample, fracture mode was also produced through intergranular or transgranular mode(indicated by "T" on the microstructure), even though aluminum titanates, existing at grain boundaries, induced useful crack deflections for toughness enhancement. The reason seems to be why the amount of the aluminum titanate is under the effective value needed to affect the fracture mode change. The two samples, thus, have the nearly same fracture mode, as shown in Fig. 3(a) and (b). The investigation is supported by the measured toughness value in Table 1. In case of A-T-L composite, fracture was occurred through somewhat different mode from that in both pure and A-T sample. Seeing that crack went through $LaPO_4$ particles, $LaPO_4$ acted as crack absorber, as shown in Fig. 3(c). It is thus thought that improvement in toughness by the addition of a weak interphase, i.e. weak second phase of particulate type can be expected.

4. Conclusions

To improve the fracture toughness of alumina ceramics, its microstructure was controlled by the addition of TiO_2 and $LaPO_4$. In case of A-T sample, the effects of increasing grain size by TiO_2 and TEA of Al_2TiO_5, formed by the reaction of Al_2O_3 with the excess TiO_2 over the solubility limit at heat-treatment temperature, were used for the toughness enhancement. The toughness enhancement, however, was not found in spite of strength degradation. In case of A-T-L sample, the $LaPO_4$ suppressed the grain growth of alumina and changed the rod shape of aluminum titanate grains into the rectangular type as well. According to the investigation of crack paths, the weak interphase of $LaPO_4$ prevented crack propagation into alumina matrix. The crack propagation behavior, thus, seems to be responsible for the improvement in toughness of A-T-L composites.

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