

Effect of Tetragonal ZrO₂ Addition on the Mechanical Properties of α -Alumina/La- β -Aluminate Composite

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정방정 ZrO₂의 첨가가 α -Alumina/La- β -Aluminate 복합체의 기계적 성질에 미치는 영향

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ABSTRACT

Alumina composite was fabricated by introducing tetragonal ZrO₂ in alumina composite of α -alumina reinforced with in-situ formed La- β -aluminate (LaAl₁₁O₁₈). The powder mixture of composition (100-x)[88 Al₂O₃ + (La₂O₃ + 11 Al₂O₃)] + x vol% ZrO₂ was prepared with x from 0 to 40. Dense composites fabricated by hot-pressing exhibited bending strength up to 1200 MPa. The grain growth inhibiting effect of ZrO₂ grains and La- β -aluminate platelets, and possibly the stress-induced phase transformation of ZrO₂ have resulted in the high bending strength. The fracture toughness of the composite also increased up to 8.5 MPa·m^{1/2}. The enhancement in toughness can be explained by transformation and microcrack toughening of ZrO₂ and by crack deflection and bridging of La- β -aluminate platelets and ZrO₂.

요 약

In-situ 반응에 의하여 형성된 La- β -aluminate(LaAl₁₁O₁₈)로 강화된 알루미나 복합체에 정방정 ZrO₂를 첨가하여 알루미나 복합체를 제조하였다. 사용된 분말 혼합체의 조성은 (100-x)[88 Al₂O₃ + (La₂O₃ + 11 Al₂O₃)] + x vol% ZrO₂이었으며, x는 0부터 40까지 변화시켰다. 열간가압성형에 의하여 얻어진 치밀한 소결체는 1200 MPa의 곡강도값을 나타내었다. 이러한 높은 곡강도값은 첨가한 ZrO₂ 입자와 기존의 La- β -aluminate platelet의 지지 입자에 대한 입성장 억제 효과와 ZrO₂의 응력유기 상변태 효과로부터 기인하였다. 상기 복합체의 파괴 인성도 역시 8.5 MPa·m^{1/2}까지 증가하였는데, 이러한 파괴인성의 증가는 ZrO₂의 상변태 강화와 미세균열 강화, 그리고 La- β -aluminate와 ZrO₂ 입자의 균열 deflection과 bridging의 효과로 설명되어질 수 있다.

1. Introduction

Alumina is one of the most important technical ceramics and has been used in various fields due to its attractive properties such as high melting point, high hardness, excellent high-temperature stability, and high wear-resistance. However, it has also critical disadvantage of brittleness under mechanical and/or thermal

stress resulting from its low fracture toughness. For wider applications of alumina ceramics, therefore, the high strength and toughness are required.

To increase the strength and the toughness of alumina ceramics, many researches have been performed by reinforcing the fibers or whiskers. However, there are many problems such as controlling interfacial properties between fibers or whiskers and matrix, difficul-

ties in homogeneous mixing, and full densification. One of the solutions to such problems may be the in-situ formation of a compatible reinforcing second phase in the matrix. For example, Kim et al.¹⁾ introduced alumina ceramics reinforced with β''' -alumina ($\text{NaMg}_2\text{Al}_7\text{O}_{25}$) formed through in-situ reaction sintering. The alumina reinforced with β''' -alumina sintered to near theoretical density, showing bending strength to 600 MPa and fracture toughness to $5 \text{ MPa}\cdot\text{m}^{1/2}$. Kang et al.²⁾ also reported an alumina matrix composite reinforced with in-situ formed La- β -aluminate ($\text{LaAl}_{11}\text{O}_{18}$). La- β -aluminate is one of the rare earth aluminates and thermally more stable than other plate-shaped aluminate compounds having β -alumina structure³⁾. The α -alumina/La- β -aluminate composite sintered to near theoretical density and showed bending strength of up to 700 MPa and fracture toughness of $3.3 \text{ MPa}\cdot\text{m}^{1/2}$. Chen et al.⁴⁾ researched in-situ alumina/aluminate platelets composites which are similar to Kang et al.'s to some extent and reported that toughness was increased by in-situ formation of aluminate platelets. The in-situ composites mentioned above still have the disadvantage; the intrinsically low cohesive strength of the layer-like aluminates limits the maximum toughness derivable from their reinforcement⁴⁾. However, the strength increases remarkably because the grain growth is inhibited by the presence of reinforcements in the matrix^{1,2)}.

The aim of the present work is to increase the fracture toughness of alumina ceramics reinforced with La- β -aluminate platelets while maintaining the favorable strength. Tetragonal ZrO_2 , which is well known to show the transformation and microcrack toughening phenomena, was introduced in alumina ceramics reinforced with La- β -aluminate platelets. The effect of ZrO_2 addition on the mechanical properties and the microstructures has been investigated.

2. Experimental Procedure

2.1. Starting Materials

Commercially available high purity (99.99%) Al_2O_3 powder (AKP-30, Sumitomo Chemical, Japan), $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (No. 5220, Unocal Molycorp., U.S.A.) and spray-dried ZrO_2 powder stabilized with 2 mol% Y_2O_3 (TZ-2Y, Tosoh Corp., Japan) were used in this work. The mean particle sizes of Al_2O_3 and ZrO_2 powder reported by

the suppliers are $0.3\sim 0.4 \mu\text{m}$ and $0.3 \mu\text{m}$, respectively. $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ was used as La_2O_3 source for the purpose of the homogeneous mixing between La_2O_3 and Al_2O_3 , resulting in the promotion of uniform in-situ reaction in the whole specimen.

2.2. Sample Preparation and Testing Procedure

Al_2O_3 and ZrO_2 powders were suspended in distilled water and adjusted to pH 2.5 by using the diluted 5 N- HNO_3 to achieve a more stable suspension⁵⁾. The above suspension was ball-milled with high purity alumina ball and jar for 16 h and readjusted to pH 2.5. An aqueous solution of $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ was added in order to make the slurry with the composition of $(100-x)[88 \text{ Al}_2\text{O}_3 + (\text{La}_2\text{O}_3 + 11 \text{ Al}_2\text{O}_3)] + x \text{ vol}\% \text{ ZrO}_2$ (x varied from 0 to 40). The slurry was dried on a hot plate while stirring and calcined in air at 600°C for 12 h. The calcined powder was gently ground in alumina mortar and hot-pressed using a graphite die at 1500°C , 1550°C , 1600°C , and 1650°C for 0.5, 1, and 3 h under 30 MPa in Ar atmosphere.

Densities of the specimens were determined by the Archimedes principle. Microstructures were investigated using scanning electron microscopy (JSM 35-CF, Jeol, Japan) after polishing and thermal etching at 1450°C for 30 min in air. From the microstructures of the specimens the average grain sizes of Al_2O_3 and ZrO_2 grains were measured by linear intercept method⁶⁾. For bending strength measurements, the hot-pressed tablets were cut into $3\times 4\times 25 \text{ mm}$ bars, ground and polished with $1 \mu\text{m}$ diamond paste. 3-point bending strength was determined using universal testing machine (Instron, U.S.A.) with a span of 18 mm at crosshead speed of 0.5 mm/min and at least 6 measurements were made for one condition. Fracture toughness was measured by Vickers indentation method⁷⁾ with 10 kg load and at least 20 measurements were made for one sample. To examine the extent of the stress-induced phase transformation of ZrO_2 before and after the fracture test, quantitative analysis was performed by X-ray Diffractometer (D/MAX-3C, Rigaku, Japan). Volume percents of the tetragonal and monoclinic ZrO_2 phase were calculated using Toraya et al.'s equation⁸⁾.

3. Results and Discussion

There are two compounds which are normally form-

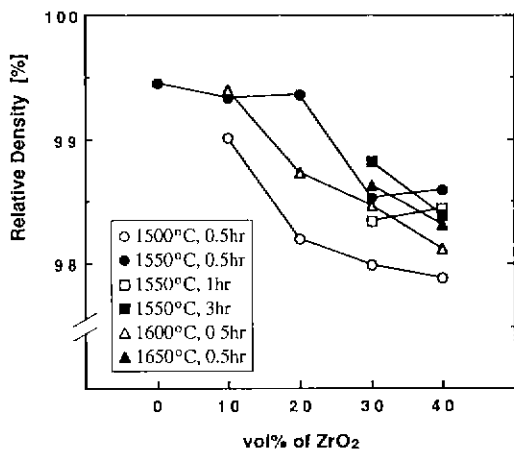


Fig. 1. Density versus volume percent of ZrO₂ hot-pressed under 30 MPa in Ar atmosphere.

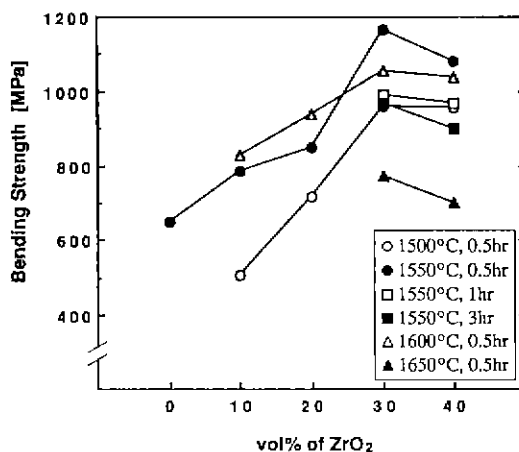


Fig. 2. Bending Strength versus volume percent of ZrO₂ hot-pressed under 30 MPa in Ar atmosphere.

ed in Al₂O₃-La₂O₃ system: LaAlO₃, a cubic perovskite⁹, and LaAl₁₁O₁₈, a hexagonal compound with the β -alumina structure⁹. LaAlO₃ is an intermediate phase formed around 800°C¹⁰ and as temperature increases to 1400°C, it reacts with Al₂O₃ to give LaAl₁₁O₁₈. The formation of LaAl₁₁O₁₈ is nearly completed at about 1600°C².

The change in relative densities of the hot-pressed specimens with different hot-pressing conditions and volume percent of added ZrO₂ is shown in Fig. 1. In each composition, the theoretical density of the composite was estimated with respect to the phase fractions of Al₂O₃, La- β -aluminate, and tetragonal ZrO₂. According to the JCPDS card (No. 33-699), LaAl₁₁O₁₈ has a hexagonal structure with lattice constants of $a=b=5.561$ Å and $c=22.041$ Å. If the chemical formula and lattice constants are correct^{11,12}, the theoretical density of LaAl₁₁O₁₈ can be calculated as 4.071 g/cm³. In the calculation of theoretical density of the composite, volume percent of monoclinic and tetragonal ZrO₂ were considered (refer to Fig. 6). In Fig. 1, the densities of all specimens are above 98% of the theoretical density and show the tendency to decrease with increasing volume percent of ZrO₂. Larger amounts of ZrO₂ inclusions may hinder the densification behavior of alumina matrix which results in lower relative density. In another viewpoint, ZrO₂ particles may form agglomerates due to difficulties in homogeneous mixing and efficient ball-milling as the volume percent of ZrO₂ increases¹³⁻¹⁶. Hot-pressing over 1600°C did not lead to

higher relative density and this seems to be due to the pore isolation and/or pore growth resulting from oversintering and abnormal grain growth.

Bending strength of the hot-pressed specimens is shown in Fig. 2. As the volume percent of ZrO₂ increases, bending strength increases remarkably up to 30 vol%, beyond which it decreases slightly. The highest value obtained was 1200 MPa when 30 vol% of ZrO₂ was added, which is almost twice that of α -alumina/La- β -aluminate composite. Bending strength increases up to 30 vol% ZrO₂ although the relative densities decrease with increasing amount of ZrO₂ addition. Higher bending strength was obtained from the specimens hot-pressed at 1550°C and 1600°C than the specimens hot-pressed at 1500°C and 1650°C. It seems that the specimens hot-pressed at 1500°C have lower bending strength due to the relatively low densities as shown in Fig. 1. The lower bending strength of the specimens hot-pressed at 1650°C seems to be resulted from the excessive grain growth of matrix Al₂O₃ grains due to the relatively higher temperature than normal sintering temperature. The holding time during hot-pressing at 1550°C might influence bending strength due to the different grain size. In Fig. 2, as holding time increases, bending strength decreases. The specimen hot-pressed for 0.5 h shows the highest bending strength in this experiment.

Fig. 3 shows the microstructural development with increasing volume percent of ZrO₂ in the specimens

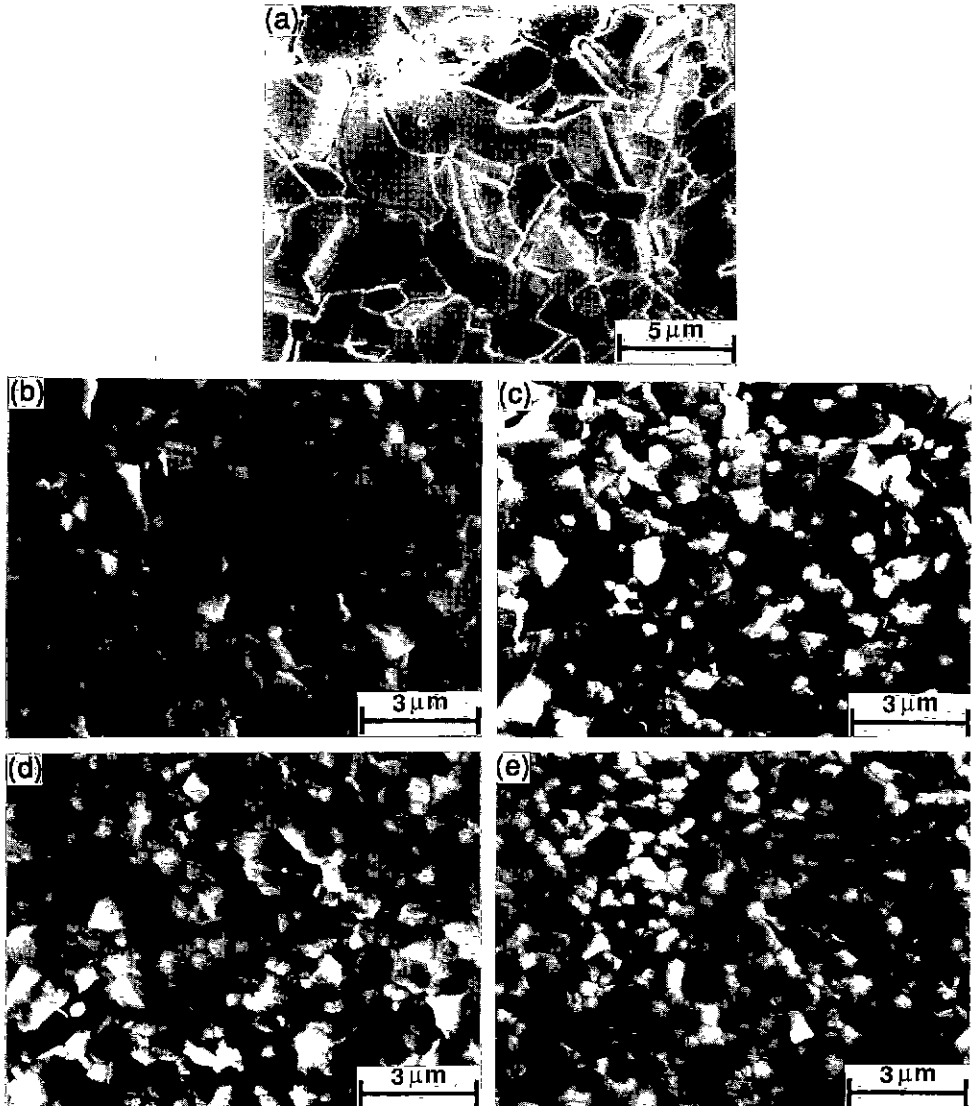


Fig. 3. Microstructures of α -alumina/La- β -aluminate (a) and α -alumina/La- β -aluminate/ZrO₂ hot-pressed at 1550°C for 0.5 hour under 30 MPa in Ar atmosphere (b), (c), (d), (e).

hot-pressed at 1550°C for 0.5 h under 30 MPa in Ar atmosphere. In 10~20 vol% region (Fig. 3(b) and (c)), ZrO₂ grains appearing as bright color are distributed intergranularly and intragranularly in the matrix of Al₂O₃ grains. In 30~40 vol% region (Fig. 3(d) and (e)), ZrO₂ grains grow larger and most of them are distributed intergranularly. Especially, the size of matrix Al₂O₃ grains decreased remarkably with increasing volume percent of ZrO₂. The micrograph of the α -alumina/La- β -aluminate composite is shown for comparison

(Fig. 3(a)). The size of ZrO₂ grains increased gradually as the amount of ZrO₂ increased. Fig. 4 is the quantitative data of the size measurements of Al₂O₃ and ZrO₂ grains in the same specimens shown in Fig. 3. Fig. 3 and Fig. 4 indicate that the most pronounced effect of the addition of ZrO₂ in α -alumina/La- β -aluminate composite is the grain growth inhibition of the matrix. Namely, the addition of ZrO₂ in α -alumina/La- β -aluminate matrix inhibits grain growth of matrix Al₂O₃ grains effectively. Therefore, this may be the reason why the

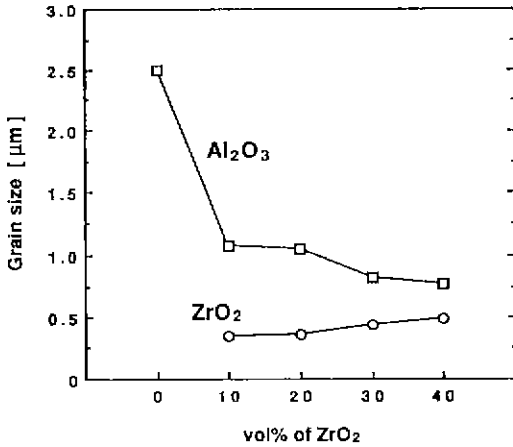


Fig. 4. Grain size variation in the specimens hot-pressed at 1550°C for 0.5 hour under 30 MPa in Ar atmosphere.

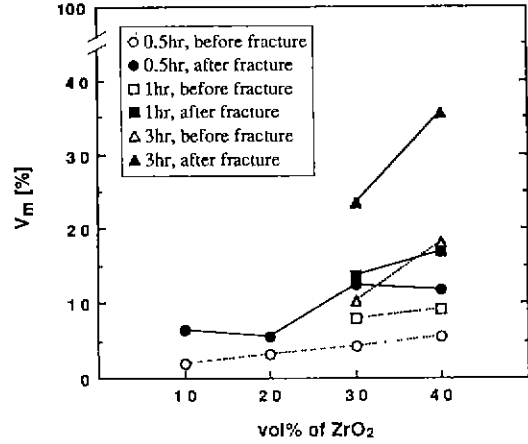


Fig. 6. Volume percent of monoclinic ZrO₂ phase in the specimens hot-pressed at 1550°C under 30 MPa in Ar atmosphere before and after the fracture occurs.

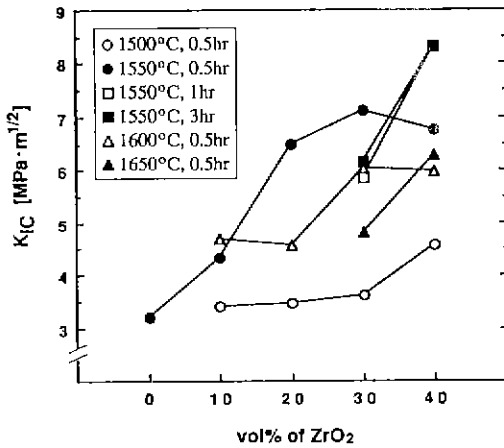


Fig. 5. Fracture toughness versus volume percent of ZrO₂ hot-pressed under 30 MPa in Ar atmosphere.

excellent strengthening effect occurs in α -alumina/La- β -aluminate/ZrO₂ system.

Fracture toughness of the specimens is shown in Fig. 5. The maximum fracture toughness, 8.5 MPa·m^{1/2}, was obtained in the specimen containing 40 vol% ZrO₂ which was hot-pressed at 1550°C for 3 h under 30 MPa in Ar atmosphere. This value is about three times higher than that of monolithic alumina or α -alumina/La- β -aluminate composite. The fracture toughness of the specimens increased gradually with ZrO₂ content. In order to examine the extent of the stress-induced

phase transformation of ZrO₂ which seems to contribute to the increase in fracture toughness, the volume percent of monoclinic and tetragonal ZrO₂ phases were analyzed. Fig. 6 shows the measured volume percent of monoclinic ZrO₂ phase in the specimens hot-pressed at 1550°C with various hot-pressing times before and after the fracture test. In Fig. 6, blank and filled symbols represent the data of the specimens before and after the fracture occurs, respectively. While most of the ZrO₂ grains were retained as tetragonal phase before the fracture occurred, some portion of the ZrO₂ grains was transformed from tetragonal to monoclinic phase after the fracture occurred. Besides, the higher the volume percent of added ZrO₂, the larger the extent of ZrO₂ grains transformed. Therefore, the enhancement in fracture toughness in Fig. 5 seems to be due to this transformation toughening of ZrO₂. ZrO₂ grains which exist at grain boundaries in the matrix as tetragonal phase will undergo the stress-induced phase transformation to monoclinic phase, absorbing the energy of the external stress. Besides, this stress-induced phase transformation seems to contribute to the increase in bending strength as well as fracture toughness by means of the energy absorption^{14,16,17,19}.

The specimens containing 30 vol% and 40 vol% of ZrO₂ show considerable amounts of transformed monoclinic ZrO₂ even before the fracture test. The microcracks might be produced by this spontaneous transfor-

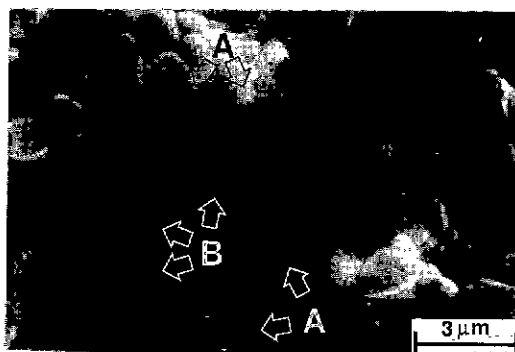


Fig. 7. Microstructure of α -alumina/La- β -aluminate/ ZrO_2 showing intergranular (A) and intragranular (B) particles.

mation. These microcracks will possibly contribute to the toughening of the composite by means of deflecting and/or branching the propagating crack^{13,18}. Therefore, fracture toughness seems to increase gradually with increasing volume percent of ZrO_2 (Fig. 5) due to the stress-induced phase transformation and the microcrack toughening phenomena. In this viewpoint of microcracking, the slight decrease in bending strength (Fig. 2) in case of 40 vol% addition of ZrO_2 seems to

be due to the defect formation around spontaneously-transformed monoclinic ZrO_2 grains.

Fig. 6 also suggests that the volume percent of monoclinic phase after the fracture test is not considerable (below 40%), which seems to be due to the relatively small portion of effective transformable tetragonal ZrO_2 phase. This might be due to the existence of many intragranular ZrO_2 grains (B in Fig. 7) which are less sensitive to the transformation than intergranular ones (A in Fig. 7) located at the grain boundaries or triple junctions^{16,19}.

Fig. 8 shows the mode of crack propagation after Vickers indentation. The crack front is deflected along ZrO_2 grains (a) and La- β -aluminate platelets (b and c), resulting in longer crack path. As shown in Fig. 8 (c) and (d), the crack stops propagating and a newly created crack begins to propagate from other position, which is known as the crack bridging phenomena²⁰. La- β -aluminate platelets and/or ZrO_2 grains will relieve effectively the stress concentration at a crack tip and consequently the crack seems to stop propagating. If the stress applied from the process zone of the crack exceeds a certain limit, a new crack will be created in other position which will undergo the same bridging

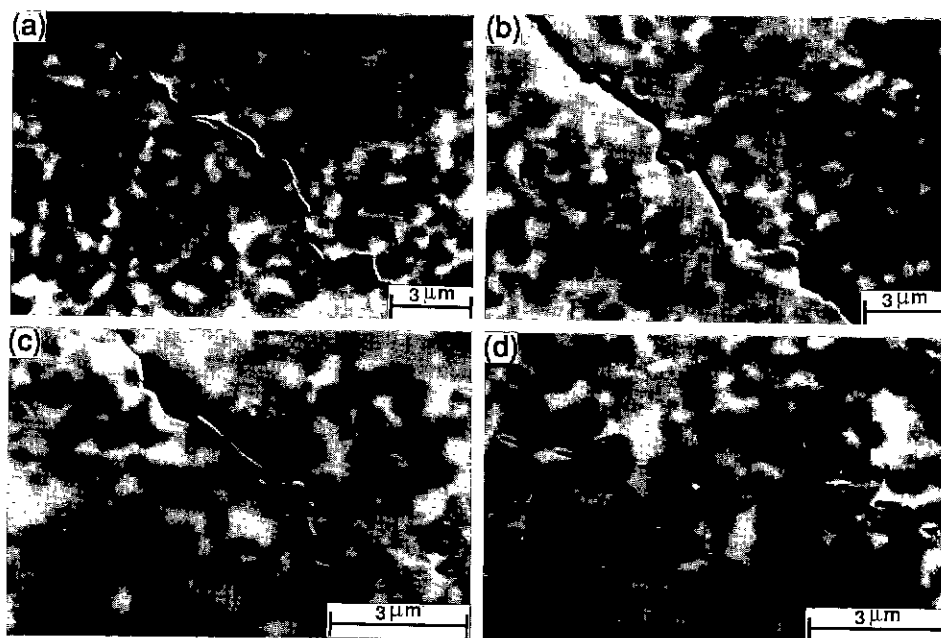


Fig. 8. Microstructures of α -alumina/La- β -aluminate/ ZrO_2 showing crack deflection (a), (b) and crack bridging (c), (d).

process repeatedly. This crack bridging phenomena may result in the enhancement of fracture toughness effectively.

4. Conclusions

By introducing the ZrO₂ particles in α -alumina/La- β -aluminate composite, the bending strength and the fracture toughness of the composite increased remarkably. Bending strength increased up to 30 vol% of ZrO₂, beyond which it decreased slightly. The maximum value obtained was 1200 MPa which is twice that of α -alumina/La- β -aluminate composite. This strengthening of α -alumina/La- β -aluminate/ZrO₂ composite was due to the grain growth inhibiting effect of ZrO₂ grains and La- β -aluminate platelets as well as due to the stress-induced phase transformation of ZrO₂. Fracture toughness showed maximum value of 8.5 MPa·m^{1/2} with 40 vol% of ZrO₂ addition, which is about three times that of monolithic alumina or α -alumina/La- β -aluminate composite. The enhancement in fracture toughness is thought to be due to the transformation toughening as well as the microcrack toughening. The crack deflection and bridging mechanisms of La- β -aluminate platelets and ZrO₂ grains might also influence the enhancement in fracture toughness.

REFERENCES

1. H.D. Kim, S.Y. Lee, J.W. Ko, and H.W. Kang, "Production of Alumina Ceramics Reinforced with β'' -Alumina," U.S. Pat. No. 5081082, January 14, 1992.
2. S.W. Kang, J.W. Ko, and H.D. Kim, "Formation of La- β -Aluminate in α -Alumina Matrix and Its Influence on Mechanical Properties," *J. Korean Ceram. Soc.*, **29** (1), 23-28 (1992)
3. R.S. Roth and S. Hasko, "Beta-Alumina-Type Structure in the System Lanthana-Alumina," *J. Am. Ceram. Soc.*, **41**(4), 146 (1958).
4. P.L. Chen and I.W. Chen, "In-Situ Alumina/Aluminate Platelet Composites," *J. Am. Ceram. Soc.*, **75**(9), 2610-2612 (1992).
5. I.A. Aksay, F.F. Lange, and B.I. Davis, "Uniformity of Al₂O₃-ZrO₂ Composites by Colloidal Filtration," *J. Am. Ceram. Soc.*, **66**(10), c190-c192 (1983).
6. E.E. Underwood, "Quantitative Stereology", Addison-Wesley Publishing Company, 1970.
7. B.R. Lawn and E.R. Fuller, "Equilibrium Penny-Like Cracks in Indentation Fracture," *J. Mater. Sci.*, **10**, 2016-2024 (1975).
8. H. Toraya, M. Yoshimura, and S. Somiya, "Calibration Curve for Quantitative Analysis of the Monoclinic-Tetragonal ZrO₂ System by X-Ray Diffraction," *J. Am. Ceram. Soc.*, **67**(6), c119-c121 (1984).
9. I.A. Bondar; pp. 327-336 in Proceedings of the Seventh Conference on the Silicate Industry, Budapest, June 1963. Edited by Ferenc Tamas. Hungarian Academy of Sciences, Budapest, 1965.
10. R.C. Ropp and B. Carroll, "Solid-State Kinetics of La-Al₁₁O₁₈," *J. Am. Ceram. Soc.*, **63**(7-8), 416-419 (1980).
11. R.C. Ropp and G.G. Libowitz, "The Nature of the Alumina-Rich Phase in the System La₂O₃-Al₂O₃," *J. Am. Ceram. Soc.*, **62**(11-12), 473-475 (1978).
12. M. Gasperin, M.C. Saine, A. Kahn, F. Laville, and A.M. Lejus, "Influence of M²⁺ Ions Substitution on the Structure of Lanthanum Hexaaluminates with Magnetoplumbite Structure," *J. Solid State Chem.*, **54**, 61-69 (1984).
13. N. Claussen, J. Steeb, and R.F. Pabst, "Effect of Induced Microcracking on the Fracture Toughness of Ceramics," *Am. Ceram. Soc. Bull.*, **56**(6), 559-562 (1977).
14. F.J. Esper, K.H. Friese, and H. Geiger. "Mechanical, Thermal and Electrical Properties in the System of Stabilized ZrO₂ (Y₂O₃)/ α -Al₂O₃," pp. 528-536 in Advances in Ceramics, Vol. 12, Science and Technology of Zirconia II. Edited by N. Claussen, M. Ruhle, and A.H. Heuer. American Ceramic Society, Columbus, OH, 1984.
15. F.F. Lange, B.I. Davis, and I.A. Aksay, "Processing-Related Fracture Origins: III, Differential Sintering of ZrO₂ Agglomerates in Al₂O₃/ZrO₂ Composite," *J. Am. Ceram. Soc.*, **66**(6), 407-408 (1983).
16. T.S. Yen and J.K. Guo, "The Role of ZrO₂ in TZP and ZTA": pp. 573-582 in Advances in Ceramics, Vol. 24, Science and Technology of Zirconia III. Edited by S. Somiya, N. Yamamoto, and H. Hanagida. American Ceramic Society, Westerville, OH, 1988.
17. S. Hori, M. Yoshimura, and S. Somiya, "Strength-Toughness Relations in Sintered and Isostatically Hot-Pressed ZrO₂-Toughened Al₂O₃," *J. Am. Ceram. Soc.*, **69**(3), 169-172 (1986).
18. E.P. Butler, "Transformation-Toughened Zirconia Ceramics," *Materials Sci. & Tech.*, **1**, 417-432 (1985).
19. A.H. Heuer, N. Claussen, W.H. Kriven, and M. Ruhle, "Stability of Tetragonal ZrO₂ Particles in Ceramic Matrices," *J. Am. Ceram. Soc.*, **65**(12), 642-650 (1982).
20. P.L. Swanson, C.J. Fairbanks, B.R. Lawn, Y.W. Mai, and B.J. Hockey, "Crack-Interface Grain Bridging as a Fracture Resistance Mechanism in Ceramics: I, Experimental Study on Alumina," *J. Am. Ceram. Soc.*, **70**(4), 279-289 (1987)