Formation of La-β-Aluminate in α-Alumina Matrix and Its Influence on Mechanical Properties

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La-β-Aluminate의 형성이 α-Alumina의 기계적 성질에 미치는 영향

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ABSTRACT

Alumina ceramics was reinforced by in-situ formation of La-β-aluminate in α-alumina matrix. The powder mixture of which composition is $(100-12x)Al_2O_3 + x(La_2O_3 + 11Al_2O_3)$ was prepared for the formation of La-β-aluminate in α-alumina matrix. The amount of La-β-aluminate in the matrix was controlled by varing x which is number of moles. The dense composite was produced by sintering at 1600℃ in air or hot-pressing at 1550℃ under 30 MPa. Bending strength and fracture toughness were increased, resulting from the grain growth inhibition and the crack deflection and crack bridging mechanism when La-β-aluminate was produced in α-alumina matrix.

요 약

In-situ 반응에 의하여 α-alumina 기지내에 La-β-aluminate를 형성시킴으로써 알루미나 세라믹스를 강화하였다. $(100-12x)Al_2O_3 + x(La_2O_3 + 11Al_2O_3)$의 조성을 가지는 분말 혼합체를 이용하였으며, 생성되는 La-β-aluminate의 양은 몰수 x에 의하여 조절하였다. 1600℃에서 공기 중 상압소결에 의하여, 혹은 1550℃에서 30 MPa의 열간 가압 성형에 의하여 치밀한 소결체를 얻을 수 있었다. La-β-aluminate가 형성되어 곡강도와 파괴인성이 증가하였으며, 이는 입성장 억제 효과와 균열 진행 경로의 deflection과 bridging에 의한 것으로 생각된다.

1. Introduction

Alumina ceramics has many advantages such as high melting point, high hardness, high temperature stability, high temperature strength and high wear resistance but it has also critical disadvantage of brittleness under mechanical and/or thermal stress. So. the wide application of alumina ceramics has been limited in the field demanding high strength. To strengthen the alumina ceramics many researches on the reinforcement by fiber or whisker have been done. But, there are many problems such as interfacial cracking and diffuculties in homogeneous mixing and full densification. By the way, Ko et al.[1] have discussed the reinforcement of α-alumina matrix by forming elongated or plate-shaped β'''-alumina.

$LaAl_{11}O_{18}$, which is one of the rare earth aluminates. is thermally more stable than other β-type alumina and has smaller platelet size than β'''-alumina. So, in this study, in-situ reaction for the formation of dense α-alumina matrix dispersed with plate-shaped $LaAl_{11}O_{18}$ has been investigated in order to develope the stronger and tougher alumina than monolithic alumina ceramics.

2. Experimental Procedure

In this study, Al_2O_3 and $La(NO_3)_3 \cdot 6H_2O$ were used

Table 1. Impurities of the Materials Used.　(ppm)

	Al_2O_3*	La(NO$_3$)$_3$·6H$_2$O**
Si	10	
Na	2	<10
Mg	2	
Cu	<1	<10
Fe	5	<10
Ca		<100
Mn		<10
Ba		<20
Sr		<10
Cr		<10
Ni		<10
PN		<10
K		<10
Cl		<10
CeO$_2$		<25
Pr$_6$O$_{11}$		<50
Nd$_2$O$_3$		<50
Sm$_2$O$_1$		<50

*AKP-30, Sumitomo, Japan
**No. 5220, Unocal, Molycorp., U.S.A.

Table 2. Phases to be Formed by Calculation Through Rational Analysis.　wt%(vol%)

| x	α-Al$_2$O$_3$	LaAl$_{11}$O$_{18}$
0	100	0
0.5	93.0 (93.1)	7.0 (6.9)
1.0	86.1 (86.4)	13.9 (13.6)
1.5	79.4 (79.7)	20.6 (20.3)
2.0	72.8 (73.2)	27.2 (26.8)

as starting materials and the impurities of these materials are shown in Table 1. The reason for the use of La(NO$_3$)$_3$·6H$_2$O as La$_2$O$_3$ source is for the homogeneous mixing between La$_2$O$_3$ and Al$_2$O$_3$ and the promotion of uniform reaction in whole specimen. La(NO$_3$)$_3$ ·6H$_2$O was dissolved in distilled water and the appropriate amounts of alumina powder were added to above solution to make slurry with the composition of (100-12x)Al$_2$O$_3$+x(La$_2$O$_3$+11Al$_2$O$_3$), x: number of moles. The equilibrium compositions after sintering with respect to x were calculated through rational analysis and tabulated in Table 2.

The wet mixture was dried under IR lamp while stirring and calcined in air at 600℃ for 12 hours. Calcined powder was compacted uniaxially under a pressure of 25 MPa, followed by the isostatic pressing under a pressure of 300 MPa. The powder compacts were sintered at 1600℃ for 1, 3 and 10 hours in air. The powder mixture (about 13g) was also hot-pressed at 1550℃ for 30 minutes under 30 MPa in Ar atmosphere.

Densities of the specimens were determined by the Archimedes principle. After grinding and polishing the surface of the specimen, phases were analyzed by using X-ray diffractometer (Rigaku, D/Max-3C System) and scanning electron microscopy (JEOL, JSM 35-CF). Three point bending strength was measured for hot-pressed specimen by using a universal testing machine (Schenck Trebel, UPM-120) with a crosshead speed of 0.5 mm/min and a support span of 18 mm. Fracture toughness was measured for hot-pressed specimen by the Vicker's indentation method[2] with a load of 98 N.

3. Results and Discussion

There are two compounds which are normally formed in La$_2$O$_3$-Al$_2$O$_3$ system:LaAlO$_3$, a cubic perovskite[3], and LaAl$_{11}$O$_{18}$, a hexagonal compound with the β-Al$_2$O$_3$ structure[4]. Ropp and Carroll[5] have observed that LaAl$_{11}$O$_{18}$ began to be formed via LaAlO$_3$ at around 1400℃ and completely formed at around 1600℃ by firing La$_2$O$_3$/Al$_2$O$_3$(=1/11) mixture for 24 hours. Kato et al.[6] have reported that LaAl$_{11}$O$_{18}$ was formed at lower temperature, 1200℃, for 2 hours by coprecipitation from La(NO$_3$)$_3$·6H$_2$O and Al(NO$_3$)$_3$·6H$_2$O. And they have commented that the discrepancy in the formation temperature of LaAl$_{11}$O$_{18}$ might be attributed to the difference in the preparation method; i.e.. coprecipitation and mixing of two oxides. Also, Tsukuma and Takahata[7] have reported that LaAl$_{11}$O$_{18}$ was formed at 1450℃ by the following reaction.

$$10Al_2O_3+La_2O_3·Al_2O_3 \rightarrow La_2O_3·11Al_2O_3$$
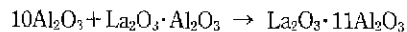
So, in this study, the pre-experiment was done to investigate the reaction sequence in case of starting from La(NO$_3$)$_3$·6H$_2$O and Al$_2$O$_3$. The powder mixture with the composition of La$_2$O$_3$:Al$_2$O$_3$=1:11 was calcined in air at 600℃ for 12 hours and sintered at 1300℃, 1400℃, 1450℃, 1500℃, 1600℃ and 1700℃ for 3 hours,
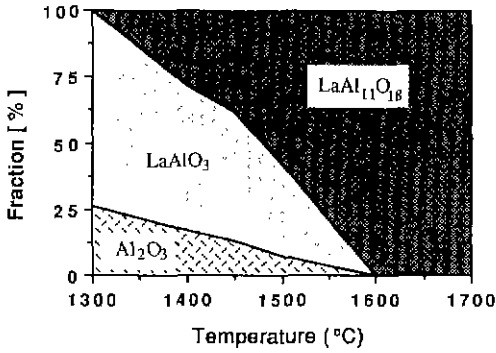
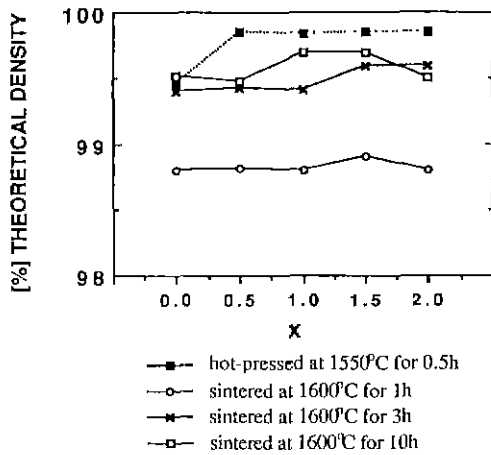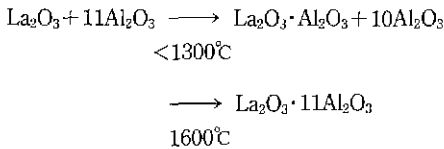**Fig. 1.** Volume fraction of the phases present at various temperatures.

—■— hot-pressed at 1550°C for 0.5h
—○— sintered at 1600°C for 1h
—✕— sintered at 1600°C for 3h
—□— sintered at 1600°C for 10h

Fig. 2. Densities with different x values.

Fig. 3. Bending strength for the specimens with different x values hot-pressed at 1550°C for 30 min under 30 MPa in Ar atomosphere.

Fig. 4. Fracture toughness for the specimens with different x values hot-pressed at 1550°C for 30 min under 30 MPa in Ar atmosphere.

X-ray diffractometer was used to analyze the phases of each specimen. The results are shown in Fig. 1 and the reaction sequence can be summerized as follows.

$$La_2O_3 + 11Al_2O_3 \longrightarrow La_2O_3 \cdot Al_2O_3 + 10Al_2O_3$$
$$< 1300°C$$

$$\longrightarrow La_2O_3 \cdot 11Al_2O_3$$
$$1600°C$$

$LaAlO_3$ is an intermediate phase and formed around 800°C[5] and as temperature increases to 1400°C, it reacts with Al_2O_3 to give $LaAl_{11}O_{18}$. The formation of $LaAl_{11}O_{18}$ is nearly completed at 1600°C, i.e., the sintering temperature of this study.

Fig. 2 shows the relative densities of the specimens sintered at 1600°C for 1, 3 and 10 hours and hot-pres-
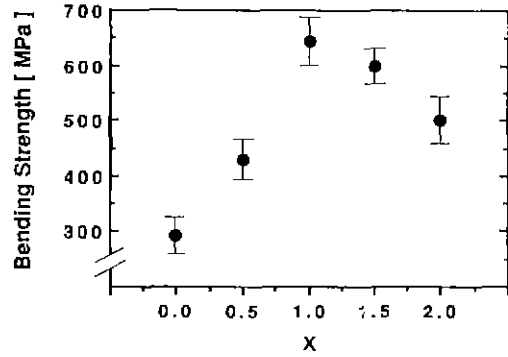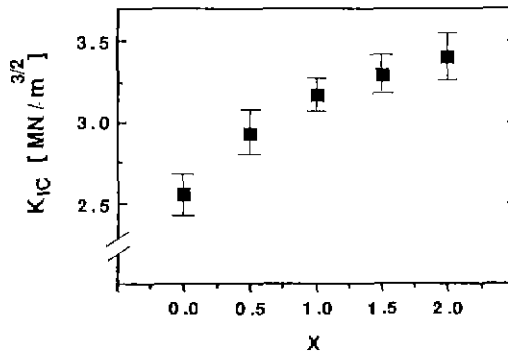
sed at 1550°C for 30 minutes. Here, although the exact theoretical density of $LaAl_{11}O_{18}$ is not known, it can be estimated from JCPDS card (33-699). According to JCPDS card, $LaAl_{11}O_{18}$ has hexagonal structure with $a = 5.561$Å and $c = 22.041$Å. So, if the chemical formula and lattice parameters are correct, the theoretical density of $LaAl_{11}O_{18}$ can be calculated to be 4.071 g/cm^3.[8,9] In Fig. 2 the increase in density with the increase in sintering time is understandable and the densities of most specimens were above 99% to the theoretical density for each composition. And the specimen hot-pressed at 1550°C for 30 minutes under a pressure of 30 MPa had higher density than sintered specimen. So, the formation of plate-shaped $LaAl_{11}O_{18}$ in α-alumina matrix does not seem to impede the densification of the matrix.
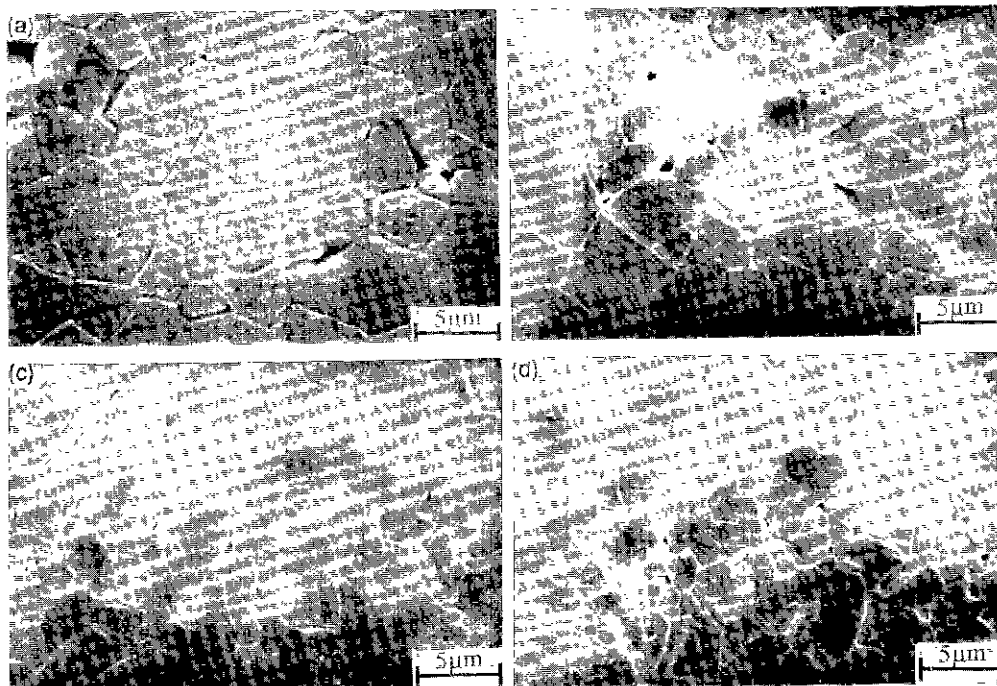
Fig. 5. Microstructures of the specimens sintered at 1600°C for 3 h in the system $Al_2O_3 + x(LaAl_{11}O_{18})$.
a) x=0 b) x=0.5 c) x=1.0 d) x=1.5

Bending strength and fracture toughness for hot-pressed specimen are shown in Fig. 3 and Fig. 4. The highest bending strength obtained was 700 MPa which is more than twice that of monolithic alumina. The bending strength increased up to x=1.0 beyond which decreased slightly. This tendency implies that there is an opimum fraction of $LaAl_{11}O_{18}$ in α-alumina matrix. By the way, the fracture toughness measured by the Vicker's indentation technique showed slight increase only with increase in x value. In order to see the role of $LaAl_{11}O_{18}$ in α-alumina matrix, the microstructures have been investigated.

Fig. 5 shows the microstructural development with increase in x value. As x value increases, the formation of $LaAl_{11}O_{18}$ increases remarkably Plate-shaped $LaAl_{11}O_{18}$ grains are homogeneously distributed in α-alumina matrix. As the amount of $LaAl_{11}O_{18}$ increases, the grain size of α-alumina matrix is decreased noticeably. So, the result in Fig. 3 that the bending strength increases as the amount of $LaAl_{11}O_{18}$ increases is understandable because it is well known that generally ceramic materials with smaller grain size have higher bending strength than those with larger grain size. But, as the amount of $LaAl_{11}O_{18}$ increases superabundantly, in case of x>1.0, they are touched each other (Fig. 5(d)). So, when the external stress is applied, crack seems to be initiated in that place and results in lower bending strength. In this α-alumina/La-β-aluminate system, the optimum amount of $LaAl_{11}O_{18}$ seems to be x=1.0.

In order to see the mode of crack propagation, Vicker's indentations were made on the polished surface of the specimen hot-pressed at 1550°C for 30 minutes. In Fig. 6, the crack front deflects when the crack tip meets the $LaAl_{11}O_{18}$ platelets and result in longer crack path. In some cases the crack stops propagating and newly created crack propagates from other position. The $LaAl_{11}O_{18}$ platelets which are formed in α-alumina matrix will dissipate effectively 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 limitation, a crack will be created in other position, that is, carck bridging phenomena occurs. And the latter crack will undergo the same process repeatedly. But, in spite of
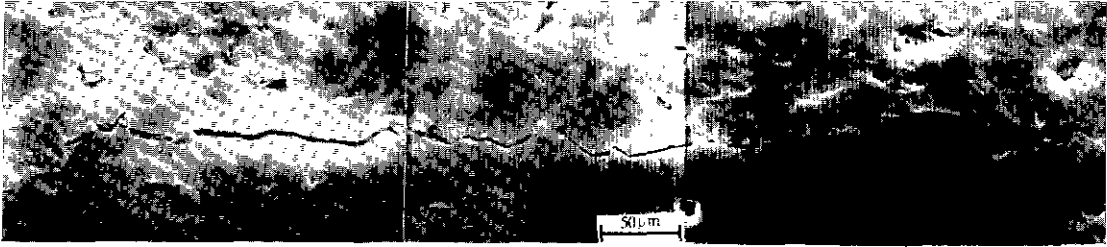
Fig. 6. Crack propagation mode in the system $Al_2O_3 + x(LaAl_{11}O_{18})$ hot-pressed at 1550°C for 3 h under 30 MPa.

Fig. 7. Microstructures of α/β'''-alumina (a) and α/β-La-aluminate (b).
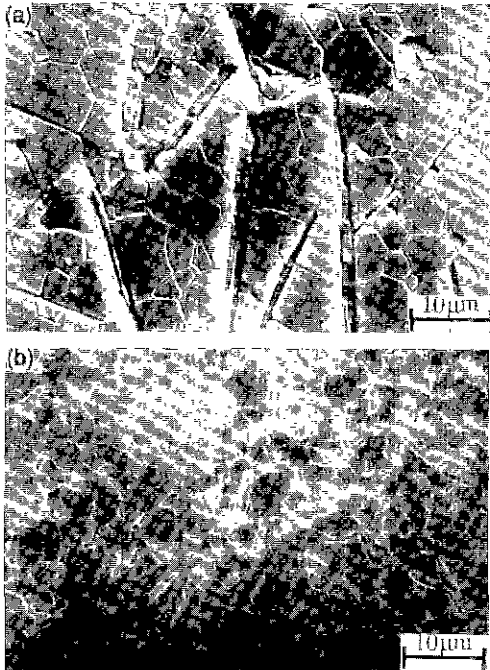
Fig. 8. Schematic diagrams of α/β'''-alumina (a) and α/β-La-aluminate (b).

this crack bridging effect, increase in fracture toughness in α-alumina/La-β-aluminate system was not remarkable compared with α-alumina/β'''-alumina system that Ko et al.[1] have reported, although the experiment conditions of both are almost same. The reason seems to be the smaller size of $LaAl_{11}O_{18}$ platelet. The size of $LaAl_{11}O_{18}$ platelet(~5 μm) is much smaller than that of β'''-alumina (~30 μm) as shown in Fig. 7. The smaller platelets may result in the smaller deflection angle than the larger platelets do[10] and this may be one of the reasons why this system shows lesser toughening effect than that with α-alumina/β'''-alumina.
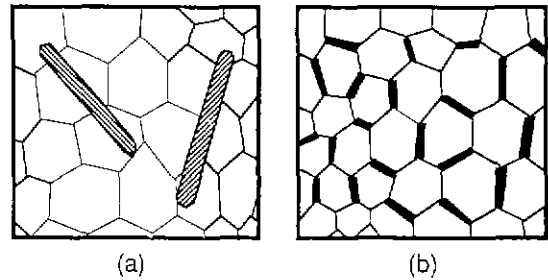
On the other hand, because the size of $LaAl_{11}O_{18}$

platelet is smaller than that of β'''-alumina, $LaAl_{11}O_{18}$ platelets can be distributed more uniformly and frequently at the grain boundaries of α-alumina matrix, if volume fractions of $LaAl_{11}O_{18}$ and β'''-alumina in α-alumina matrix are same (Fig. 8). The more frequent occurrence of $LaAl_{11}O_{18}$ platelets at grain boundaries seems to be very effective to retard the grain growth of matrix because $LaAl_{11}O_{18}$ platelets can inhibit the grain boundary migration. The remarkable grain growth inhibiting effect by $LaAl_{11}O_{18}$ platelets results in the remarkable increase in bending strength.

And, there seem to be other advantages in the reinforcement by $LaAl_{11}O_{18}$. Although the amount of the $LaAl_{11}O_{18}$ platelets increases to some extent, strengthening effect is still available due to the smaller size. On the other hand, in α-alumina/β'''-alumina composite the bending strength decreased rapidly in the range $x > 1.0$[1]. Also, the formation of $LaAl_{11}O_{18}$ in α-alumina matrix (1600°C, 3 h) is easier than that of β'''-alumina (1600°C, >10 h).

4. Conclusion

Introduction of plate-shaped La-β-aluminate in α-alu-

mina matrix through reaction sintering makes the alumina ceramics stronger. Reaction sequence for the formation of $LaAl_{11}O_{18}$ seems to be the formation of $LaAlO_3$ at around 800℃ followed by the solid state reaction of $LaAlO_3$ and Al_2O_3 to produce $LaAl_{11}O_{18}$ at around 1400℃. This reaction is completed around 1600℃. Strengthening of alumina by $LaAl_{11}O_{18}$ platelets is thought to be due to the grain growth inhibiting effect and the increase in fracture toughness seems to be due to the crack deflection and crack bridging mechanisms. Comparing the two systems, α-alumina matrix reinforced with β‴-alumina and La-β-aluminate, we can tentatively conclude that short-length-platelets contribute more to the strength than to the toughness. Short-length-platelets also make the larger loading in α-alumina matrix possible.

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