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In-situ synthesis of rodlike $LaAl_{11}O_{18}$ in Al_2O_3 powder by a coprecipitation method

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Abstract

Composite powders of rodlike $LaAl_{11}O_{18}$ grains distributed in an Al_2O_3 matrix were prepared by a coprecipitation method using $La(NO_3)_3{\cdot}6H_2O$ and $Al(NO)_3{\cdot}9H_2O$ as starting materials. The formation temperature of the $LaAl_{11}O_{18}$ phase was analyzed by XRD and the morphology of the synthesized powders was observed by SEM with EDX analysis. The results showed that the rodlike $LaAl_{11}O_{18}$ phase could be formed at low temperature and that it was distributed homogeneously in the equiaxed Al_2O_3 powder. The average aspect ratio of the $LaAl_{11}O_{18}$ grains and the average grain size of the Al_2O_3 obtained by calcining the dried gel at 1500°C for 1 h were 3–5 and 0.6 μm, respectively. TEM and HREM were used to characterize the rodlike $LaAl_{11}O_{18}$ grains and showed that the crystallographic orientation of the $LaAl_{11}O_{18}$ grain for the elongated direction was [001]. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Powders-chemical preparation; Platelets; Al_2O_3; In-situ synthesis; $LaAl_{11}O_{18}$

1. Introduction

Alumina is one of the most useful engineering materials because of its superior hardness, chemical stability and refractory character. However, the application as engineering parts is handicapped by its brittleness. One possible approach is to make composites by introducing other materials into the alumina matrix. In the last decade, ceramists have pursued toughening using microstructures reinforced with a high aspect ratio second phase and fabricated by the addition of whiskers, fibers and platelets.[1] Conventional processes for fabricating reinforced alumina matrix composites involve physically mixing the alumina powders with the reinforcements from separate sources. However, this processing cannot achieve a homogeneous distribution of the second phase in the alumina matrix, thus degrading the mechanical properties of the composites.[2]

Moreover the high cost of the reinforcements poses a significant barrier to commercialization, while the processing and handling of the reinforcements are also associated with severe health hazards.[3] These problems have led to a search for alternative fabrication routines. The in-situ processing of platelets as second phases in the alumina matrix seems to be an effective approach to microstructural toughening.

Recently, Yasuoka, et al.[4] fabricated high-strength and high-fracture toughness rodlike grain $A1_2O_3$/$LaAl_{11}O_{18}$ ceramics by solid reaction; Jang, et al.[5] reported that a hot-pressing temperature above 1500°C was required to form the $LaAl_{11}O_{18}$ phase in the Al_2O_3/$LaAl_{11}O_{18}$ composite by a solid reaction. In these situations, the $LaAl_{11}O_{18}$ grains are formed in the compacted powers during the sintering process and have some difficulties to become rodlike due to the constrained grain growth. A new approach is proposed first to synthesize rodlike $LaAl_{11}O_{18}$ grains in Al_2O_3 powder and then to sinter the composite powders to obtain the platelet reinforced composites. In this paper, we prepared in-situ grown rodlike $LaAl_{11}O_{18}$ grains distributed homogeneously in Al_2O_3 powder by a coprecipitation method.

2. Experimental procedure

The 25 vol.% $LaAl_{11}O_{18}$ and 75 vol.% Al_2O_3 composite powders were synthesized using $Al(NO_3)_3{\cdot}9H_2O$

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solution (4.5 mol·l^{-1}), $La(NO_3)_3 \cdot 6H_2O$ solution (4.5 mol·l^{-1}) and NH_4OH solution (0.2 mol·l^{-1}) as starting materials. $Al(NO_3)_3$ and $La(NO_3)_3$ solutions were prepared by dissolving the solids in distilled water, respectively. To yield a composite powder with the composition of 25 vol.% $LaAl_{11}O_{18}$ and 75 vol.% Al_2O_3, the two solutions were mixed with a molar ratio of 0.019:1(La_2O_3:Al_2O_3). The $NH_3 \cdot H_2O$ solution was added slowly to the rapidly stirred mixed solutions at 25°C in a thermostant (Model 501, China), and the slurry pH value was kept in the range of 9–10 during coprecipitation. The pH value was controlled by a pH meter (pHSJ-4, REX, China) Then the precipitate was aged in the container with constant stirring intensively for 0.5 h without removing the supernatant solutions, followed by filtering and washing twice with distilled water and ethanol, respectively. After drying at 70–80°C for 24 h, the gel was milled with ethanol for 24 h in high purity alumina media by adding AIF_3 and then dried. Finally, the dried gel was calcined for 1 h at different temperatures. A flow chart of the process for preparing the composite powders is shown in Fig. 1. The phase composition of the powder was identified by X-ray diffraction (D/max-radiffractometer, Japan) with Ni filtered CuK_α radiation. The particle size and morphology were characterized by scanning electron microscopy (EPMA-8705QHz) with energy dispersive X-ray analysis. TEM (JEM-200cx, JEOL, Japan) and HREM (JEM-400cx, JEOL, Japan) were also used for the analysis of the rodlike grains.

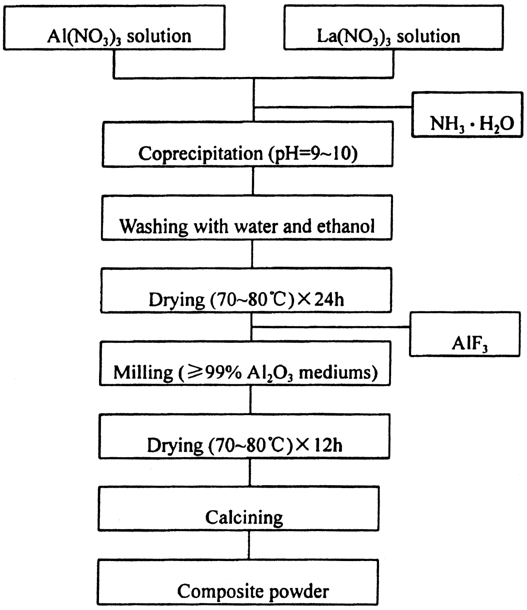

Fig. 1. Flow chart for the preparation of the composite powders.

3. Results and discussion

Fig. 2 shows the phase compositions of the dried gel calcined at different temperatures for 1 h. The dried gel calcined at 800°C gave diffraction peaks for γ–Al_2O_3 and a small amount of α-Al_2O_3 phase with amorphous background. The powder calcined at 1200°C showed a relatively high degree of crystallinity and also with some amorphous phase, the main peaks being $LaAlO_3$, $LaAl_{11}O_{18}$ and α-Al_2O_3, respectively. Though La^{3+} has a stabilizing effect on the transition alumina due to its incorporation in the crystalline structure,[6] milling with high purity alumina media and the addition of AlF_3 have potential synergistic effects in reducing the transformation temperature of the transition alumina to

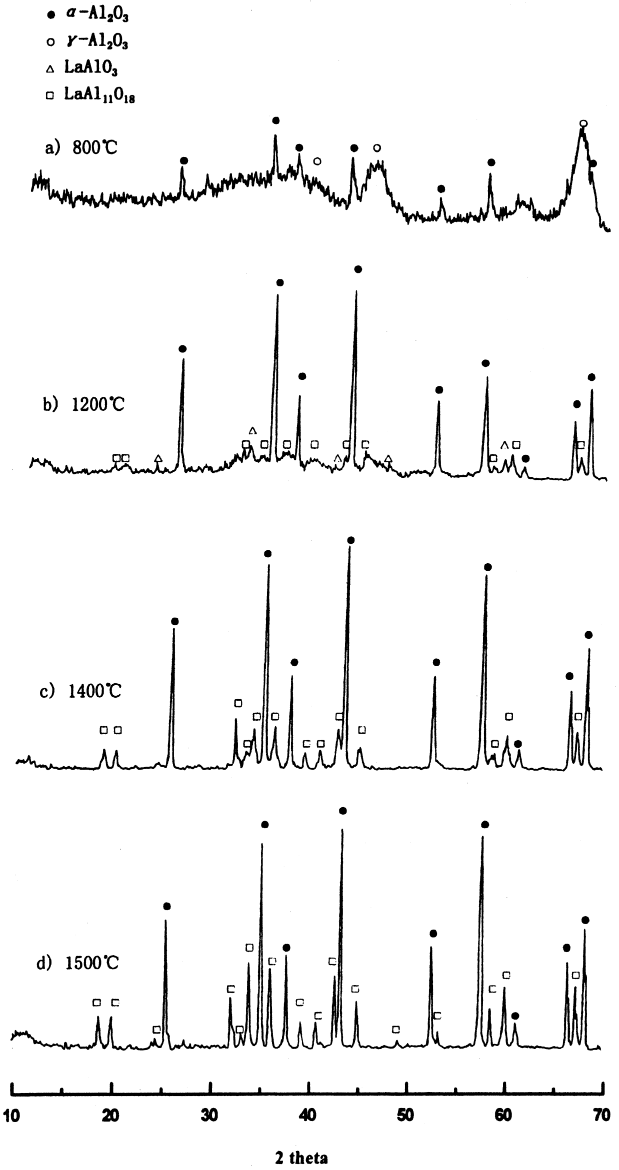

Fig. 2. Comparisons of XRD patterns of powders calcined at different temperatures.

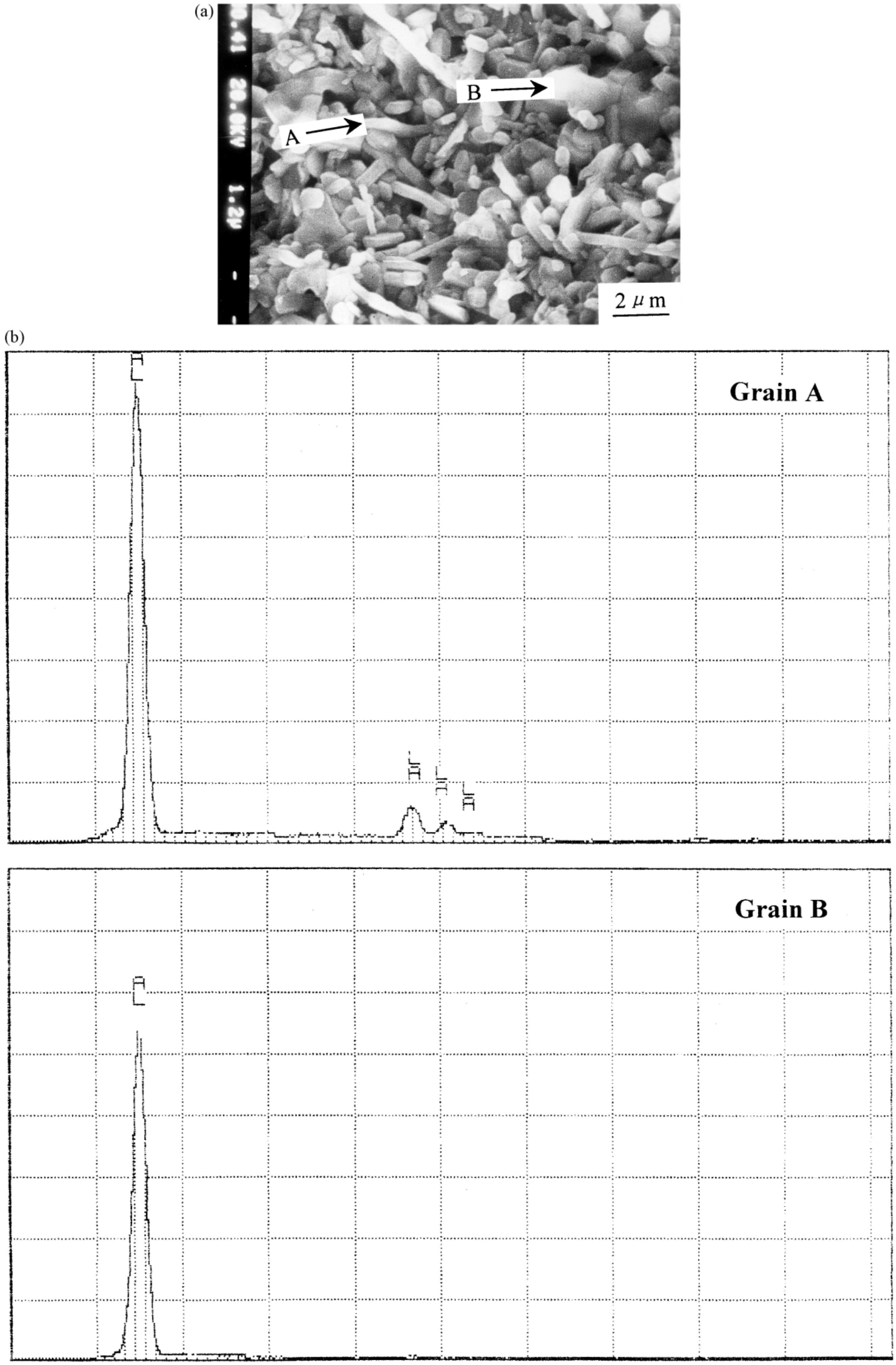

Fig. 3. (a) SEM micrograph of the composite powder; (b) EDXA spectrum of points A and B.

alpha alumina by forming an intermediate compound of AlOF.[7,8] So γ-Al_2O_3 can be converted to α-Al_2O_3 at low temperature and enhance the activity of α-Al_2O_3 with La_2O_3 and $LaAlO_3$ because of that α-Al_2O_3 power formed at lower temperature has a smaller grain size and thus the surface energy is relatively high.

The XRD curves for the gels calcined at 1400 and 1500°C have well-defined peaks whose positions correspond to $LaAl_{11}O_{18}$ and α-Al_2O_3 The degree of crystallinity of the gel calcined at 1500°C was the higher. It was found that the $LaAlO_3$ phase formed at low temperature was an intermediate phase being converted to $LaAl_{11}O_{18}$ at higher temperatures.[9] It was, therefore, suggested that $LaAl_{11}O_{18}$ formation in the Al_2O_3-La_2O_3 system occurred as follows:

$$La_2O_3 + Al_2O_3 \rightarrow 2LaAlO_3$$

$$LaAlO_3 + 5Al_2O_3 \rightarrow LaAl_{11}O_{18}$$

The SEM micrograph [Fig. 3(a)] shows that the composite powders calcined at 1500°C contained rodlike grains distributed homogeneously in an equiaxed grain powder. The average length and width of the rodlike grains were about 3.5 and 0.8 µm, respectively and the average equiaxed grain size was 1 µm. The particle size

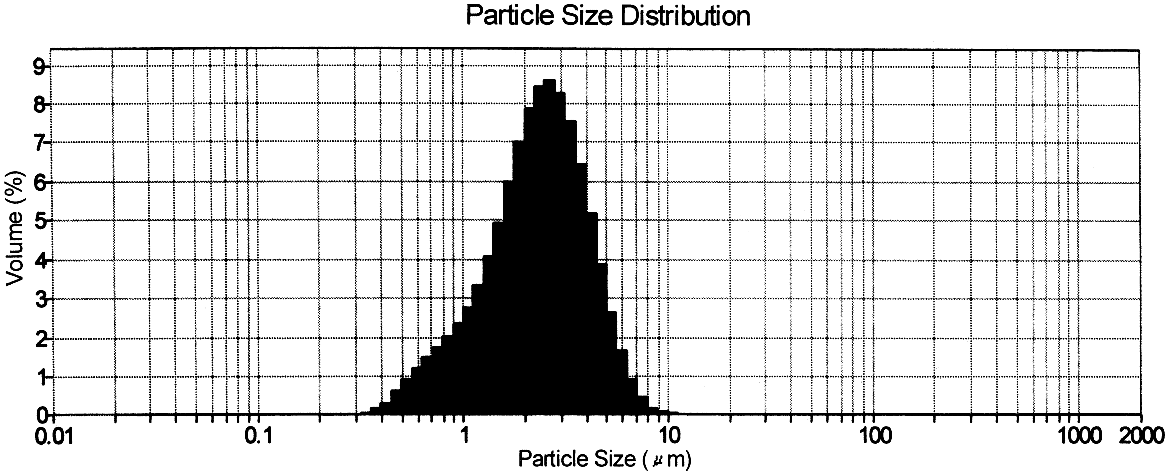

Fig. 4. Particle size distribution of the composite powders.

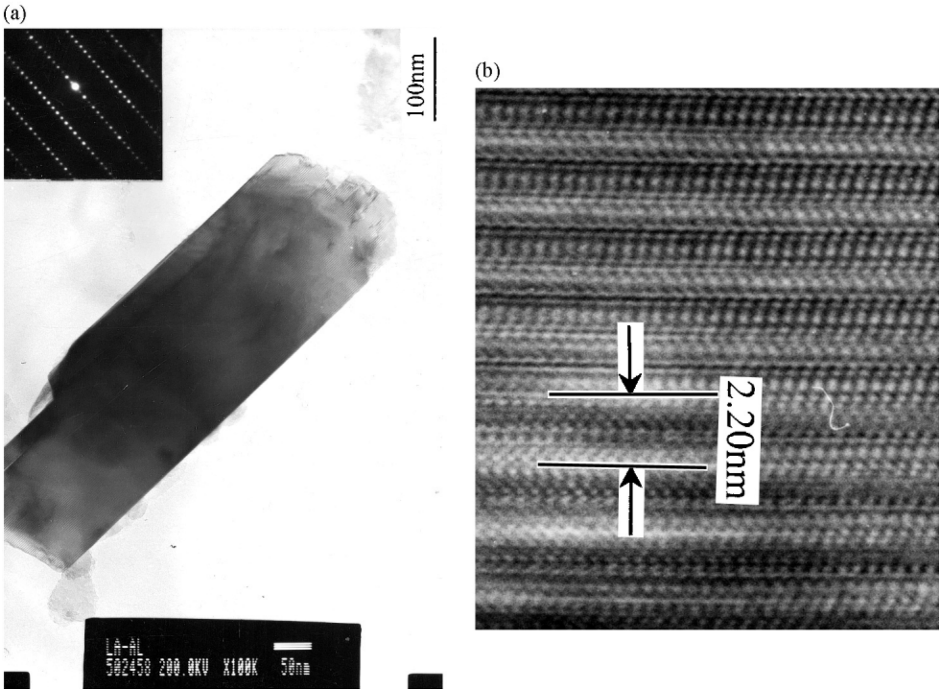

Fig. 5. (a). Micrograph and SAED pattern of $LaAl_{11}O_{18}$ grain; (b) the HREM of rodlike $LaAl_{11}O_{18}$ grain.

distribution of the powders was analyzed using a Mastersizer 2000 Ver. analyzer, with $d_{50} = 2.4$ μm, as shown in Fig. 4. Necking between powder grains can be seen from the micrograph due to the high calcining temperature. The combination of XRD results and EDX analysis indicated that the rodlike grains with aspect ratio of 3–5 are the $LaAl_{11}O_{18}$ phase and the equiaxed grains are the Al_2O_3 phase. Fig. 3(b) shows the EDX analysis of the A and B sites in Fig. 3(a), the AlK_α and LaK_α peaks are clearly shown in Fig. 3 The rodlike grains (point A) in Fig. 3(a) contained the elements La and Al, and the equiaxed grains (point B) contained only Al. It was found that incorporating small amounts of La_2O_3 into $A1_2O_3$ by coprecipitation improved the composite powder uniformity and resulted in enhanced reactivity of the compounds of La_2O_3 and Al_2O_3 to form $LaAl_{11}O_{18}$, which was slow or difficult to form by the conventional solid-state reaction technique alone.[10] This was attributed to the improved chemical homogeneity and intimate mixing of constituents on a molecular scale. The rodlike $LaAl_{11}O_{18}$ grains could be explained by the anisotropic growth habit of $LaAl_{11}O_{18}$ because of the markedly different lattice parameters of a_0 (0.556 nm) and c_0 (2.204 nm) and thus the grain growth of $LaAl_{11}O_{18}$ can occur possibly in one direction.[5] But the anisotropic grain growth in this system has not been quantitatively studied. Larger space in the composite powder compared with the space in compacted green, is beneficial for rodlike $LaAl_{11}O_{18}$ grain growth. The density of composite power is 0.57 g/cm^3 and the density of compacted green is 2.12 g/cm^3.

Fig. 5 shows a high-resolution micrograph and selected-area electron diffraction (SAED) pattern of the rodlike $LaAl_{11}O_{18}$ grains. The SAED pattern of the rodlike grains showed a clear crystalline pattern, and the rodlike grains were found to be single crystals elongated along [001]. In the high-resolution micrograph, a lattice image corresponding to [001] was clearly seen and no disarray or discontinuity of the lattice image was detected in the rodlike grains.

4. Conclusion

In-situ development of rodlike $LaAl_{11}O_{18}$ grains in Al_2O_3 matrix powder was prepared by coprecipitation using $La(NO_3)_3{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ as the starting materials. The reaction sequence for producing $LaAl_{11}O_{18}$ phase required the formation of $LaAlO_3$ at lower temperature, this being followed by a solid-state reaction between $LaAlO_3$ and Al_2O_3 at higher temperature. The rodlike $LaAl_{11}O_{18}$ phase can be formed at 1500°C and the HREM analysis indicated that the crystallographic orientation of the rodlike $LaAl_{11}O_{18}$ for the elongated direction was [001]. The composite powders are suitable for preparing whisker or platelet reinforced Al_2O_3 ceramic composites.

Acknowledgments

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