Preparation and properties of porous lanthanum doped alumina ceramic composites with self-organization

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Porous lanthanum doped alumina ceramic composite was prepared by self-organization and solid-state reaction between Al2O3 and La2O3. Crystal phases, microstructure and density of ceramics were examined to characterize novel composites in the system of Al2O3 and La2O3. After heat treatment at 1300°C and 1400°C, LaAl12O19 plate-like crystals were formed through the solid-state reaction of LaAlO3 with Al2O3. The addition of large amounts of La contributed to the increase of LaAl12O19 plate-like crystals and their cross-linking microstructure. The porous alumina composites maintained high surface areas of 20 m2/g after heating at 1300°C, and 11 m2/g at 1400°C. The bending strength of La added alumina composite was 57 MPa after heating at 1400°C.

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1. Introduction

The development of the catalysts used for a high-temperature combustion system becomes essential for the recent concerns over global environmental problems. Alumina is widely used as a catalyst support, because of its high specific surface areas, surface characteristics and crystal structure are suitable for catalytic combustion. However, in general, α-alumina supports significantly decrease in surface areas under high-temperature conditions and then the catalysts lose the catalytic activity.3 Therefore, it is necessary to improve thermal stability of alumina catalytic supports. It has been known that the addition of lanthanum species greatly improves the thermal stability of alumina supports.2–4,8–10,12–20 Limestone or dolomite supports have been put to practical use in exhaust treatment, especially for automotive catalysts. However, the heat resistance is not enough under extremely high temperature combustion when the temperature is over 1300°C. It has been reported that the alumina powder supports are improved by forming complex oxides between La2O3 and Al2O3.3,16

In this paper, we will prepare the newly porous alumina composite with La-addition, which has heat resistance under high temperatures over 1300°C. We examined the microstructural changes of ceramics in the system of La2O3 and Al2O3, and determined the preparation route of the porous ceramic composite.

2. Experimental

2.1 Sample preparation

The starting materials were pure α-Al2O3 powdered (> 99.9%, Sumitomo Chemical Co., Ltd.) and lanthanum (III) nitrate (La(NO3)3·6H2O; Wako Pure Chemical Industries, Ltd.). La-added alumina powders were prepared by an impregnation process using aqueous lanthanum (III) nitrate. The impregnated samples were then freeze-dried in a vacuum after freezing at −30°C. The powders of alumina with La of 0.1–10 mol% per Al in Al2O3 were heated at 600°C, followed by grinding, and then used as raw materials for ceramic composites. The raw material powders of La-added alumina, mixed with the paraffin wax (LUVAX–1266; Nippon Seiro Co., Ltd., Japan) were ball-milled in toluene for 3h and dried at room temperature. The compact body was uniaxially compressed at 45 MPa into plates of 50 × 5 × 2 mm in size. After calcination at 600°C, they were heated at 1250°C, 1300°C or 1400°C for 3 h in air.

2.2 Characterization

The X-ray powder diffraction (XRD) patterns of powdered samples were obtained with Rigaku Co., rint–2000 diffractometer using Cu Kα radiation, operated at 40 kV and 40 mA. The microstructures (the fracture surfaces) were examined by a scanning electron microscopy (JEOL Ltd., JSM6000F) at 10 kV. The BET specific surface areas were measured by nitrogen adsorption of N2 at 77 K after the pre-heating treatment of samples at 200°C for 1 h. Three-point bending tests were performed by a Shimadzu Autograph AGS–G using 20 mm span and cross head speed of 0.5 mm/min.

3. Results and discussion

3.1 Solid state reaction

Figure 1 shows the XRD patterns for a series of the samples with different La content, which were heated at 1300°C for 3h. In the sample up to with 0.3 mol% of La contents, only α-Al2O3 phase was observed, and no other phase derived from lanthanum species was detected. As the lanthanum content increased, the XRD amplitude of α-Al2O3 peaks decreased. For the samples with 1.5–3 mol% of La contents, the new phases corresponding to LaAlO3 and layer-structured LaAl12O19 were derived from the solid-state reactions. In the samples over 5 mol% of La contents, α-Al2O3 was not detected, and the XRD amplitude of LaAl12O19 peaks increased as the La content increased. Figure 2 shows the XRD patterns for the samples which were heated at 1400°C for 3 h. For a sample with 0.1 mol% of La contents, only α-Al2O3 phase was observed. For the samples with 0.3–5 mol% of La content
contents, both the LaAlO₃ and La₂Al₄O₄ phases were detected in addition of α-Al₂O₃ phase. The XRD peak intensity of LaAlO₃ became lower and that of La₂Al₄O₁₇ was higher, compared to those for the sample heated at 1300°C. Thus, the solid-state reaction between Al₂O₃ and LaAlO₃ formed La₂Al₄O₁₇ at an elevated temperature from 1300°C to 1400°C, as follows,

\[
\text{LaAlO}_3 + 5\text{Al}_2\text{O}_3 \rightarrow \text{La}_2\text{Al}_4\text{O}_{17} \quad (1)
\]

LaAlO₃ was formed by an equal molar reaction between La₂O₃ and Al₂O₃ below 1300°C. In the sample with 10 mol% of La contents, the amount of La₂Al₄O₁₇ increased more and Al₂O₃ did not remain at all after at 1300°C and 1400°C. La₂O₃ had been consumed as a source to form LaAlO₃ and La₂Al₄O₁₇ during solid-state reactions in Al₂O₃ matrix with the addition of La species.

3.2 Bulk density and open porosity

Figures 3 and 4 show the bulk densities and the open porosities of lanthanum doped alumina ceramic composites as a function of La content. At 1300°C, the samples with La content up to 0.3 mol% had an almost constant bulk density in the range of 1.67 to 1.73 × 10³ kg/m³. However, for the 1.5 mol% La-added sample, the bulk density was up to 1.82 kg/m³ and the open porosity was down to 52.8%. When La contents were over 3 mol%, the bulk densities decreased and open porosities increased. Finally, for 10 mol% La-added sample, the porous ceramic composite with the maximum porosity of 63% was obtained. The same tendency of density and porosity as the samples heated at 1300°C versus La content was shown for the samples heated at 1400°C. For 10 mol% La-added sample heated at 1400°C, the porous ceramic composite with a large porosity of 60% was obtained.

3.3 Microstructure

Figure 5 shows the SEM photographs of fracture surfaces in the composites heated at 1300°C with different La content. For the 1.5 mol% La-added sample, the heterogeneous structure is observed, where small amounts of LaAl₁₁O₃₅ plate-like crystals have formed locally in α-Al₂O₃ matrix. For the 3 mol% La-added sample, both α-Al₂O₃ and γ-Al₂O₃ have existed and the LaAl₁₁O₃₅ plate-like crystals are frequently observed. For 5 mol% La-added sample, the large amount of LaAl₁₃O₃₅ plate-like crystals with about 20–30 nm in thickness are observed in the mixed matrix of fine γ-Al₂O₃ and LaAlO₃ grains. For 10 mol% La-added sample, LaAl₁₃O₃₅ plate-like crystals have grown up more and LaAlO₃ grains are observed. The well-dispersed LaAl₁₃O₃₅ crystals lead to the formation of many pores in both composites. Figure 6 shows the SEM photographs of the fracture surfaces of composites heated at 1400°C. The 1.5 mol% La-added sample shows the heterogeneous structure the same as that heated at 1300°C. For 3 and 5 mol% La-added samples, the LaAl₁₁O₃₅ plate-like crystals are highly dispersed in α-Al₂O₃ and LaAlO₃ grains. For 10 mol% La-added sample, the LaAl₁₃O₃₅,
plate-like crystals have occupied a great part of the composite body, however the small amount of LaAlO$_3$ grains are present. The continuous pores consist of a cross-linking structure of LaAl$_{11}$O$_{18}$ plate-like crystals. Especially, 5 mol% and 10 mol% La added samples have homogeneous porous structures with well-developed LaAl$_{11}$O$_{18}$ network. The morphology results in highly open-porous structure which was indicated by the measurement value as shown in Fig. 4. These SEM images indicate that the characteristic feature and development of the network structure of LaAl$_{11}$O$_{18}$ plate-like crystals which should provide a porous ceramic after self-organization via solid state reaction in the system of Al$_2$O$_3$ and La$_2$O$_3$.

3.4 Specific surface area

The high surface area is an important factor of the catalytic activity at high temperature combustion. Figure 7 shows the specific surface areas of 5 mol% and 10 mol% La-added alumina composites heated at 1250°C, 1300°C and 1400°C. At 1250°C, both 5 mol% and 10 mol% La-added samples had high surface areas of 41 m$^2$/g and 27 m$^2$/g, respectively. However, the surface areas significantly decreased with only a 50°C rise in heat treatment temperature from 1250°C to 1300°C. In the temperature of 1250°C or less, added La$_2$O$_3$ mainly improves the thermal stability of alumina by surface modification of alumina particles. On the other hand, the high thermal stability is not achieved by such a dispersed phase of La$_2$O$_3$ over 1300°C, because LaAl$_{11}$O$_{18}$ particles form in them. Therefore, a different type of thermal stabilization mechanism due to the network of small LaAl$_{11}$O$_{18}$ plate-like crystals is necessary to maintain the surface area under the high temperature. Actually, 5 mol% La-added alumina composite with a well-developed LaAl$_{11}$O$_{18}$ network had a surface area of 20 m$^2$/g at 1300°C, which was about twice as high as that of 10 mol% La-added alumina composite. The 5 mol% La-added alumina composite maintained a high surface area of over 10 m$^2$/g after heating at 1400°C.

3.5 Bending strength

Figure 8 shows the bending strength of 5 mol% and 10 mol% La-added alumina composites heated at 1250°C, 1300°C and 1400°C. The strength values of 5 mol% and 10 mol% La-added composites heated at 1250°C were 31 and 32 MPa, respectively. The bending strength of 5 mol% La-added composite was improved to 57 MPa with an elevated heat treatment temperature at 1400°C. On the other hand, the bending strength of 10 mol% La-added composite decreased to 21 MPa after heat treatment at
1400°C. Figure 9 shows the SEM photographs of LaAl$_{11}$O$_{18}$ cross-linking structures in (a) 5 mol% and (b) 10 mol% La-added alumina composites heated at 1400°C for 3 h in air.

This novel material is potentially useful as catalytic support for high temperature combustion.

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