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Thick-film coating of hexaaluminate catalyst on ceramic substrates for high-temperature combustion

Hiroshi Inoue, Koshi Sekizawa, Koichi Eguchi*, Hiromichi Arai

Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University,
6-1 Kasuga-koen, Kasuga 816-8580, Japan

Abstract

Structural and chemical stabilities of substituted hexaaluminate catalyst films coated on some ceramic substrates were investigated for high-temperature combustion applications. The thermal stability of the hexaaluminate catalyst films on α-SiC substrate was greatly enhanced by the insertion of both, a neat hexaaluminate and mullite intermediate layer. Pure alumina substrate was preferable in depositing the substituted hexaaluminate catalyst film to pure mullite, mullite-zirconia composite, or partially stabilized zirconia substrates. The thermal stability of the hexaaluminate catalyst films, coated on these oxide ceramic substrates, greatly depended on the extent of diffusion of components between the film and substrate at high temperatures. The substituted hexaaluminate microparticles in the film rearranged during the sintering process above 1400°C, and their (001) plane oriented parallel to the surface of the substrate. Manganese introduced in the substituted hexaaluminate films or disks gradually decreased with an increase in the heat-treatment temperature because of its volatilization. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hexaaluminate catalyst; Ceramic substrates; Combustion; Hexaaluminate film; SLMA

1. Introduction

Many studies on catalytic combustion have been extensively carried out for high-temperature applications, such as in gas turbines and jet engines. Since catalytic oxidation of lean fuels proceeds at lower temperatures, catalytic combustion suppresses both, unburned hydrocarbons and thermal NO_x emission, and attains high energetic efficiency [1–3]. Since catalysts are exposed to a wide range of temperatures, from 500°C to 1300°C, the catalysts are required to cover several different kinetic processes and/or their transient regions. Sadamori et al. [4] suggested multi-stage-catalysts with different active materials and thermal stabilities to deal with this problem. In high-temperature regions (above 800°C) both, homogeneous gas phase and heterogeneous catalytic reactions take place. Since, the gas phase reaction is stabilized by the catalytic reaction, catalysts exposed to high temperatures are required to maintain a high surface area and catalytic activity under such severe conditions.

Hexaaluminate-related compounds [5–8] are the most promising catalyst materials applicable under the high-temperature conditions. Some hexaaluminate compounds retain high surface areas; e.g. above $20\ m^2\ g^{-1}$, after calcination at 1300°C. The surface areas are an order of magnitude larger than that of

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*Corresponding author. Fax: +81 92 5730342.

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Al_2O_3, which is a typical washcoat material used below 1200°C. In addition, partial substitution for the Al-site in the hexaaluminate lattice by some transition metals, such as Mn and Fe, gives rise to a high oxidation activity. No significant lowering of the surface area is brought about by the substitution. $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ (SLMA) is one of the successful designs in hexaaluminate catalysts. Since these active species are dispersed in the hexaaluminate lattice, severe volatilization or migration of the active species and drastic deterioration of the activity should be avoided. However, it is required to improve the thermal shock resistance of the hexaaluminate honeycomb because of its high thermal expansion coefficients (ca. $8\times10^{-6}\,K^{-1}$).

We reported a new structural design of the hexaaluminate catalyst which consisted of an α-SiC substrate with high thermal stability and thermal shock resistance, and a hexaaluminate catalyst film. Other structural ceramics were also investigated as the substrate for high-temperature combustion catalysts. An α-SiC, pure alumina (AP) and pure mullite (MP), mullite-zirconia composite (MZ), and partially stabilized zirconia (PSZ) were used as substrates, and the structural and chemical stability of hexaaluminate catalyst films coated on these substrate are discussed.

2. Experimental

Hexaaluminate catalysts, $BaMnAl_{11}O_{19-\alpha}$ (BMA) and $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ (SLMA), were prepared by hydrolysis of mixed metal alkoxides. Details of the preparation process have been described in a previous report [9]. The resultant gel of BMA and SLMA was calcined at 1200–1450°C for 5 h in air. The resulting powders were dispersed in ethanol and stirred vigorously to prepare 12 wt.% BMA and SLMA slurries. Since Mn in the hexaaluminate lattice promoted the reaction between the substrate and film, mullite and neat hexaaluminate were employed as intermediate buffer layers [10,11]. Mullite ($Al_6Si_2O_{13}$) precursor was prepared by drying an absolute ethanol solution containing calculated amounts of $Si(OC_2H_5)_4$ and $Al(NO_3)_3\cdot9H_2O$. $Ba_{0.75}Al_{11.0}O_{17.25}$ (BA) precursor was also prepared by the hydrolysis of mixed metal alkoxides. The precursors, thus obtained, were dried and calcined at 1100°C for 5 h in air. Resulting mullite and BA powders were added to ethanol and stirred vigorously to prepare a 6 and 12 wt.% slurry, respectively.

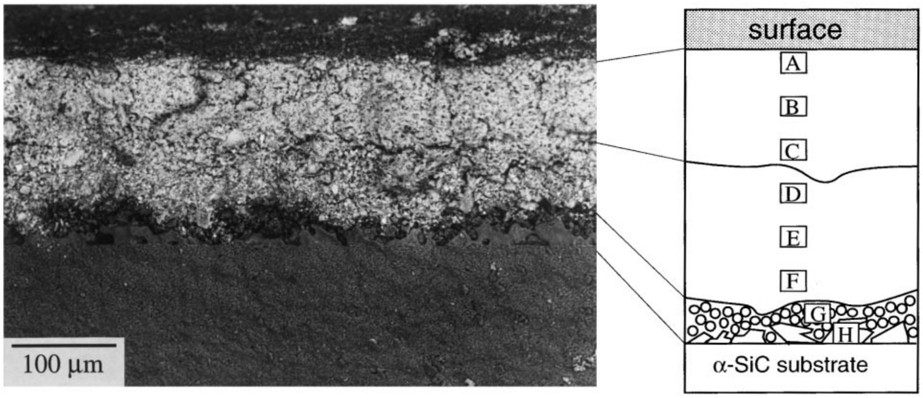
Dense α-SiC, pure alumina (AP) and pure mullite (MP), mullite-zirconia composite (MZ), and partially stabilized zirconia (PSZ) were used as 'substrates'. These substrates were dipped into the slurry dispersions and dried at room temperature. This coating process was repeated 3–5 times. The samples were calcined at 1200° or 1300°C for 5 h in air. The alternate sequence of dipping and calcination was repeated to develop a certain film thickness. Finally, samples were calcined at 1300–1600°C for 5 h in air, in order to investigate the thermal stability of the formed films. X-ray diffraction (XRD) and scanning electron microscope (SEM) with energy-dispersive X-ray spectrometer (EDX) were employed to investigate the crystalline phase and the interface between the film and substrate.

3. Results and discussion

3.1. Heat resistance of Mn-substituted hexaaluminate film on α-SiC substrate

The thermal stability of the hexaaluminate films, coated directly on α-SiC substrate, was significantly affected by the reaction with SiO_2 which grew at the surface of the substrate through heat treatments. The barium hexaaluminate (BA) film, coated on α-SiC substrate was stable up to 1300°C and the characteristics of the hexaaluminate bulk materials were retained even in slurry-coated hexaaluminate films. On the other hand, SLMA and BMA films reacted with the substrate to form other crystalline phases above 1200°C. The thermal stability of the Mn-hexaaluminate catalyst films on α-SiC substrate was deteriorated due to overreaction between the film and substrate.

To improve the thermal stability of Mn-hexaaluminate/α-SiC, double intermediate layers of BA and mullite were inserted and characterized (Fig. 1). The quadruple-layered sample of BMA/BA/mullite/α-SiC was prepared and, subsequently, heat treated at 1400°C for 5 h in air. The BMA and BA powders were calcined at 1450°C for 5 h in air prior to slurry coating. A backscattered electron image of the fracture surface of the heated sample is shown in Fig. 1 together with



	Fraction / atomic%	
	Mn	Si
A	7.1	1.5
B	7.9	0.7
C	9.5	0.4
D	4.1	6.9
E	5.0	2.3
F	3.9	3.3
G	0.2	30.7
H	2.0	54.6

Fig. 1. Backscattered electron image and schematic illustration of fracture surface of quadruple-layered sample of $BaMnAl_{11}O_{19-\alpha}$/$Ba_{0.75}Al_{11.0}O_{17.25}$/$Al_6Si_2O_{13}$/α-SiC after heat treatment at 1400°C for 5 h in air. Source powder for hexaaluminate slurries was calcined at 1450°C for 5 h in air.

its schematic phase distribution. Compositional data were taken from eight positions, A–H, in the cross-sectional view of the sample by EDX (Fig. 1). The porous microstructures of BMA and BA films were maintained even after heat treatment at 1400°C. In the bottom of the mullite intermediate layer, large glassy grains (H) containing a large amount of SiO_2 were formed. It indicates that the mullite layer effectively suppressed the diffusion of the SiO_2 into the hexaaluminate layers. EDX analysis also revealed that Si and Mn migrated into the BA intermediate layer from the lower mullite intermediate and upper BMA layers, respectively. This indicates that the BA intermediate layer is functioning as a buffer layer to avoid the direct contact between the Mn component and SiO_2. The high thermal stability of the quadruple-layered sample appears to be achieved by the buffer actions of these intermediate layers. Thermal expansion coefficients of the materials constituting the quadruple layer, i.e. α-SiC, mullite, BA, and BMA, are 4.3×10^{-6}, 5.6×10^{-6}, 6.8×10^{-6}, and ca. 8×10^{-6} K^{-1}, respectively. The stacking sequence of the gradient layers is preferable in relieving thermal shock.

3.2. *Thermal stability of Mn-substituted hexaaluminate film coated on oxide ceramic substrates*

Figs. 2 and 3 show SEM images and XRD patterns of the SLMA films prepared on MP, MZ, PSZ, and AP substrates and, subsequently, kept at 1400°C for 5 h in air. Significant grain growth was observed in the films prepared on the MP and MZ substrates. The grain growth of the film on the MP substrate was observed even after heat treatment at 1300°C. The diffraction peaks of these samples were assigned to SLMA and the substrate with small impurities of α-Al_2O_3 and $SrAl_2Si_2O_8$. It is apparent that the thermal stability of the SLMA film on the MP and MZ substrates is low and that the coated film was partially transformed into α-Al_2O_3 and $SrAl_2Si_2O_8$ phases after heat treatment. Since both, MP and MZ substrates included the mullite phase, it is suggested that the mullite phase reacted with the SLMA phase and, consequently, α-Al_2O_3 and $SrAl_2Si_2O_8$ phases were formed as equilibrium phases at 1400°C. On the other hand, no significant grain growth was observed in the SLMA films prepared on the PSZ and AP substrates. These films had a homogeneous microstructure and microcrystals <1 μm which are sinter-bonded with each other. The microstructure of the surface of the films was almost the same as that of the sintered disk which was prepared by uniaxial pressing of the SLMA powder and heating at 1400°C for 5 h in air. These results indicates that the SLMA film on the PSZ or AP substrates have a high thermal stability.

Elemental analysis was carried out on the surface of the films and the sintered disk (no substrate) after the heat treatment at 1400°C (Table 1). Silicon was detected at the surface of the films coated on the MP and MZ substrates. Atomic fractions of Al in these films were larger than that in the sintered disk.

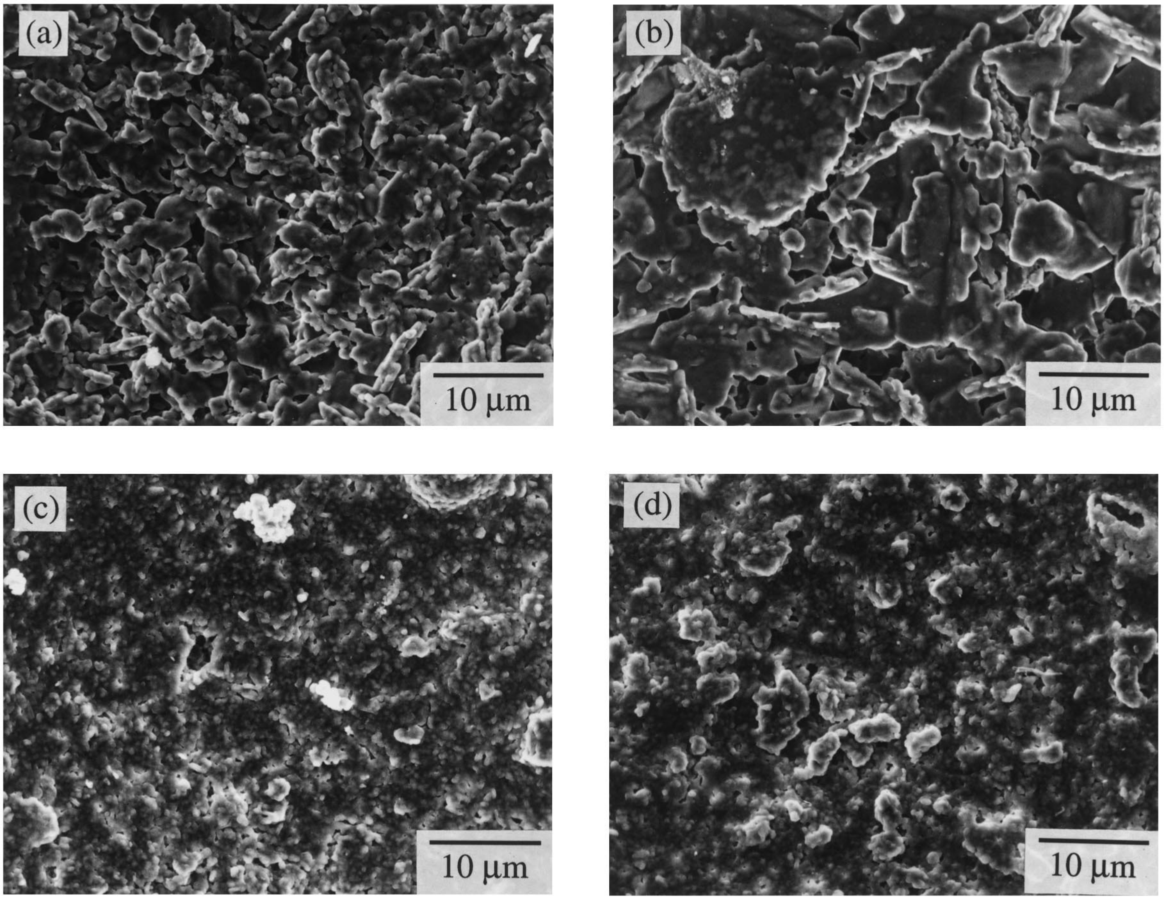


Fig. 2. SEM images of the hexaaluminate films coated on (a) pure mullite (MP), (b) mullite-zirconia composite (MZ), (c) partially stabilized zirconia (PSZ), and (d) pure alumina (AP) calcined at 1400°C.

Components of the substrates migrated to the topmost part of the SLMA film. On the other hand, the composition in the SLMA films prepared on the PSZ and AP substrates was almost the same as that of the sintered disk. This shows that no significant elemental diffusion occurred between the SLMA film and substrates. The SLMA film was stable in the SLMA–PSZ and SLMA–AP systems at 1400°C. The phases constituting the film and the substrate are, therefore, important for the high thermal stability of the film.

Table 1
Composition of the hexaaluminate film on the various ceramic substrates after calcination at 1400°C

Substrate	Fraction/atom (%)					
	Al	La	Mn	Si	Sr	Zr
No substrate	83.9	3.5	7.0	–	5.6	–
Pure mullite	94.9	0.7	1.2	2.5	0.7	–
Mullite-zirconia	93.3	1.2	1.5	3.2	0.7	0.1
Partially stabilized zirconia	87.4	3.0	4.3	–	5.3	–
Pure alumina	86.5	3.0	5.4	–	5.1	–

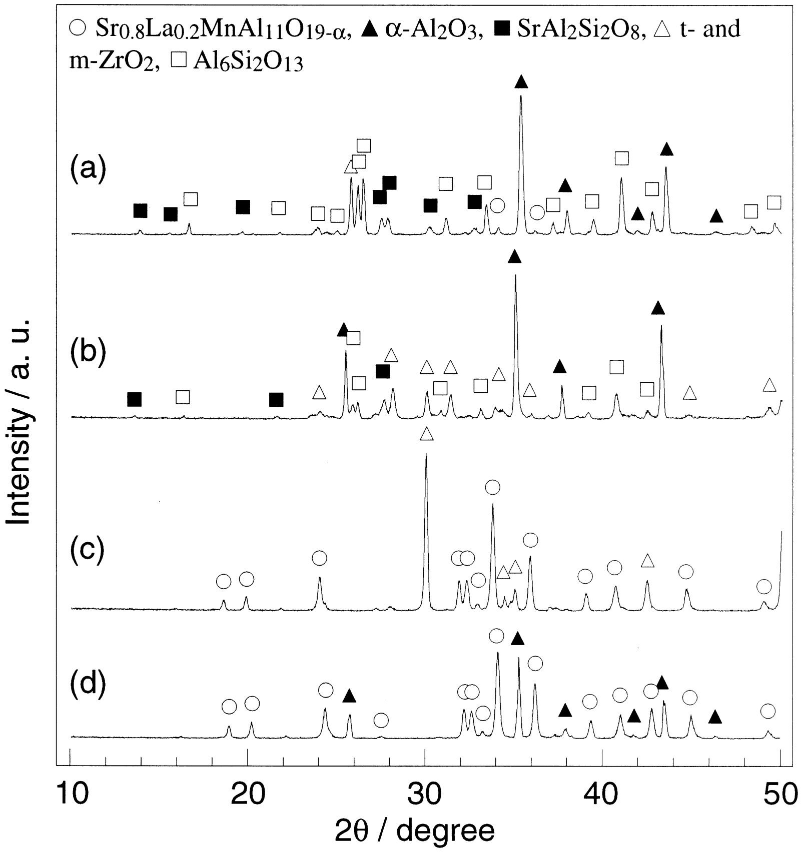


Fig. 3. XRD patterns of the hexaaluminate films coated on (a) pure mullite (MP), (b) mullite-zirconia composite (MZ), (c) partially stabilized zirconia (PSZ), and (d) pure alumina (AP) calcined at 1400°C.

Therefore, it is concluded that PSZ and AP are the promising materials of honeycomb body to be coated with the SLMA.

3.3. *Comparison of the thermal stability of SLMA films on AP and PSZ substrates*

To elucidate the reason for the high thermal stability of SLMA film on the PSZ and AP substrates, the samples were calcined at 1500°C for 5 h and characterized by SEM/EDX and XRD. Both films possessed a porous microstructure in which platelike large particles were sintered together (Fig. 4). It was also observable at the interface between the film and substrate that the microparticles and the substrate were sinter-bonded. Sintering and grain growth of the platelike particles in the film proceeded analogously to that during calcination at 1400°C. The morphological change of the film during the calcination was smaller on the AP than on the PSZ substrates. The film prepared on the AP substrate is supposed to possess a larger specific surface area. XRD patterns in Fig. 5 indicated that the hexaaluminate structure of the SLMA films on the PSZ and AP substrates were maintained after heat treatment at 1500°C. The microparticles observed by SEM corresponded to SLMA. It indicates that no significant reaction occurred between the SLMA film and PSZ or AP substrate after heat treatment. EDX analysis revealed that only Mn in the film migrated into the inner part of the substrates, which occurred more severely with the PSZ than with the AP substrates.

After calcination at 1600°C, the difference in the microstructure between the SLMA films prepared on

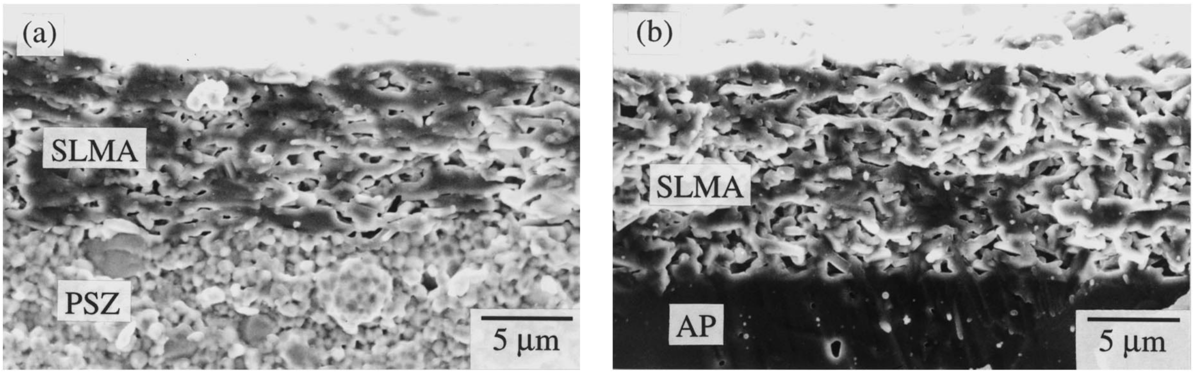


Fig. 4. Cross-sectional images of the hexaaluminate films coated on (a) partially stabilized zirconia (PSZ), and (b) pure alumina (AP) calcined at 1500°C.

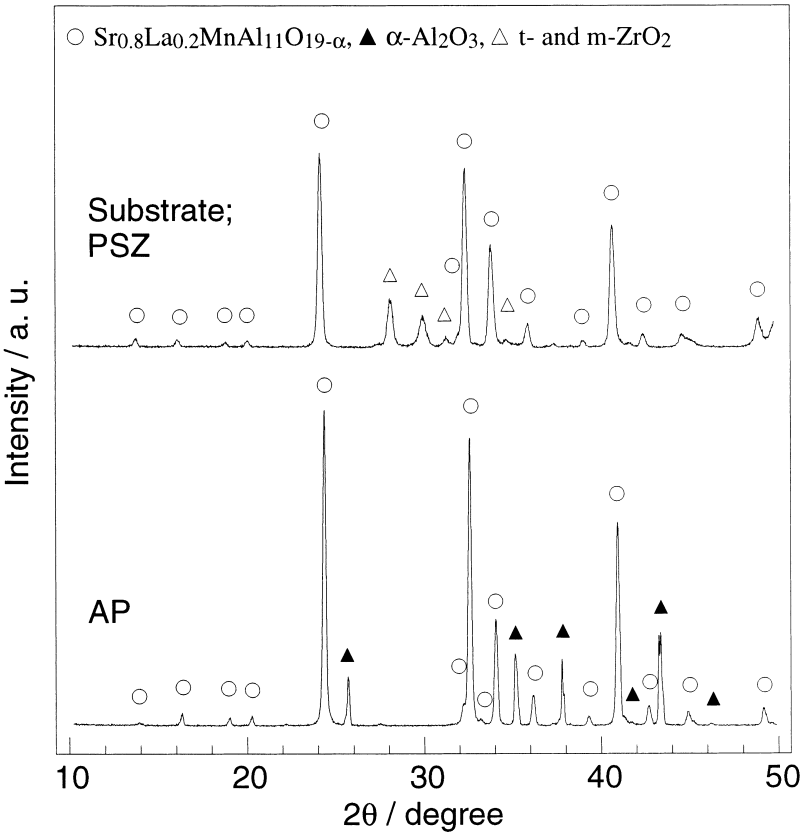


Fig. 5. XRD patterns of the hexaaluminate films coated on (a) partially stabilized zirconia (PSZ), and (b) pure alumina (AP) calcined at 1500°C.

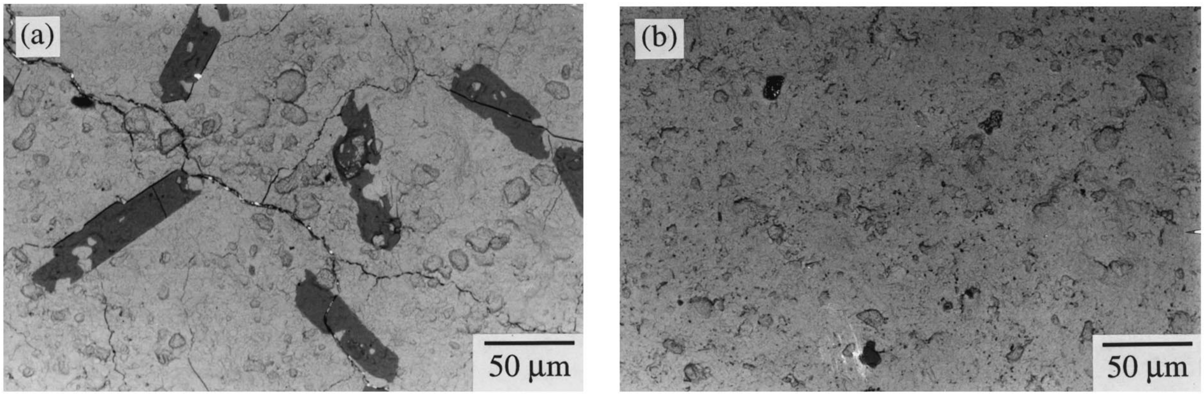


Fig. 6. Backscattered electron image of the hexaaluminate film on (a) partially stabilized zirconia (PSZ), and (b) pure alumina (AP) calcined at 1600°C.

the PSZ and AP substrates became distinct. Backscattered electron images of the SLMA film heated at 1600°C for 5 h in air are shown in Fig. 6. In SLMA/PSZ, many large dense grains and cracks were observable. The cationic component in the large grains was analyzed to be only Al by EDX, and XRD patterns of this sample were assigned to α-Al_2O_3. These observations indicate that the large grains observed by SEM correspond to α-Al_2O_3. Results of elemental analysis on the fracture surface of SLMA/PSZ and SLMA/AP are shown in Table 2. Although, the components of the PSZ substrate hardly migrated into the SLMA film, Sr of the SLMA diffused into the substrate. XRD patterns of the sample were assigned to PSZ, SLMA, and α-Al_2O_3 phases. Since a large amount of α-Al_2O_3 phase led to a local increase of the density, cracks were also created by the large dense grains.

On the other hand, neither cracks nor exfoliation were observed in the microstructure of SLMA/AP after heat treatment at 1600°C (Table 2). XRD patterns indicate that SLMA/AP consisted of the SLMA and AP phases without impurities. The atomic fractions of Sr, La, and Al in each part of the film were uniform and almost the same as those of the SLMA disk sintered at 1600°C. The amount of Mn diffusion in the substrate was insignificant as compared to that in the PSZ substrate. It is concluded that the thermal stability of SLMA film coated on an oxide

Table 2
Composition of the hexaaluminate film on the partially stabilized zirconia (PSZ) and pure alumina (AP) after calcination at 1600°C for 5 h

Sample position	Fraction/atom (%)					
	Al	La	Mn	Sr	Y	Zr
SLMA/PSZ						
top of the film	87.8	3.5	3.2	4.8	0.0	0.7
middle of the film	88.5	3.3	3.2	4.8	0.0	0.2
bottom of the film	88.1	3.7	3.6	4.3	0.0	0.3
top of the substrate	5.0	1.2	0.9	3.9	10.0	79.0
inner part of the substrate	3.2	0.7	1.1	3.2	9.3	82.5
SLMA/AP						
top of the film	89.2	3.0	2.2	5.6		
middle of the film	88.4	3.2	2.9	5.5		
bottom of the film	89.0	3.3	3.1	4.6		
top of the substrate	99.6	0.2	0.3	0.0		
inner part of the substrate	99.6	0.2	0.2	0.0		

ceramic substrate greatly depends on the extent of diffusion of components constituting the film and the substrate at a high temperature. SLMA/AP showed excellent thermal stability among these ceramic composites.

3.4. Sintering behavior and composition of SLMA microcrystal in the film

The relative intensity of each diffraction peak assigned to the SLMA film was dependent on the kind of substrate as shown in Fig. 5. The difference in the relative peak intensity implies preferential orientation of the SLMA microparticles in the film. To elucidate this preferential orientation, XRD patterns of SLMA/AP held at various temperatures are summarized in Fig. 7. In disordered SLMA powder, the most intense XRD peak was the (107) line. The other diffraction peak intensities were referenced to that of the (107) line. The intensity of each peak, assigned to the SLMA phase calcined at 1300°C, was almost the same as that of the calcined SLMA powder. This indicates that SLMA microparticles were randomly oriented in the slurry coating process. When the heat treatment temperature was raised up to 1400°C, the relative intensities of the (002), (006), (008), (0010), and (0014) lines from the SLMA phase increased systematically. The growth of these [00n] peaks became more obvious at 1500°C or higher temperatures. This suggested that the SLMA microparticles began to rearrange preferentially by making the basal plane of the thin platelike hexaaluminates parallel to the surface of the substrate. XRD measurement was also carried out for the sample which was prepared by mechanical grinding of the SLMA and AP mixture. The relative intensity of each diffraction peak of the

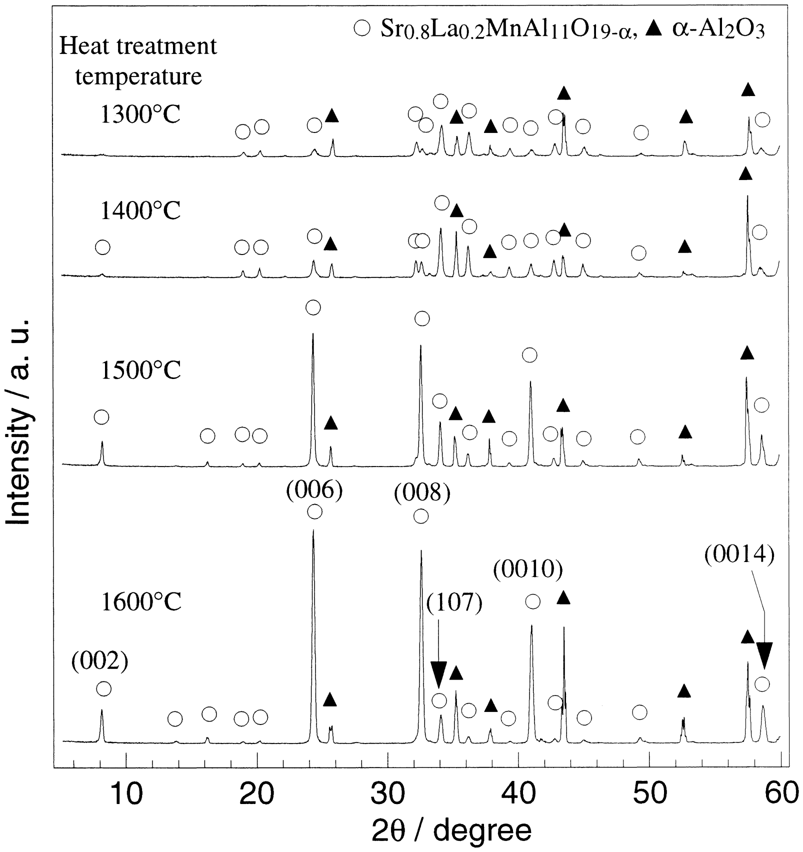


Fig. 7. XRD patterns of the $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ (SLMA) films coated on pure alumina (AP).

ground SLMA sample was the same as that of the calcined SLMA powder.

A similar change in the relative intensity of the each peak assigned to the SLMA phase was also observed for SLMA/PSZ and the SLMA disks which were prepared by uniaxial pressing of the SLMA powder calcined at 1200°C into a disk, and subsequently heated above 1500°C. The rearrangement of platelike particles in the powder compact on the sintering process was also reported by Ichikawa et al. [12].

The Mn content in SLMA films prepared on PSZ and AP substrates decreased with an increase in the heat-treatment temperature, as shown in Tables 1 and 2. Since Mn is the redox center for oxidation of hydrocarbons over the SLMA catalyst, the Mn content of the SLMA film is an important parameter in evaluating the catalytic activity. The dependence of the Mn content in the film, the sintered disk, and the calcined powder on the heat-treatment temperature was estimated (Fig. 8). The Mn content at the surface of the disk and film sample monotonously decreased with increasing sintering temperature in air. In addition, the sample disk sintered at 1300°C possessed a rather low Mn content as compared to the powder. With the decrease of Mn content due to volatilization, grain growth of the hexaaluminate particles was facilitated, especially at the surface. It is required to optimize the coating and heating process to prepare SLMA-coated honeycombs by taking the operating conditions into consideration. The optimization of the Mn concentration in the film is suggested to be important, since the depletion of Mn from the surface of the film due to volatilization decreases the number of the active centers of the catalytic reaction.

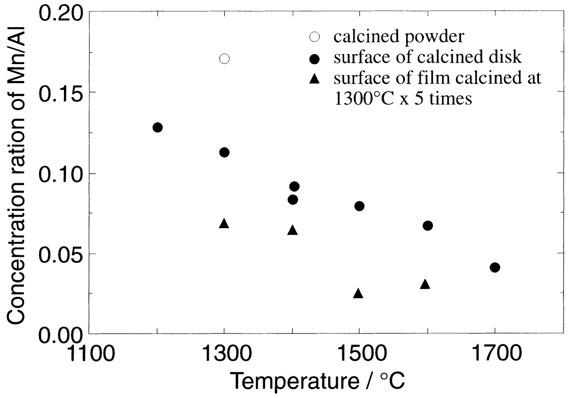


Fig. 8. Concentration ratio of Mn/Al in $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ powder, disk, and films after various heat treatments.

4. Conclusions

Thick film coating of hexaaluminate catalyst on thermally stable ceramic substrates was investigated for high-temperature combustion. Insertion of an intermediate layer between the film and substrate is effective for hexaaluminate/α-SiC. The thermal stability of the hexaaluminate films depended on both, the coated hexaaluminate species and calcination temperature of the hexaaluminate prior to dipping. The prepared quadruple layered sample of BMA/BA/mullite/α-SiC maintained the porous microstructure of the upper BMA and BA films, even after heat treatment at 1400°C. The high thermal stability was achieved by the buffer actions of these intermediate layers suppressing the reaction between the hexaaluminate film and SiO_2. SLMA/PSZ and SLMA/AP also maintained the porous microstructure up to 1500°C in a stable manner. Although, many large α-Al_2O_3 grains and cracks were formed for SLMA/PSZ because of the selective diffusion of Sr from the film into the substrate after heat treatment at 1600°C, SLMA/AP maintained its crystalline phases and morphology. Hexaaluminate film rearranged so as to preferentially orient the (001) plane parallel to the substrate surface of increasing temperatures. This preferential orientation of the hexaaluminate was supposed to result from the rearrangement and the grain growth which proceeded to decrease the volume of the film on the sintering process.

Acknowledgements

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