J Mater Sci (2006) 41:7401–7405
DOI 10.1007/s10853-006-0799-8

Forming and sintering of porous calcium-hexaaluminate ceramics with hydraulic alumina

T. Nagaoka · T. Tsugoshi · Y. Hotta ·
M. Yasuoka · K. Watari

Received: 25 May 2005 / Accepted: 29 November 2005 / Published online: 20 September 2006

Abstract We have developed a new eco-friendly fabrication process for porous ceramics using hydraulic alumina (HA) and water. In the present study, we fabricated porous calcium-hexaaluminate ($CaAl_{12}O_{19}$, CA6) ceramics using this new process. A boehmite gel 3-D network was formed by the hydration of HA in HA/$CaCO_3$ mixed slurry. The HA/$CaCO_3$ mixed slurry was hardened by the formation of this 3-D network. Even without the addition of an organic binder, green bodies containing the 3-D network demonstrated high compressive strength and retained their original shapes. Furthermore, the water acted as a fugitive material in the green bodies. Consequently, the open porosity of the CA6 ceramics could be controlled over a wide range of 42–62.7% by the addition of water (ratio of water to HA/$CaCO_3$ mixed powder: 0.4 to 1.6 by weight) without the use of organic fugitive materials. The results of evolved gas analysis-mass spectrometry measurements showed that the emissions from the hardened green body consisted mostly of water. Consequently, the new fabrication process for porous calcium-hexaaluminate ceramics was confirmed to be eco-friendly.

Introduction

Hexaaluminates are promising materials for these high-temperature applications. These compounds have plate-like morphology and high sintering resistance because of the layered crystal structure. Then hexaluminates are already the subject of extensive research for catalytic applications [1–3]. Furthermore, one of these compounds has relatively high strength [4]. Consequently porous hexaaluminate ceramics are expected to use for filter materials, light structural components and catalysts carriers at high temperatures.

These porous ceramics can be fabricated using organic binders such as polyvinyl alcohol and methyl cellulose to consolidate the powder mixture and fugitive materials such as acrylic beads, starch and latex to create pores [5–9]. The role of a binder is to provide green strength so that a green body can be formed and will retain its desired shape before heating. Acrylic beads, carbon powder, and starch are widely used as fugitive materials for creating pores in porous ceramics [9, 10]. The pore size and porosity of porous ceramics can be adjusted by adjusting the sizes of the fugitive materials and the amounts added.

However, these organic binders and fugitive materials must be completely thermally decomposed so that they do not remain in the sintered body as carbon or ash. Moreover, large volumes of gases such as carbon dioxide and hydrocarbon species are emitted from the green body during heating. CO_2 is believed to be one of the greenhouse gases responsible for global warming, while emitted hydrocarbons can be malodorous as well as harmful. It is necessary to pyrolytically decompose the hydrocarbon species further to defuse them, which requires thermal energy, thus further increasing emissions of CO_2. Therefore, total volume of emitted CO_2 gas in the ceramic processing rises with increasing

---

T. Nagaoka (✉) · T. Tsugoshi · Y. Hotta · M. Yasuoka ·
K. Watari
National Institute of Advanced Industrial Science
and Technology (AIST) Chubu, 2266-98, Anagahora,
Shimoshidami, Moriyama-ku, Nagoya 463-8560, Japan
e-mail: t.nagaoka@aist.go.jp

amounts of emitted hydrocarbon species. It is therefore important to develop an eco-friendly ceramic fabrication process employing inorganic substances that can reduce the amounts of organic substances used.

Hydraulic inorganic binders are promising materials for the consolidation of starting powders in green bodies with water by hydration and conversion into ceramics during heating [11, 12]. During this process, the emission of harmful gases is unlikely. Hydraulic alumina (HA) is an important mineral phase of hydraulic inorganic binders, and has been studied for use as a hydraulic inorganic binder in high-alumina castable refractory [13]. The main phase of HA is ρ-Al_2O_3, an intermediate alumina. The hydration of ρ-Al_2O_3 forms bayerite and boehmite gel as follows [13]:

$$\rho\text{-}Al_2O_3 + H_2O \rightarrow \underset{\text{(Bayerite)}}{Al_2O_3 \cdot 3H_2O} + \underset{\text{(Boehmite gel)}}{Al_2O_3 \cdot 1\text{-}2H_2O}.$$

This hydration process is not affected by a CO_2 atmosphere, with other hydraulic inorganic binders such as calcium monoaluminate ($CaAl_2O_4$), calcium dialuminate ($CaAl_4O_7$), and barium monoaluminate ($BaAl_2O_4$). Furthermore, hydrated HA is converted during heating into α-Al_2O_3, one of the main components of oxide ceramics. HA, therefore, has potential for use as a hydraulic inorganic binder in alumina-based ceramics processing. Another unique advantage of using HA is microstructure control of the green body by hydration of HA: it appears possible to control the mechanical properties of the green body, sinterability and microstructure of the sintered body by controlling the composition and morphology of the HA hydrates.

Added water is predicted to create numerous pores through the dewatering process during heating, acting as a fugitive material that does not produce any harmful gases, suggesting that a sintered body with high porosity is obtained if a large amount of water can be held in the green body. As mentioned above, the HA and water are expected to act as eco-friendly agents for consolidating the starting powders and creating pores.

This paper reports on the new eco-friendly fabrication process for porous calcium-hexaaluminate ($CaAl_{12}O_{19}$, CA6) ceramics, one of the hexaaluminate ceramics with a wide range of porosities using HA, $CaCO_3$ and water. The major gas species evolved during heating were also investigated by means of gas analysis.

Experimental procedure

Sample preparation

Hydraulic alumina (HA, BK-105, 99.7% purity, Sumitomo Chemical Co., Ltd., Japan) with a mean particle size of 5 μm and $CaCO_3$, (reagent grade, 99.9% purity, Wako Pure Chemical Co., Ltd., Osaka, Japan) were used as starting powders. Water contents of the HA measured by thermo gravimetric analysis was 9.8 mass%. The molar ratio of HA and $CaCO_3$ was 6.0, which coincides to the stoichiometric valence of CA6. A planetary ball mill with a pair of alumina pots containing alumina balls (diameter: 5 mm) was used to mix the HA and $CaCO_3$ powder. The HA and $CaCO_3$ were ground with methanol in the mill pot at 300 rpm for 1 h. The ground mixtures were dried at 60 °C for 30 min in a vacuum, and then screened through a #150-mesh sieve.

The mixed powder and distilled water were mixed using a mortar and pestle. The ratio of water to HA/$CaCO_3$ mixed powder by weight (water ratio, hereinafter referred to as "WR") ranged from 0 to 1.6. Then the mixed powder/water mixture was uniaxially pressed (WR = 0–0.4) or cast into the molds to form rectangular bars ($20 \times 8 \times 8$ mm) for compressive strength measurements, after which the molds were kept tightly covered with laboratory film. The samples in the molds were cured at 25 °C for 24 h in a container kept at over 90% relative humidity. The samples were taken out of the molds after 24 h. The hardened samples (green bodies) were slowly dried at room temperature, and then sintered at 1,600 °C for 2 h in air. To protect the green bodies from cracking during dehydration, a slow heating rate (10 °C/h) was applied at low temperatures.

Characterization of the porous alumina-based ceramics

Green densities were calculated from the samples using simple volume and mass measurements. Compressive strength measurements of the green bodies were performed using a mechanical test machine (AG-1S, Shimadzu, Japan) and measured by a 5 kN load cell. The green bodies were loaded at a displacement rate of 0.5 mm/min. Compressive strength was calculated by dividing the peak load by the area (8×8 mm^2). The number of the samples used was two and three. X-ray diffraction (XRD) analysis was performed on the hydrated HA/$CaCO_3$ mixed slurry with WR = 1.2 to study the crystalline phase evolution as a function of curing time. The measurements were performed using an X-ray diffractometer (RAD-RU powder diffractometer, Rigaku, Tokyo, Japan) with Cu Kα radiation (40 kV, 400 mA). The fracture surfaces of the samples were observed using a scanning electron microscope (SEM) (Model JSM-6340F, JEOL, Japan). Samples for XRD analysis and SEM observation were immersed in methanol and acetone for 10 min each and dried to stop the hydration. The bulk density and open porosity of the sintered samples were measured using Archimedes' method. The pore size distributions of the sintered samples were measured using the mercury intrusion method. Mercury porosimetry (Model 9420, Shimadzu Corp., Japan) provided pore-size distribution data for the sintered samples. The porosity values obtained by Archimedes' method and mercury porosimetry were in good agreement (within 5%).

The major gas species evolved by pyrolysis of the hydrated HA/$CaCO_3$ samples prepared by this new process and a conventional α-Al_2O_3/$CaCO_3$ sample with an organic binder (commercially available polyvinyl alcohol) and fugitive material (acrylic beads) were investigated by means of evolved gas analysis-mass spectrometry (EGA-MS) [14].

Results and discussion

Forming with hydraulic alumina

In the early stages of curing, the mixed starting powder with water (WR = 0.4–1.6) did not solidify, especially for samples with large amounts of water (WR > 0.8). However, all the samples hardened in molds after curing at 25 °C for < 24 h. Figure 1 shows the green density and average compressive strength of the cured samples. The green density and average compressive strength decreased from 1.77 to 1.29 g/cm^3 and from 11.8 to 0.2 MPa, respectively, as the water ratio increased (WR = 0.4–1.6). Although the compressive strength of the green bodies with high levels of water (WR = 1.2–1.6) was lower (< 1.7 MPa) than that of green bodies without water (2.9 MPa), these green bodies retained their original shapes.

Figure 2 shows the XRD patterns of the HA and $CaCO_3$ mixture with water (WR = 1.2) cured at 25 °C for various times. XRD indicates that $CaCO_3$ was the major crystalline phase and two broad peaks, believed to be χ-Al_2O_3 and ρ-Al_2O_3, were observed in the sample before hydration. The XRD patterns of the sample cured for 8 h was almost the same as those of the HA powder before hydration. A small broad peak, believed to be that for boehmite gel, was observed in the sample cured for 16 h. As the curing time increased, the peak intensity of the boehmite gel increased.

Figure 3 shows SEM photographs of the fracture surfaces of the green bodies without water and WR = 1 cured at 25 °C for 24 h. A three-dimensional (3-D) network is observed in the sample cured for 24 h, as shown in Fig. 3b. The results of the XRD analysis show this 3-D network to be boehmite gel. This result, together with the result of the compressive strength test, indicates that the boehmite gel 3-D network hardened the HA/$CaCO_3$ slurry and holds a large amount of water.

Microstructure of porous CA6 ceramics

XRD analysis revealed that CA6 was single crystalline phase in the sintered (1,600 °C for 2 h) samples and no other calcium-aluminate phase was detected. Figure 4

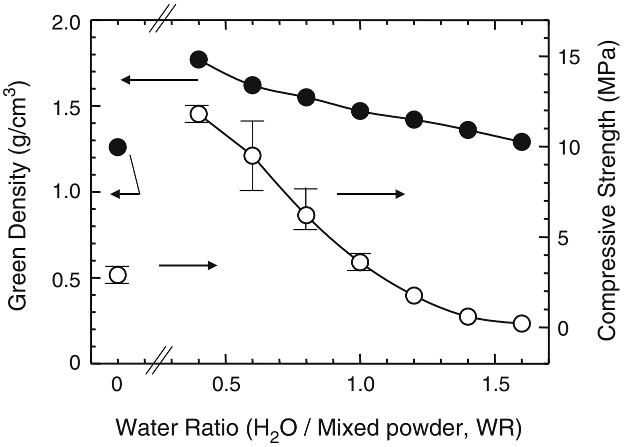


Fig. 1 Green density and compressive strength of the samples with different water ratios (WR = 0–1.6) cured at 25 °C for 24 h

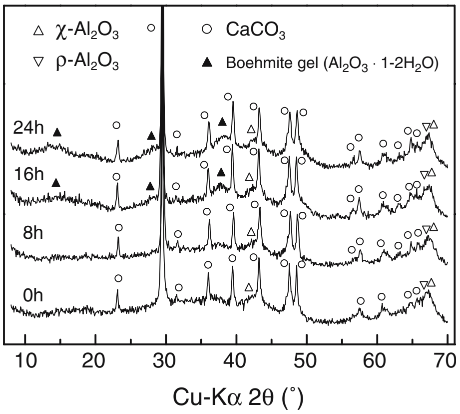
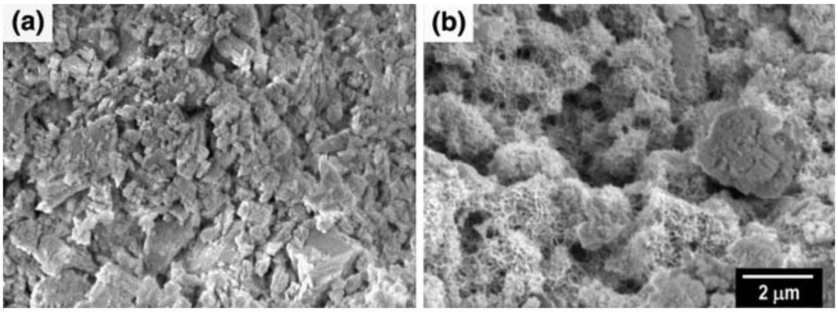


Fig. 2 XRD patterns of the samples with WR = 1 cured at 25 °C. Note: 0 h indicates HA/$CaCO_3$ mixed powder before hydration

Fig. 3 SEM photographs of the samples (**a**) HA/$CaCO_3$ mixed powder and (**b**) HA/$CaCO_3$ mixed powder with WR = 1 cured at 25 °C for 24 h



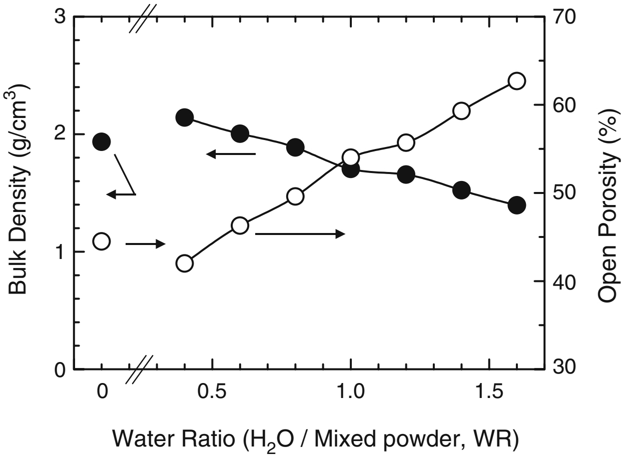
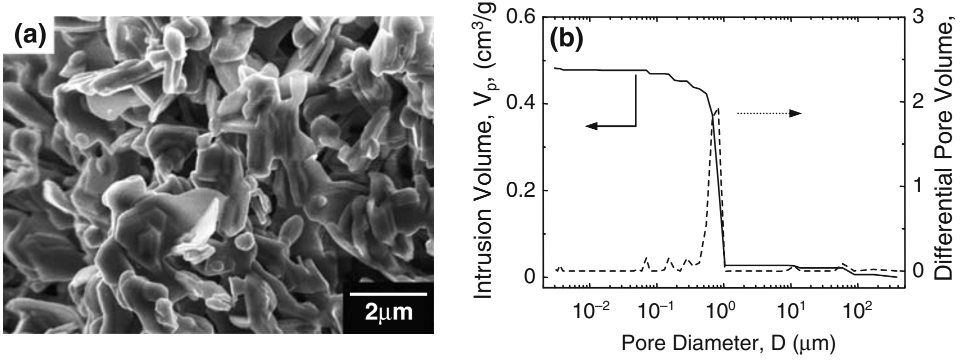


Fig. 4 Bulk density and open porosity of the samples with different water ratios sintered at 1,600 °C for 2 h

shows the bulk density and open porosity of the samples sintered at 1600 °C for 2 h. The bulk densities of the sintered samples decreased slightly from 2.14 to 1.40 g/cm^3 with increasing water ratio (WR = 0.4–1.6). The results of measurements by Archimedes' method show that the pores in the sintered samples were almost all open pores. The open porosity increased from 42.0% to 62.7% linearly with increasing water ratio (WR = 0.4–1.6). Although the addition of a large amount of water was expected to create a large pore volume, the open porosity increased only by 42.0 to 62.7 vol% due to shrinkage of the samples during heating. Nevertheless, the water acted as a fugitive material in the green bodies. In this study, it is conceivable that not only the addition of water but also dehydration from HA, decomposed CO_2 gas from $CaCO_3$ and interlocking of the CA6 platelike grains contribute to CA6 pore formation. In these factors, the addition of water also proved useful in controlling the wide range of open porosities seen in porous CA6 ceramics.

Figure 5a shows SEM photograph of the porous CA6 ceramics using the HA/$CaCO_3$ mixed powder with water (WR = 1.6) sintered at 1,600°C for 2 h. A well-developed 3-D network structure was observed in the sintered sample. CA6 plate-like grains were connected to each other via thick necks. Figure 5b shows the pore size distribution of the porous CA6 ceramics sintered at 1,600°C. Median pore diameter of these samples with WR = 1.6 was 0.78 μm. The distribution pattern shows a relatively narrow pore size distribution, however the mixed powder and water were mixed using a mortar and pestle. This result shows that the added water was dispersed homogeneously in the HA/$CaCO_3$ mixed powder and acted as a fugitive material of uniform size. In addition, since this porous CA6 ceramics has a narrow pore size distribution, it has potential for use as a filtration material. Thus, porous CA6 ceramics with a wide range of open porosity and a narrow pore size distribution can be produced by this new process using HA/$CaCO_3$ mixed powder and water.

Fig. 5 (**a**) SEM micrograph and (**b**) pore size distribution of the sample with WR = 1.6 sintered at 1,600 °C for 2 h



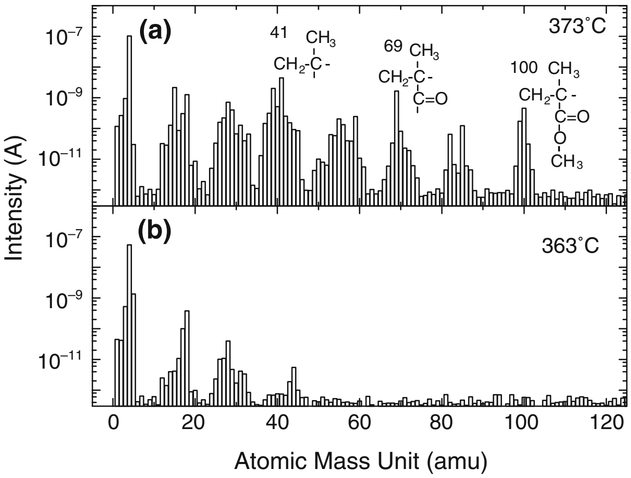


Fig. 6 EGA-MS spectra of green bodies: (**a**) α-Al_2O_3/$CaCO_3$ green body with 1 mass% organic binder (polyvinyl alcohol) and 20 mass% fugitive material (acrylic beads) and (**b**) hardened green HA/$CaCO_3$ (WR = 1)

EGA-MS measurement

Figure 6a shows the EGA-MS spectrum obtained from the α–Al_2O_3/$CaCO_3$ green body with 1 mass% polyvinyl alcohol as the organic binder and 20 mass% acrylic beads as the fugitive material at 373 °C. The peak intensities of the larger fragmented ions are high. These fragmented ions, such as 41, 69 and 100 amu are thought to be hydrocarbon species, e.g., C_3H_5, C_4H_5O and $C_5H_8O_2$, respectively, originating as pyrolyzed species of the polyvinyl alcohol and acrylic beads. These emitted hydrocarbon species can be malodorous as well as harmful. On the other hand, in the case of the hardened HA/$CaCO_3$ green body prepared using this new process (WR = 1), although the peak intensity of 18 amu, identified as H_2O due to the dehydration of the hydrated HA, was high, larger ion fragments, considered to be hydrocarbons, were rare. Since the emitted hydrocarbons can be harmful, it is necessary to pyrolytically decompose these gases further to defuse them, which requires thermal energy, thus further increasing emissions of CO_2. In this new process, the peak intensities of hydrocarbon were low, with the peak intensity of CO_2 (2.92×10^{-13} A) being 30.5% of that (9.58×10^{-13} A) emitted when using the conventional method. Therefore, our approach using HA as a hydraulic inorganic binder and water as a fugitive material in the fabrication of porous CA6 ceramics is confirmed to be an environmentally friendly technology.

Conclusions

A new eco-friendly fabrication process was developed employing HA and water. In this study, porous calcium hexaaluminate ceramics ($CaAl_{12}O_{19}$, CA6), one of the porous hexaaluminate ceramics, were prepared by this new process. The HA/$CaCO_3$ samples with water were hardened by the formation of a boehmite gel 3-D network. Even without the addition of an organic binder, hardened HA/$CaCO_3$ samples (green bodies) had high compressive strength and retained their original shapes. The green bodies contained a large amount of water, which acted as a fugitive material. Consequently, the open porosity of the sintered CA6 ceramics could be controlled by the addition of water without the use of organic fugitive materials. The results of evolved gas analysis-mass spectrometry measurements confirm that our approach, using HA as a hydraulic inorganic binder and water as a fugitive material in the fabrication of porous CA6 ceramics, is an environmentally friendly technology.

References

1. Inoue H, Sekizawa K, Eguchi K, Arai H (1997) J Am Ceram Soc 80:584
2. Machida M, Eguchi K, Arai H (1988) J Am Ceram Soc 71:1142
3. Machida M, Eguchi K, Arai H (1987) J Catal 103:385
4. Nagaoka T, Kanzaki S, Yamaoka Y (1990) J Mater Sci Lett 9:219
5. Benbow JJ, Oxley EW, Bridgwater J (1987) J Chem Eng Sci 42:2151
6. Kristffersson A, Roncari E, Galassi C (1998) J Eur Ceram Soc 18:2123
7. Kristffersson A, Carlström E (1997) J Eur Ceram Soc 17:289
8. Sawyer CB, Reed JS (2001) J Am Ceram Soc 84:1241
9. Lyckfeldt O, Ferreira JMF (1998) J Eur Ceram Soc 18:131
10. Lindqvist K, Linden E (1997) J Eur Ceram Soc 17:359
11. Nagaoka T, Iwamoto Y, Kikuta K, Hirano S (2000) J Am Ceram Soc 83:1613
12. Nagaoka T, Iwamoto Y, Kikuta K, Hirano S (2001) Ceram Trans 112:831
13. Hongo Y (1979) Taikabutsu 31:647
14. Tsugoshi T, Furukawa M, Ohashi M, Iida Y (2001) J Thermal Anal Calorim 64:1127