In Situ Synthesis and Microstructure of Porous CaAl_4O_7 Monolith and $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ Composite

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多孔質 CaAl_4O_7 単相及び $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ 複合材料の *In Situ* 合成と微細構造

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In situ processing and microstructure of calcium dialuminate (CaAl_4O_7)-based porous materials have been investigated. Powder mixtures of CaCO_3 and $\alpha\text{-Al}_2\text{O}_3$ (1 : 2 in molar ratio, doped with 0.5 mass% LiF), and CaCO_3 , $\alpha\text{-Al}_2\text{O}_3$, and ZrO_2 (2 : 2 : 1 with 0.5 mass% LiF) were prepared by a high-energy ball-mill process. Reactions of the powder mixtures during heating processes were revealed by high-temperature X-ray diffraction (HT-XRD), and by thermogravimetry and differential thermal analysis (TG-DTA). Porous CaAl_4O_7 monolith and its $\text{CaAl}_4\text{O}_7/50$ mol% CaZrO_3 composite have been successfully synthesized using reactive pressureless sintering (at 1100–1200°C, for 2 h in air) of powder mixtures. Both porous monolith and composite had homogeneous microstructure and very narrow pore-size distribution with mean pore size of ~ 1 μm . These porous materials, which are expected to have good thermal shock resistance, can be applied to high-temperature gas filters and lightweight structural components.

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1. Introduction

Calcium dialuminate, CaAl_4O_7 , is a refractory compound (melting point: $1765 \pm 25^\circ\text{C}$) in the $\text{CaO-Al}_2\text{O}_3$ binary system.^{1,2)} CaAl_4O_7 is a component phase of high-alumina cements,³⁾ and often called as “ CA_2 ” in the cement industry. CaAl_4O_7 is also found in natural terrestrial rocks and meteorites.⁴⁾ It was termed “grossite” in the mineralogical field in 1994.⁴⁾ Although calcium aluminates, except $\text{CaAl}_{12}\text{O}_{19}$ (CA_6), react with water to form hydrates, CaAl_4O_7 has much lower hydration rate than $\text{Ca}_3\text{Al}_2\text{O}_6$ (C_3A), $\text{Ca}_5\text{Al}_6\text{O}_{14}$ (C_5A_3), and CaAl_2O_4 (CA).⁵⁾

Recently, Jonas et al.^{6,7)} reported that CaAl_4O_7 is a promising, non-silicate high-temperature structural ceramic with high-thermal shock resistance, because of its low thermal expansion among aluminates ($\alpha = 4.1 \times 10^{-6}/^\circ\text{C}$ up to 900°C ⁶⁾). Thus, they prepared CaAl_4O_7 monolith,⁶⁾ $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ composites,⁶⁾ and $\text{CaAl}_4\text{O}_7/\text{MgAl}_2\text{O}_4$ composites,⁷⁾ and investigated the microstructure and thermal properties. Despite the favorable thermal property of CaAl_4O_7 phase, it is generally difficult to synthesize single-phase CaAl_4O_7 ; for example, Jonas et al. prepared CaAl_4O_7 phase by three-step calcination, successively at 1200, 1300 and 1450°C , and repeated several times after pulverizing. However, some residual intermediate reaction products (possibly CaAl_2O_4) were still observed.^{6,7)}

The present authors have recently reported that novel porous $\text{CaZrO}_3/\text{MgO}$ composites with 3-D network structure can be synthesized via single-step reactive sintering of highly-pure mixtures of dolomite and zirconia powders.⁸⁾ It has been found that the combination of LiF-doping and planetary ball-milling was fairly effective to accelerate the *in situ* reactions and to produce homogeneous microstructure.⁸⁾ Such porous composites are promising filter materials with good structural stability at high-temperatures.

In this study, we have synthesized CaAl_4O_7 monolith and $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ composites via single-step reactive sintering of CaCO_3 , Al_2O_3 , and ZrO_2 with LiF-doping, similarly to

the above-mentioned $\text{CaZrO}_3/\text{MgO}$ system. By changing sintering temperature, both porous (with very narrow pore-size distribution; sintered at $1100\text{--}1200^\circ\text{C}$) and dense materials (sintered at $1300\text{--}1400^\circ\text{C}$) were successfully obtained. This paper mainly focuses on processing of the porous products; the reaction behavior, microstructure and pore structure of the porous CaAl_4O_7 monolith and the $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ composites will be described.

2. Experimental procedure

2.1 Source and processing

Commercially available CaCO_3 (99.5% purity, Kojundo Chemical Laboratory Co., Ltd.), $\alpha\text{-Al}_2\text{O}_3$ (99.99% purity, 0.15 μm particle size, 14 m^2/g , Taimei Chemicals Co., Ltd.), pure ZrO_2 (99.9%, 46 nm particle size measured by XRD, Sumitomo Cement Co., Ltd.) and LiF (99.9%, Wako Pure Chemical Ind., Ltd.) were used as the starting powders.

To synthesize CaAl_4O_7 monolith, CaCO_3 and Al_2O_3 powders (1 : 2 in molar ratio) with LiF (0.5 mass% for total starting powders) were wet-ball milled in ethanol for 6 h by using a high-energy planetary ball-mill process (acceleration: 6 G). The mixed slurries were dried, subsequently dry-ball-milled for 24 h, and then, sieved through a 100-mesh screen. The mixed powders were cold isostatically pressed at 200 MPa after mold-pressing. The green compacts (15 mm in diameter and ~ 5 mm in thickness) were sintered in air at 1100° to 1400°C for 2 h.

To produce $\text{CaAl}_4\text{O}_7/50$ mol% CaZrO_3 composite, the mixture of CaCO_3 : Al_2O_3 : $\text{ZrO}_2 = 2 : 2 : 1$ in molar ratio (doped with 0.5 mass% LiF) was used as the starting materials, and treated in the same manner as above.

2.2 Analyses of the reaction behavior of the mixed powders

The reaction behavior of the mixed powders was studied by *in situ* high-temperature X-ray diffraction (HT-XRD) in an X-ray diffractometer (Scintag, X1 system) with a vertical-type goniometer, a Si solid-state detector, and a Peltier

refrigerator. A Pt direct heating stage ($10\text{ mm} \times 50\text{ mm} \times 0.15\text{ mm}$) was used. Figure 1 shows a schematic illustration of the Pt heating stage. XRD patterns of the mixed powders were acquired using $\text{Cu K}\alpha$ radiation operated at 45 kV and 40 mA in the range between room temperature and 1300°C in air. The heating rate for HT-XRD was $10^\circ\text{C}/\text{min}$, which was the same as that for the bulk sintering. Each measurement was conducted after 3-min holding.

The reaction behavior of the mixed powders was also studied via thermogravimetry and differential thermal analysis (TG-DTA) up to 1500°C ($10^\circ\text{C}/\text{min}$) in a static air atmosphere.

2.3 Characterization of the bulk materials

Constituent phases of the sintered materials were ana-

Fig. 1. Schematic illustration of a direct heating stage for high-temperature *in situ* X-ray diffraction. A Pt strap heater attached with Pt-Pt/Rh thermocouple was used. Measurements were conducted in air.

lyzed by an X-ray rotating anode diffractometer (Model Rotaflex, Rigaku, Tokyo), $\text{Cu K}\alpha$ at 40 kV and 100 mA. The microstructure was characterized using a scanning electron microscope (SEM; Model 6330F, JEOL, Tokyo).

The porosity and the pore-size distribution of the sintered materials were determined by mercury porosimetry (Poresizer 9320, Micromeritics, Norcross, GA, USA). Mercury intrusion was carried out at pressures between 0 to 207 MPa. Cylindrical pore model⁹⁾ was used for the calculation of the total pore volume (V_p), specific surface area (S_p), median pore diameter ($D = 4V_p/S_p$), and porosity (P).

3. Results and discussion

3.1 HT-XRD and TG-DTA analyses of the mixed powders

Figures 2 (a) and (b) show HT-XRD patterns for (a) the $\text{CaCO}_3\text{-Al}_2\text{O}_3$ mixture (1 : 2 in molar fraction, with 0.5 mass% LiF), and (b) the $\text{CaCO}_3\text{-Al}_2\text{O}_3\text{-ZrO}_2$ mixture (2 : 2 : 1 in molar fraction, with 0.5 mass% LiF), respectively. As can be seen from Fig. 2 (a), CaCO_3 began to decompose at $<800^\circ\text{C}$ to form CaO , following Eq. (1).

At 800°C , diffraction peaks of CaO were clearly observed, and those of CaCO_3 disappeared. At $\sim 800\text{--}900^\circ\text{C}$, CaO started to react with Al_2O_3 to form an intermediate phase, viz. CaAl_2O_4 (CA), following Eq. (2).

A direct reaction between CaCO_3 and Al_2O_3 may be also taken place in some extent. At 1100°C , the peak-intensities of CaAl_2O_4 decreased, and CaAl_4O_7 phase began to be generated, following Eq. (3).

At 1300°C , intermediate CaAl_2O_4 phase completely disappeared, and only CaAl_4O_7 was identified. Note that the

Fig. 2. (a) High-temperature *in situ* X-ray diffraction (HT-XRD) patterns for the $\text{CaCO}_3\text{-Al}_2\text{O}_3$ mixture (1 : 2 in molar fraction) doped with 0.5 mass% LiF, following the reactions $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \uparrow (<800^\circ\text{C})$, $\text{CaO} + \text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_2\text{O}_4$ ($800\text{--}900^\circ\text{C}$), and then, $\text{CaAl}_2\text{O}_4 + \text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_4\text{O}_7$ ($\sim 1100^\circ\text{C}$); (b) HT-XRD patterns for the $\text{CaCO}_3\text{-Al}_2\text{O}_3\text{-ZrO}_2$ mixture (2 : 2 : 1) doped with 0.5 mass% LiF. The formation of CaAl_4O_7 was retarded because of the insufficient particle contact, i.e., dilution effect by ZrO_2 addition. The reaction $\text{CaO} + \text{ZrO}_2 \rightarrow \text{CaZrO}_3$ was also observed at $900\text{--}1200^\circ\text{C}$. Intermediate c- ZrO_2 (ss) was also identified at 1100°C .

peaks from the Pt direct-heating element increased at 1300°C, which demonstrates the increase in the exposed area of Pt.

As shown in Fig. 2(b), the formation mechanism of CaAl_4O_7 in the $\text{CaCO}_3\text{--Al}_2\text{O}_3\text{--ZrO}_2$ mixture was almost the same as the $\text{CaCO}_3\text{--Al}_2\text{O}_3$ system, but the formation was delayed because of the insufficient particle contact, i.e., a dilution effect by additional CaO and ZrO_2 . The CaZrO_3 formation started at 900°C, and was substantially completed at 1300°C. Intermediate cubic- ZrO_2 solid-solution was also identified at >1100°C, but its intensities decreased with elevating temperature; cubic- ZrO_2 solid-solution might form some ordered compound (CaZr_4O_9),¹⁰⁾ but peaks from the ordering were invisible in this study, due to kinetic (intrinsic) and/or resolutional (extrinsic) reasons. Details of the $\text{ZrO}_2\text{--CaZrO}_3$ system were given in the literature.¹⁰⁾ In contrast to Fig. 2(a), the peaks from Pt direct-heating element almost disappeared at 1300°C because a rather dense product covered the heater surface. The formation of dense product at 1300°C was also observed for a sintered bulk material as shown later.

Throughout, the lines of the HT-XRD patterns are noticeably sharp caused by “mineralization” action of the LiF. It helps to clarify complex reactions by producing sharp-line X-ray patterns at levels where the LiF is unobservable; this might be advantageously used more often for difficult transportation at syntheses.¹¹⁾

Figure 3 demonstrates the TG-DTA diagrams for (a) the LiF-doped $\text{CaCO}_3\text{--Al}_2\text{O}_3$ mixture (1 : 2 in molar fraction),

Fig. 3. TG-DTA diagrams for (a) the $\text{CaCO}_3\text{--Al}_2\text{O}_3$ mixture (1 : 2 in molar fraction), and (b) the $\text{CaCO}_3\text{--Al}_2\text{O}_3\text{--ZrO}_2$ mixture (2 : 2 : 1), doped with 0.5 mass% LiF for both systems. Measurements were conducted in air atmosphere at 10°C/min.

and (b) the LiF-doped $\text{CaCO}_3\text{--Al}_2\text{O}_3\text{--ZrO}_2$ mixture (2 : 2 : 1 in molar fraction), respectively. From Fig. 3(a), CaCO_3 started to liberate CO_2 gas at $\sim 500^\circ\text{C}$, and clearly decomposed into CaO and CO_2 at $700\text{--}800^\circ\text{C}$, judged from the weight loss and large endothermic peak at 766°C . A sharp exothermic peak at 866°C is attributable to the formation of intermediate CaAl_2O_4 phase. Shallow increase of DTA curve at $>900^\circ\text{C}$ is attributed to the progress of the reactions, and gentle endothermic peak at $\sim 1300\text{--}1400^\circ\text{C}$ is probably caused by the vaporization of LiF. The TG-DTA curves of the $\text{CaCO}_3\text{--Al}_2\text{O}_3\text{--ZrO}_2$ system are similar to those of the $\text{CaCO}_3\text{--Al}_2\text{O}_3$ system (Fig. 3(b)). However, the aforementioned exothermic peak (at $\sim 870^\circ\text{C}$) by CaAl_2O_4 formation became small, presumably because of the dilution effect. It seems to merge with the shallow increase in DTA curve at $>900^\circ\text{C}$. The small exothermic peak at 939°C can be explained by the formation of CaZrO_3 , but it was unclear due to the concurrent CaAl_4O_7 formation. In addition, rather complicated exo- and endothermic peaks were observed $\sim 1350^\circ\text{C}$. Possible reasons of these peaks may be; (1) the further formation of CaZrO_3 from cubic- ZrO_2 solid-solution (exo.), (2) the liquid phase formation via multi-phase eutectic reactions (endo.), and (3) the LiF vaporization (endo.). As a whole, the TG-DTA results were in fairly good agreement with the HT-XRD study.

3.2 Phase analysis and microstructure of the bulk materials

XRD patterns of the CaAl_4O_7 monolith and the $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ composite sintered at 1200°C are shown in Figs. 4 (a) and 4 (b), respectively. It is clearly demonstrated in Fig. 4(a) that single-phase CaAl_4O_7 was successfully fabricated by the single-step reactive sintering process. Moreover, the bulk materials sintered at 1100, 1300 and 1400°C from the LiF-doped $\text{CaO--Al}_2\text{O}_3$ system yielded almost identical XRD patterns; thus, in the powder compacts, the whole reactions substantially completed even at 1100°C , due to the sufficient particle contact and the reaction time (two-hour holding at maximum temperatures). Similarly to the monolithic CaAl_4O_7 system, the $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ composite sintered at 1200°C consisted of only these two phases (Fig. 4(b)). The composites sintered at different temperatures were also composed of these desired phases.

Figure 5 shows SEM micrographs of the bulk porous

Fig. 4. XRD patterns of the bulk porous materials sintered at 1200°C : (a) CaAl_4O_7 monolith and (b) $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ composite.

Fig. 5. SEM micrographs of the bulk porous materials sintered at 1200°C: (a) CaAl_4O_7 monolith and (b) $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ composite.

materials sintered at 1200°C: (a) CaAl_4O_7 monolith and (b) $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ composite. Equiaxed grains ($\sim 1 \mu\text{m}$) with bright contrast in Fig. 5(b) corresponds to CaZrO_3 phase. CaAl_4O_7 grains in both figures were elongated to some degree because of their crystalline anisotropy.⁴⁾ Both monolith and composite had well-developed necks and uniform open-porous structure, which was realized by the liquid formation via LiF doping, in analogy with the porous $\text{CaZrO}_3/\text{MgO}$ composites in the previous study.⁸⁾ Note that open-porosity values of these two materials were equally 32% by chance, as described below.

Figure 6 illustrates the total pore volume and the pore-size distribution of the monolith and composite sintered at 1200°C. These two materials had very narrow pore size distribution with mean size of $\sim 1 \mu\text{m}$. The pore-size distributions in these materials fairly resemble to those of the porous $\text{CaZrO}_3/\text{MgO}$ composites, which were produced similarly using carbonate source, LiF-doping and reactive sintering with CO_2 liberation.⁸⁾ Hence, we can deduce that this reactive sintering method is effective to make such uniformly open-porous materials not only for CaAl_4O_7 , $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$, and $\text{CaZrO}_3/\text{MgO}$ systems, but also other various oxides.

Table 1 summarizes the pore structure of CaAl_4O_7 monoliths and the $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ composites prepared at different sintering temperatures. Samples sintered at 1100°C and 1200°C for both monolith and composite had the uniform open-pore structure as shown in Fig. 6. The porosity values of these porous materials are acceptable for the use of gas filters at high temperatures, as well as that of lightweight structural components. Samples sintered at

Fig. 6. Pore size distribution determined by mercury porosimetry for the bulk porous materials sintered at 1200°C: (a) CaAl_4O_7 monolith and (b) $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ composite.

Table 1. Pore Structure of the CaAl_4O_7 Monoliths and $\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ Composites

Sintering temperature (°C)	V_p (cm^3/g) ^a	S_p (m^2/g) ^b	D_{top} (nm) ^c	D_{median} (nm) ^d	p (%) ^{††}
CaAl_4O_7 monolith					
1100	0.227	1.72	713	528	39
1200	0.163	0.69	995	945	32
1300	0.048	0.56	920 (165)	343	13
1400	0.029	0.47	726 (180)	247	7.3
$\text{CaAl}_4\text{O}_7/\text{CaZrO}_3$ composite					
1100	0.311	1.62	927	768	52
1200	0.131	0.50	1113	1048	32
1300	0.008	0.04	792	800	2.5
1400	0.001	0.00	—	—	0.2

^aTotal pore volume. ^bSpecific surface area, determined by mercury porosimetry.

^cPeak-top pore diameter. ^dMedian pore diameter, $D_{\text{median}} = 4V_p/S_p$.

^{††}Open porosity, $p = 100 \times V_p \times (\text{Sample mass})/(\text{Sample volume})$.

1300°C and 1400°C became much denser, particularly for the composites due to the higher sinterability of CaZrO_3 than CaAl_4O_7 . Details of microstructure and mechanical properties of the dense materials will be described in another report.

4. Conclusions

Porous CaAl_4O_7 monolith and porous $\text{CaAl}_4\text{O}_7/50\text{-mol}\%$ CaZrO_3 composite have been synthesized using *in situ* reac-

tive sintering of the $\text{CaCO}_3\text{-Al}_2\text{O}_3$ and the $\text{CaCO}_3\text{-Al}_2\text{O}_3\text{-ZrO}_2$ mixtures. Dense materials were also obtained by this pressureless reactive sintering process. A combination of HT-XRD and TG-DTA analyses clarified the reaction behavior of the mixed powders. Because of the liquid formation via LiF doping, strong necks were formed between constituent particles, similarly to the previous study on $\text{CaZrO}_3/\text{MgO}$ composite using a dolomite source.⁸⁾ Both porous monolith and composite had homogeneous microstructure and very narrow pore-size distribution with mean pore size of $\sim 1\ \mu\text{m}$. These porous materials are promising for the uses of high-temperature gas filters and lightweight structural components, and expected to have good thermal shock resistance.

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