

Coating of hydroxyapatite on cordierite through biomimetic processing

Ill Yong Kim^{a,*}, Sung Baek Cho^b and Chikara Ohtsuki^a

^aGraduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan

^bKorea Institute of Geosciences and Mineral Resources (KIGAM), Kajung-dong 30, Yusong-ku, Taejeon 305-350 Korea

Biomimetic hydroxyapatite deposition method has been used to prepare hybrids and composites. We attempted to coat hydroxyapatite layer on cordierite through a biomimetic process for fabrication of a novel functional material. The cordierite treated with calcium chloride solution was evaluated on hydroxyapatite formation in a simulated body fluid (SBF). The cordierite was hydrated by treating with calcium chloride solution, which led to the formation of silanol (Si-OH) groups on its surface. The $0.25 \text{ mol} \cdot \text{dm}^{-3}$ calcium treated cordierite formed hydroxyapatite on its surface after soaking in SBF within 7 d while the controls, slide glass and alumina plate also treated with the calcium chloride solution, did not show any change in their surface morphology before and after soaking in SBF. This processing might be available for the hybridization of hydroxyapatite and silica-based materials.

Key words: Biomimetic process, Hydroxyapatite, Cordierite, Simulated body fluid.

Introduction

Cordierite ceramics ($(\text{Mg}, \text{Fe}^{2+})_2\text{Al}_4\text{Si}_5\text{O}_{18}$) have many applications in the industrial areas, such as substrates for automobile exhaust catalysts, heat exchangers for turbine engines and filters for some metal molten [1, 2]. Because of their excellent properties, low pressure drop in the exhaust system, good thermal shock resistance, refractoriness, good washcoat adherence and catalyst are some of its most important properties.

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), a type of calcium phosphate, shows high biological affinity to living bone. Synthetic hydroxyapatite is widely used as substitute materials for filling bony defects. Moreover, hydroxyapatite has several interesting properties such as adsorption of proteins and virus, exchange of ionic species in its crystal lattice and removal of volatile organic compounds [3–5]. Previous studies reported [6, 7] a biomimetic process to coat hydroxyapatite using a simulated body fluid (SBF) or its related solutions. Kokubo and his colleagues proposed a biomimetic process that utilizes a reaction between bioactive glass and SBF [8, 9], in order to coat a hydroxyapatite layer onto a substrate. Coating of hydroxyapatite on cordierite by biomimetic process leads to the development of a novel functional material.

In biomimetic processing, there are two strategies for hydroxyapatite coating. According to the study of the hydroxyapatite formation on SiO_2 -based system [10, 11], formation of silanol (Si-OH) group leads to heterogeneous hydroxyapatite nucleation on the surface

of a material. The formed nuclei grow by consuming surrounding calcium and phosphate ions. In another route, calcium treatment is also effective on hydroxyapatite coating because release of calcium ions from the material will increase the degree of the supersaturation with respect to hydroxyapatite [12]. Therefore, hydroxyapatite formation on cordierite requires Si-OH formation by hydration and(or) treatment by a calcium salt solution. Previous study reported [13, 14] that the cordierite was hydrated by reaction with H_2O . Hydration of cordierite led to the formation of hydroxide on its surface, which induced the hydrox-yapatite nucleation. In this study, we attempted to coat hydroxyapatite on cordierite through a biomimetic processing. The hydration of the cordierite was evaluated after immersion to calcium chloride (CaCl_2) solution. Hydroxyapatite-forming ability of the calcium ion treated cordierite specimens was investigated using a simulated body fluid (SBF).

Experimental

Materials

Cordierite ($\beta\text{-Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, Ceracomb co. Ltd, Korea) was used as supplied in this study. Slide glass (S-1225, 8–10 mol% CaO , Matsunami, Japan) and alumina plate (Al_2O_3 , Nikkato, Japan) were used as controls. Rectangular specimens with dimensions of $10 \times 15 \times 1 \text{ mm}^3$ were cut from the supplied materials. The specimens were washed with ethanol and then dried at 40°C for 1 d. The calcium ions treated specimens (Ca-treated) were prepared by soaking in 0.01, 0.10 and $0.25 \text{ mol} \cdot \text{dm}^{-3}$ (M) calcium chloride (CaCl_2 , Nacalai tesque, Japan) solutions for 24 h at room temperature. Hereafter, the treated specimens are denoted as follows. The notation 0.25 Ca-treated

*Corresponding author:

Tel : +81-52-789-3184

Fax: +81-52-789-3182

E-mail: kim.ill-yong@apchem.nagoya-u.ac.jp

cordierite, for example, means that the specimen was treated using 0.25 M calcium chloride solution. After drying, the treated specimens were characterized and introduced for testing of hydroxyapatite formation through biomimetic process.

Characterization

Crystalline phase of the treated specimens were analyzed by X-ray diffraction (XRD, RINT PC 2100, Rigaku Co., Japan). Before and after immersion to calcium chloride solution, the binding energy of O1s of the specimens was measured using an X-ray photoelectron spectrometer (XPS, JPS-9000MC, JEOL, Japan). The XPS measurements were performed using a take-off angle of 10 employing an AlK α X-rays as an excitation source. The measured binding energies were corrected with reference to the binding energy of C1s (284.6 eV) of the hydrocarbon adsorbed on the sample surfaces. The surfaces of the prepared specimens was observed using a scanning electron microscope (SEM, JSM5600, JEOL Ltd, Japan), after coating the specimens with platinum. To analyze the element contents of the specimens, elementary characterization was carried out using energy-dispersive spectroscopy (EDX, EX-54140, JEOL, Japan).

Hydroxyapatite formation through biomimetic processing

Hydroxyapatite coating on cordierite by biomimetic processing was carried out using simulated body fluid (SBF) proposed by Kokubo and his colleagues [8, 9]. The Ca-treated specimens were then soaked in 30 cm³ of the SBF with ion concentrations nearly equal to those of human blood plasma as shown in Table 1. The

Table 1. Ion concentrations of simulated body fluid and human blood plasma.

	Ion concentration (mmol/dm ³)	
	Simulated fluid	Blood plasma
Na ⁺	142.0	142.0
K ⁺	5.0	5.0
Mg ²⁺	1.5	1.5
Ca ²⁺	2.5	2.5
Cl ⁻	147.8	103.0
HCO ₃ ⁻	4.2	27.0
HPO ₄ ²⁻	1.0	1.0
SO ₄ ²⁻	0.5	0.5

SBF was prepared by dissolving reagent grade chemicals of NaCl, NaHCO₃, KCl, K₂HPO₄ · 3H₂O, MgCl₂ · 6H₂O, CaCl₂ and Na₂SO₄ into distilled water. It was buffered at pH 7.25 with 50 mmol tris (hydroxymethyl)aminomethane ((CH₂OH)₃CNH₂) and 45 mM hydrochloric acid (HCl) and was kept at 36.5 °C. To evaluate hydroxyapatite-forming ability on the channel inside of honeycomb, the Ca-treated cordierite honeycomb was soaked into the SBF. After the specimens were soaked in SBF at 36.5 °C for 7 d, they were removed from the SBF. They were gently washed with distilled water and then dried at room temperature. The surface structure of the specimen was analyzed by XRD. The surface morphology of the specimen was observed under SEM.

Results

Fig. 1 shows SEM photographs of the surface of

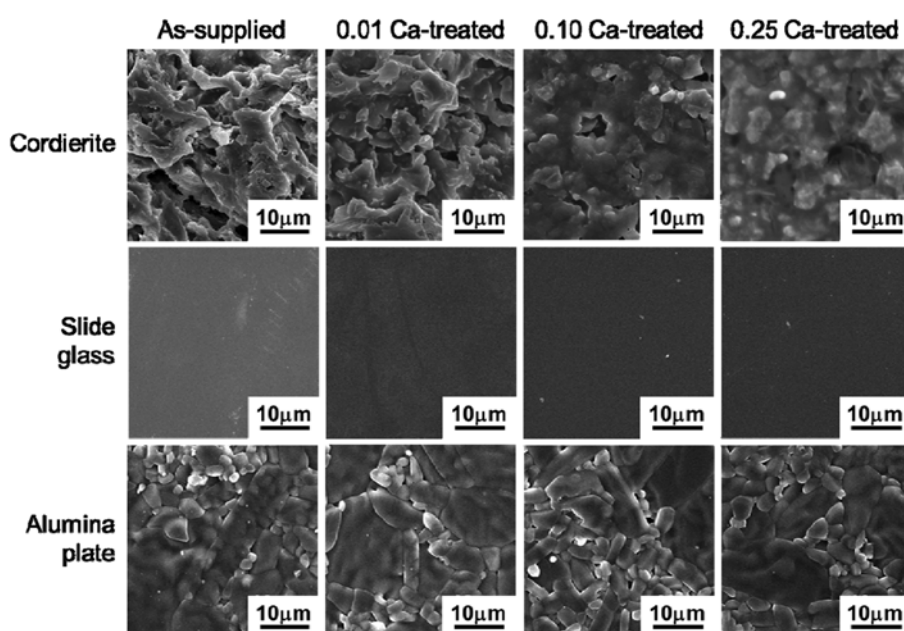
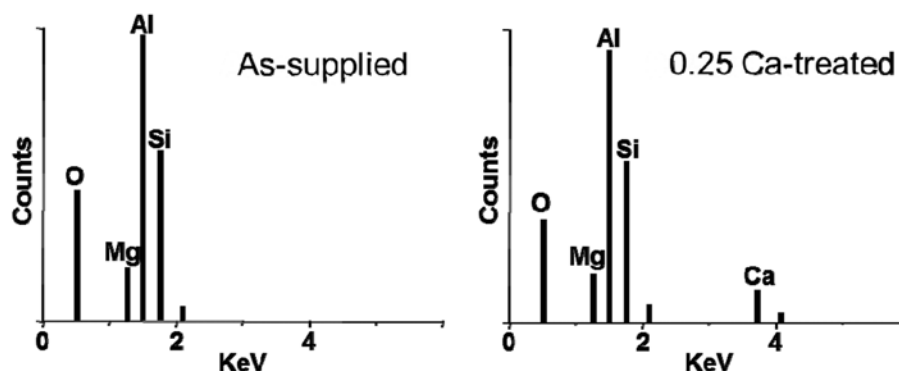


Fig. 1. SEM photographs of the surface of cordierite and control specimens before and after treatment in the calcium chloride solutions.

Table 2. Calcium concentrations of the specimens before and after soaking in calcium chloride solutions.

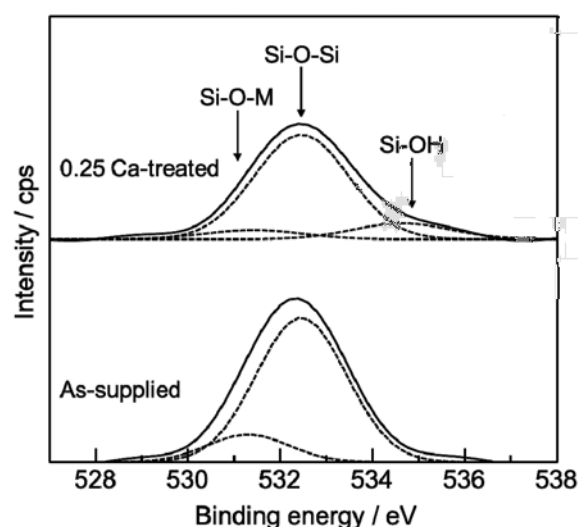
Specimen	Calcium concentration (mol %)			
	As-supplied	0.01 Ca-treated	0.10 Ca-treated	0.25 Ca-treated
Slide glass	8.40	8.31	8.85	8.90
Alumina plate	0.00	0.22	0.20	0.22
Cordierite	0.00	1.31	1.74	8.27

**Fig. 2.** EDX results of the surface of the cordierite before (as-supplied) and after the treatment in 0.25 M calcium chloride solution.

cordierite and control specimens before and after treatment in the calcium chloride solutions. Before the treatment, the as-supplied cordierite had porous structure and its surface was rough. After the treatment, the surfaces of 0.10 and 0.25 Ca-treated cordierites became smooth, which indicates the formation of Si-OH on the surface. After same treatment, slide glass and alumina plate, however, did not show any remarkable change on morphology regardless of increasing calcium chloride concentration.

Using EDX, the amount of calcium released from every Ca-treated specimen and controls were calculated. The calcium contents of the surfaces of all the specimens were summarized in Table 2. According to the Table 2, 0.25 Ca-treated cordierite has extensive amount of calcium ion release compared to other Ca-treated cordierites. Fig. 2 shows EDX results of the surface of the cordierite before and after the treatment in 0.25 M calcium chloride solution. The peak of calcium was appeared after the treatment while the peaks of oxygen, aluminum and silicon were slightly decreased. The slide glass had a slight increase in their calcium contents after treatment in the solutions with increasing calcium chloride concentration, while alumina plate did not show any change in its calcium content. The calcium contents on the surfaces of cordierite increased with increasing the calcium concentration of the solutions. The calcium content of the 0.25 Ca-treated cordierite was 8.27% in molar ratio.

The 0.25 Ca-treated cordierite was applied to be analyzed its surface by XPS. Fig. 3 shows XPS spectra of the as-supplied and 0.25 Ca-treated cordierite. The peaks ascribed to SiO₂ and Al₂O₃ bonds and to Si-O-M were observed at 532.2 and 531.2 eV, respectively. Besides, the peak intensity of Si-O-M decreased

**Fig. 3.** XPS spectra of the as-supplied and 0.25 Ca-treated cordierite.

relatively after the treatment. The peak of hydroxides was newly appeared at 534.2 eV.

Fig. 4 shows SEM photographs of the 0.25 Ca-treated specimens before and after soaking in SBF for 7 d. The deposition was observed on the 0.25 Ca-treated cordierite while the controls, slide glass and alumina plate did not show any change in surface morphology even after soaking in SBF 7 d. Fig. 5 shows XRD patterns of the 0.25 Ca-treated cordierite before and after soaking in SBF for 7 d. Two peaks were newly appeared around 26 and 32°. The peaks are assigned to 002 and envelop of 211, 112 and 300 of hydroxyapatite (JSPDS Card #72-1243), respectively. The results of hydroxyapatite formation on all the specimens in SBF were summarized in Table 3. All the control

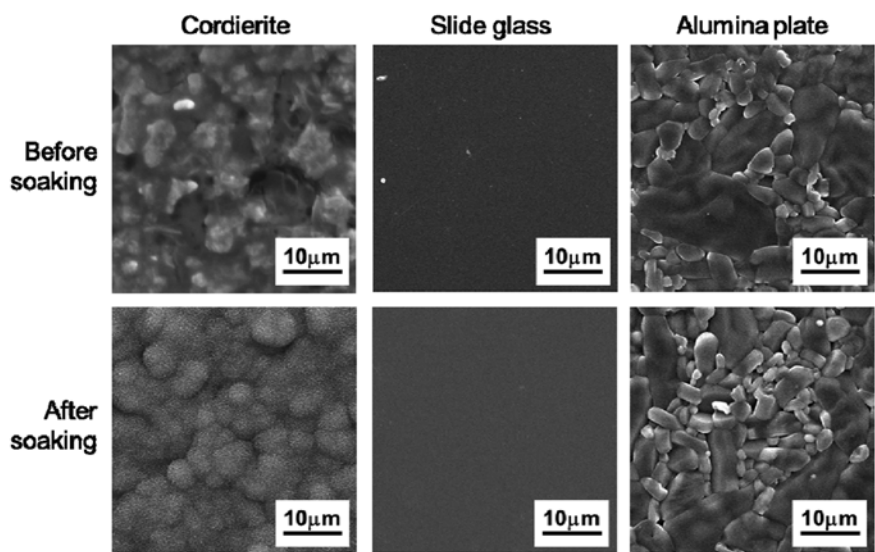


Fig. 4. SEM photographs of the 0.25 Ca-treated specimens before and after soaking in SBF for 7 d.

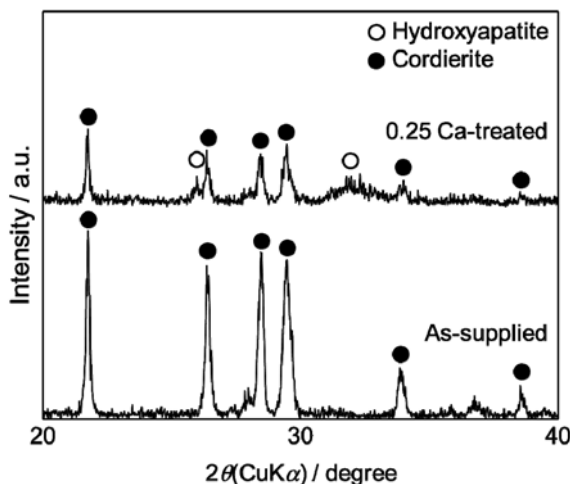


Fig. 5. XRD patterns of the 0.25 Ca-treated cordierite before and after soaking in SBF for 7 d.

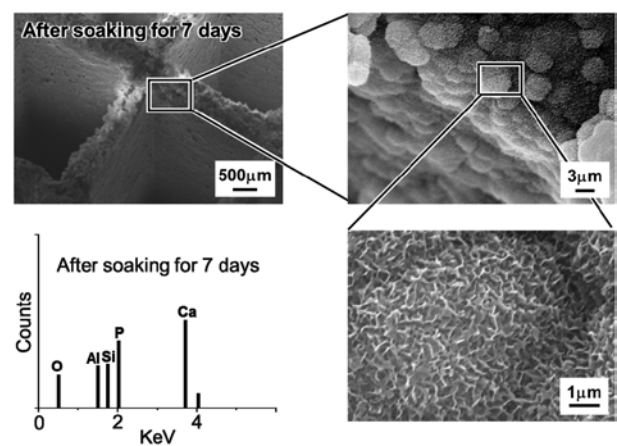


Fig. 6. SEM photographs and EDX spectra of the 0.25 Ca-treated cordierite honeycomb after soaking in SBF for 7 d.

Discussion

specimens did not form hydroxyapatite on their surfaces. Only 0.25 Ca-treated cordierite formed hydroxyapatite on its surface within 7 d.

Figure 6 shows SEM photographs and EDX spectra of the 0.25 Ca-treated cordierite honeycomb after soaking in SBF for 7 d. Hydroxyapatite formation was observed on the channel of honeycomb structure.

To form hydroxyapatite on a substrate by a biomimetic process, a functional group such as Si-OH [15], Ti-OH [16] and COOH [17] which induces hydroxyapatite nucleation and the increase of the degree of the supersaturated solution with respect to hydroxyapatite are required [10]. Calcium silicate system meets the two requirements for hydroxyapatite formation. Calcium silicate system is well known as

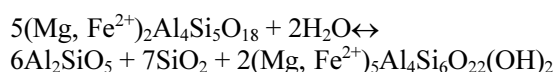
Table 3. Hydroxyapatite-forming ability of the specimens after treatment by calcium chloride solutions.

Specimen	Calcium concentration (mol %)			
	As-supplied	0.01 Ca-treated	0.10 Ca-treated	0.25 Ca-treated
Slide glass	×	×	×	×
Alumina plate	×	×	×	×
Cordierite	×	×	×	○

○ = hydroxyapatite formation, × = no hydroxyapatite formation.

an essential composition to show the hydroxyapatite formation [11]. According to the previous studies [10], the calcium release and the formation of silanol groups on the surface are important for hydroxyapatite formation. The calcium releases from the surface of the calcium silicate glass when the glass is exposed to body fluid or SBF. Then the degree of supersaturation of body fluid or SBF with respect to hydroxyapatite is increased by the calcium release. On the other hand, the silanol groups are formed on the surface of the glass by the calcium release. The silanol groups formed on the surface act as nucleation sites for hydroxyapatite. The hydroxyapatite crystals grow up as they consume surrounding calcium and phosphorous ions in body fluid or SBF. Consequently, the calcium release and the formation of silanol groups are required to form hydroxyapatite on the surfaces of SiO_2 -based materials.

According to the Hietanen's and Vernon's reports [13, 14], cordierite is hydrated by the reaction with water. The reaction is expressed, as follows:



After hydration of cordierite, hydroxides are formed. In this study, β -cordierite ($\beta\text{-Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) was used and the cordierite seemed to be hydrated in the calcium chloride solution. From the SEM photographs, the smooth surfaces were observed after soaking in calcium chloride solution. Therefore, from the results of XPS, it was confirmed that the hydroxide form might be silanol (Si-OH) groups. Besides, the SiO_2 formed through the reaction with H_2O also can be hydrated with increasing exposing periods into an aqueous solution. The formed Si-OH groups might act as the nucleation site of hydroxyapatite [16]. However, the 0.01 and 0.10 Ca-treated cordierites did not form hydroxyapatite although they were hydrated.

As above mentioned, the calcium release from the materials is important to form hydroxyapatite on its surface. In this study, 0.01, 0.10 and 0.25 mol calcium chloride solutions were used for calcium treatment. The calcium contents on the surface of 0.01, 0.10 and 0.25 Ca-treated cordierites 1.31, 1.74 and 8.27 mol%, respectively. Hydroxyapatite was formed only on the 0.25 Ca-treated cordierite among tested specimens. This result indicates that the calcium ions required for hydroxyapatite formation were released from the 0.25 Ca-treated one. The released calcium ions increase the degree of supersaturation with respect to hydroxyapatite. Accordingly, the surfaces of slide glass and alumina plate were not changed after soaking in SBF. There were no remarkable changes in their calcium contents, although the slide glass and alumina plate were treated with the calcium solutions. Consequently, it indicates that nucleation site such as Si-OH group is required as well as calcium release to form hydroxyapatite. The hybrid-

ization of hydroxyapatite and cordierite by biomimetic processing was successful after the treatment in calcium chloride solution. This processing might be available to coat hydroxyapatite layer on a mineral containing silicon dioxide, such as zeolite or the other silica-based minerals.

Conclusions

To prepare the composite of hydroxyapatite and cordierite, the hybridization was carried out through a biomimetic process using SBF. Cordierite was hydrated to form silanol groups on its surface and treated in the calcium chloride solution. The specimen treated with 0.25 mol calcium treatment formed hydroxyapatite on its surface after soaking in SBF within 7 d. It was confirmed that silanol group and calcium release are effective to form hydroxyapatite. This processing can be available for hybridization of hydroxyapatite and a silica-based material to fabricate functional materials.

Acknowledgments

This work is supported by Grant-in-Aid for Scientific Research on Innovative Areas of "Fusion Materials: Creative Development of Materials and Exploration of Their Function through Molecular Control" (No. 2206) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).

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