研 究

Effects of Hydrochloric Acid Catalyst Concentration on Crystallization of Sol-Gel Derived $\text{CaMgSi}_2\text{O}_6$ Gels

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SYNOPSIS

The sol-gel-derived diopside gels of the composition 25mol%CaO-25mol%MgO-50mol%SiO₂ are prepared adding hydrochloric acid of 1 to 4 mol/dm³ concentration in the basic step, and the crystallization behavior of the gels during heating is investigated using thermal differential analysis (DTA-TG), X-ray diffraction and Fourier transform infrared spectroscopy. The results show that the addition of hydrochloric acid leads to lower temperatures of glass formation and crystallization, due to the restriction of calcium carbonate formation, and that the suitable concentration for the single phase crystallization is 3 mol/dm³.

KEY WORDS

Diopside, biomaterial, sol-gel, crystallization, Hydrochloric acid concentration, single phase

1 Introduction

$\text{CaMgSi}_2\text{O}_6$ (Diopside) glass-ceramics in the system CaO-MgO-SiO₂ have high biologically affinity, high mechanical strength and press-formability¹⁻⁴⁾, and therefore have attracted interest as potential biomaterials. Katsui et al.⁵⁾ synthesized the diopside ceramics by heating the gels prepared using a sol-gel route from Ca metal, Mg metal and tetramethoxysilane. In this gel method, hydrochloric acid is added as a catalyst to the mixture solution during hydrolysing, with a decided amount of water. They found⁶⁾ that the use of hydrochloric acid is particularly necessary for the preparation of diopside ceramics without other crystallizing phases and subsequently develops the glass-ceramics with desirable properties through a sol-gel route. Hence, investigations of optimizing conditions adding hydrochloric acid catalyst are of interest.

In the present work, the crystallization of $\text{CaMgSi}_2\text{O}_6$ gels was studied as a function of hydrochloric acid concentration, using DTA-TG, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR).

2 Experimental procedure

The gels with a molar ratio of 1:1:2 for CaO:MgO:SiO₂ were prepared by the sol-gel process using Ca metal, Mg metal and tetramethoxysilane $\text{Si}(\text{OCH}_3)_4$ (Tokyo Kasei) as starting materials. Firstly 0.025 mol of Mg metal (Wako) was dissolved in 10ml of dehydrated methanol and 20ml of tetrahydrofuran in a glass container, and next, 0.025 mol

of Ca (Wako) metal was dissolved in the solution. Secondly, 0.05 mol of tetramethoxysilane was added to the resultant solution, following by stirring at room temperature. 10ml of methanol was added to the solution poured into another glass container, and stirred. Next, 1 mol/dm³ (sample No.; #S-1), 2 mol/dm³ (#S-2), 3 mol/dm³ (#S-3) and 4 mol/dm³ (#S-4) of hydrochloric acid was added to the solution, with 0.3 mol of water. Furthermore, the gels with only 0.3 mol (#S-5) and 0.32 mol (#S-6) of water, not adding hydrochloric acid, were also prepared. Finally the gels obtained were dried at room temperature for a few days.

The dried gels were heated at the rate of about 0.06 K/s to temperatures in the range 623 to 1473 K in air. The diopside glass formation and crystallization of the gels in the heating process were investigated by means of DTA-TG, X-ray powder diffraction and IR spectroscopy. Rigaku Denki TG8120 was used for DTA-TG analysis. The heating rate of dried gels was 0.33 K/s. X-ray powder diffraction patterns were obtained on a Mac Science MXP3 diffractometer system employing Cu K α_1 ($\lambda = 1.5405 \text{ \AA}$). The IR spectra were obtained on a Perkin Elmer 1720X Fourier Transform Infrared Spectrometer using the KBr pellet method.

3 Results and Discussion

Fig. 1 shows the TG-DTA curve for three kind of dried gels (#S-1, #S-3 and #S-6) from room temperature to 1723 K.

The DTA curves of all the three gels showed an endothermic peak at 373–473 K, due to the removal of physically bound water and some residual organic matter, followed by a wide exothermic peak around 573 K. This exothermic peak is probably due to the combustion of the unreacted organic groups of the alkoxides. Small endothermic peaks at 873–973 K on the DTA, depending on hydrochloric acid concentration, may be attributed to the beginning of glass formation process.

The first clearly detectable exothermic peak was attributed to the crystallization of diopside. The peak temperature was 1130.7 K and 1097.6 K for hydrochloric acid concentration of 1 mol/dm^3 (#S-1) and 3 mol/dm^3 (#S-3), respectively. The larger the hydrochloric acid concentration, the lower the crystallization temperature of diopside. The crystallization temperature for gel (#S-6) not adding hydrochloric acid was 1148.3 K. Larger amounts of water increased the crystallization temperature of diopside. An endothermic peak was observed at around 1653 K for the three gels, due to the melting of diopside.

A crystallization sequence for the gel of #S-3 heated in air, is given in Fig. 2. On heating at 623–873 K, calcite (JCPDS-50586) is observed, although the peak intensity was decreased with heating temperature. At 923 K, calcite

decreases drastically and two new peaks appear, in addition to extremely broadened peak around $2\theta = 30^\circ$. Former two peaks were equal to the diffraction position of the 221 and 002/202 planes of diopside. Thus, formation of the glassy diopside phase was nearly completed and the crystallization began at 923 K. All of the peaks at temperatures from 973 K to 1473 K can be indexed as monoclinic diopside. As the heat temperature is increased, the peaks attributed to diopside become more intense. In the gel of #S-4, the same result as #S-3 was obtained. The results indicates that the gels change as calcium carbonate $\rightarrow$ diopside glass $\rightarrow$ diopside crystalline, with heating temperature.

Fig. 3 shows the XRD pattern for the gel of #S-1 after heating at 1473 K in air. The pattern is similar to that for

Fig. 1 DTA-TG curve of dried gel using different hydrochloric acid catalyst concentration, heated at 0.33 K/s in air. (a) 1 mol/dm^3 (#S-1), (b) 3 mol/dm^3 (#S-3), (c) without hydrochloric acid (#S-6).

Fig. 2 XRD pattern changes of dried gel of #S-3 heated at various temperatures for 7.2 K/s in air. ■ : CaCO_3 (calcite)

Fig.3 XRD pattern of dried gel of #S-1 heated at 1473 K for 7.2 Ks in air. ▼ : α -CaSiO₃

the gel of #S-3. However, α -CaSiO₃ is detectable⁶⁾, although the peak intensity is weak. A trace amount of α -CaSiO₃ was also detected in the gel of #S-2.

A crystallization sequence for the gel of #S-6 prepared without adding hydrochloric acid, is given in Fig. 4. On heating at 623–873 K, two polytype of calcium carbonate appears. Aragonite (JCPDS-50453) appears at 623–723 K and then changes to calcite at 823 K. At 923 K, calcite nearly disappears and a glassy diopside phase appears. Then, the crystallization begins at 1023 K. Almost of the peaks at temperatures above 1023 K can be indexed as monoclinic diopside. However, a trace amount of α -CaSiO₃ is detected at 1273 K.

The results of Figs. 1–3 suggest that addition of hydrochloric acid concentration above 3 mol/dm³ realizes the single phase crystallization of only diopside. However, diopside crystalline prepared adding hydrochloric acid of 4 mol includes a considerable amount of chlorine, as confirmed by EPMA measurement. Thus, 3 mol/dm³ is suitable for high purity of diopside ceramics.

Fig. 5 shows the XRD patterns for the four gels of #S-1, #S-2, #S-3 and #S-4 after heating at 923 K in air. The patterns show that #S-1 is just before glass formation, #S-2 is just before crystallization after completing glass formation, #S-3 is just after crystallization and #S-4 is almost completing crystallization. The results indicate that the crystallization temperature of the gels decreases with increasing the hydrochloric acid concentration. This agrees with the result of TG-DTA measurement.

From above results it is clear that the addition of hydrochloric acid restricts the formation of calcium

Fig.4 XRD pattern change of dried gel of #S-6 heated at various temperatures for 7.2 Ks in air.
■ : CaCO₃ (calcite), ▲ : CaCO₃ (aragonite)

Fig.5 XRD patterns of dried gels heated at 923 K for 7.2 Ks in air. (a) 1 mol/dm³ (#S-1), (b) 2 mol/dm³ (#S-2), (c) 3 mol/dm³ (#S-3), (d) 4 mol/dm³ (#S-4). ■ : CaCO_3 (calcite)

carbonate and therefore prevents the delay of glass formation and crystallization by its existence. Calcium carbonate is formed by the reaction of the hydrolysed product, $\text{Ca}(\text{OH})_2$, with CO_2 in air during gelation and/or glass formation by heating.

The structural change of the dried gels of #S-3 in the heating process was also studied using ex-situ FTIR analysis. This spectral change with heating temperature was similar to X-ray powder diffraction pattern change shown in Fig. 2. Fig. 6 shows the FTIR spectrum for the gel heated at 873 K. The strong broad bands at about 3400 cm^{-1} and around 1650 cm^{-1} are attributed to water⁵⁾. The absorption band around at 1020 cm^{-1} , attributed to the Si-O vibration in the SiO_4 tetrahedron, shifted to 1070 cm^{-1} above 1023 K. The absorption peak around 1430 cm^{-1} is attributed to the CO_3^{2-} vibration from the presence of calcium carbonate⁷⁾.

4 Conclusions

Effects of hydrochloric acid concentration on the crystallization of sol-gel derived $\text{CaMgSi}_2\text{O}_6$ gels prepared using a sol-gel route was investigated using TDA-TG, X-ray diffraction and FTIR. It was found that the addition of hydrochloric acid leads to lower temperatures of glass formation and crystallization, due to the restriction of calcium carbonate formation, and that 3 mol/dm³ is the suitable concentration for a single phase crystallization.

Fig.6 FTIR spectra of dried gels of #S-3 heated at 873 K for 7.2 Ks in air.

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