Ceramics International **24** (1998) 243–247

PII: S0272-8842(96)00040-5
0272-8842/98 $19.00+.00

The Sintering Characteristics of $MgO–CaO–Al_2O_3–SiO_2$ Composite Powder Made by Sol–Gel Method

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(Received 21 July 1995; accepted 6 February 1996)

Abstract: The sintering sequences and characteristics of glass with composition in the quaternary phase field of the MgO-CaO-Al_2O_3-SiO_2 (MCAS) system, which was prepared by the sol–gel method, were studied with scanning electron micrograph, X-ray diffraction patterns, and other techniques. X-ray diffraction studies of specimens with a sintering temperature higher than 940°C showed that cordierite and anorthite existed as two different phases. The dielectric characteristics of the sintered MCAS composite glass were a function of sintering temperature and sintering time. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

The recent interest in the sintering of glasses arises from the fact that glasses were less prone than ceramics to processing flaws arising from packaging defects.[1,2] Cordierite ($2MgO–2Al_2O_3–5SiO_2$)[3] and cordierite-based[4] glass ceramics are promising materials for electronic packaging and offer lower dielectric constant (5.0 at 1 MHz) and thermal expansion coefficient in comparison to Al_2O_3. In the past, many other types of glass-forming system were also developed, for example, NaO-CaO-SiO_2,[5] Li_2O-Al_2O_3-SiO_2,[6] BaO-SiO_2,[7] B_2O_3-SiO_2,[8] and others.[9] Because the glass-based composites did not sinter readily to form useful monoliths, indirect routes were typically used to fabricate glass ceramics. There were two common routes, one was the glass-ceramics process[10,11] and the other was the reactive "sol–gel" process.[12,13] The sol–gel process attempted to duplicate the mixing levels of the melt process by simultaneous precipitation of the appropriate metal species as hydroxides and then dehydrating them to yield intimately mixed oxides. Using the sol–gel technique, chemically homogenized glasses and glass composite formation can be achieved in solution near room temperature. After an article was formed, densification was achieved at around 900–1000°C without sintering aid, and then the glass article is crystallized in the range of 900–1100°C.

Recently, pure and crystalline cordierite powders and cordierite-based composites were prepared by the sol–gel method using metal alkoxides.[14] Sales and Alarcon reported that cordierite-based glass ceramics could be prepared in the $MgO–CaO–Al_2O_3–SiO_2$ quarternary system by the sol–gel method. In the present investigation, glass with composition in the quarternary primary phase field of the $MgO–CaO–Al_2O_3–SiO_2$ (abbreviated as MCAS) system was prepared by the sol–gel method, using inorganic colloidal suspensions. Then the MCAS composite is used as the precursor material to prepare dense cordierite-based ceramics at less than 1000°C. The dielectric characteristics of the sintered MCAS composite glass are described in this paper. The reaction scheme and the crystallization sequences of the MCAS glass composite are also described in this article.

2 EXPERIMENTAL PROCEDURES

In the present investigation, glass of the basic composition of (in wt%) 5% MgO, 19% CaO, 26% Al_2O_3 and 50% SiO_2 (with an approximate stoichiometry of MgO: CaO: Al_2O_3: SiO_2 = 6.5:

14.5: 27.5: 51.5) was prepared by the sol–gel method. Colloidal silica was dispersed in 600 ml of deionized water and concentrated nitric acid was also added. To this acidic suspension we added magnesium nitrate hexahydrate, aluminium nitrate hexahydrate, and calcium nitrate hexahydrate. The subsequent addition of ammonium hydroxide resulted in the quantitative precipitation of magnesium, calcium and aluminium hydroxides. The solids were collected by filtration and calcined at 300°C for 1 h. The calcination step was desirable to convert any ammonium nitrate present to oxides of nitrogen and water. The powder was pressed into pellets uniaxially in a steel die. Typical dimensions of the pellets were 15 mm in diameter and 1.5 mm in thickness. Sintering of these pellets was carried out at temperatures between 800 and 1000°C under ambient condition for a duration of 40 min. These specimens were also sintered at 940°C for 20–360 min.

The microstructure of the surface of the sintered specimens was observed under a scanning electron microscope (SEM). X-ray diffraction patterns were taken at $2\theta = 4°$ per minute using CuKα radiation. The density of the sintered specimens as a function of sintering temperature with a fixed sintering time of 40 min was measured by the liquid displacement method using deionized water (Archimedes method). The shrinkage of the sintered specimens was measured by a digital meter. After painting silver paste on both sides of the specimens and firing at 700°C for about 20 min, dielectric properties were measured with a HP4192a impedance analyser. The dielectric constant was measured over the range of 1 kHz and 10 MHz.

3 RESULTS AND DISCUSSION

Figure 1 shows the SEM micrograph of grain size of the fabricated MCAS composite glass powder. In the SEM microstructural study of gel derived glass composite, particles with very small size were observed. Most particles were spheroidal and appeared to be non-agglomerated.

Dilatometry was performed to track shrinkage as a function of sintering temperature for a sintering time of 40 min. A typical dilatometory trace is shown in Fig. 2. During the initial sintering of MCAS composite glass, rapid shrinkage happened in the temperature range of 800–920°C. The shrinkage reached saturation at about 940°C. The density of the sintered MCAS composite glass is also shown in Fig. 2. Rapid densification occurred in the temperature range 800–920°C. The densification also reached saturation at about 940°C, and the specimens sintered at 940°C had a density of about 2.539 g/cm^3. The specimens sintered at 100°C were densified completely and had a density of 2.580 g/cm^3, and only few pores were observed on the surface of the sintered specimens (as shown in Fig. 3(c)). Observation of the fractured cross-section of the sintered specimens was also carried out, and in almost all cases no pores were left behind. The density of the MCAS composite glass sintered at 1000°C (2.580 g/cm^3) is slightly larger than the theoretical density of cordierite glass (2.51 g/cm^3).[15]

SEM observations on MCAS composite glass sintered at 900, 940 and 1000°C, respectively, for

Fig. 1. The SEM micrograph of fabricated MCAS composite powder.

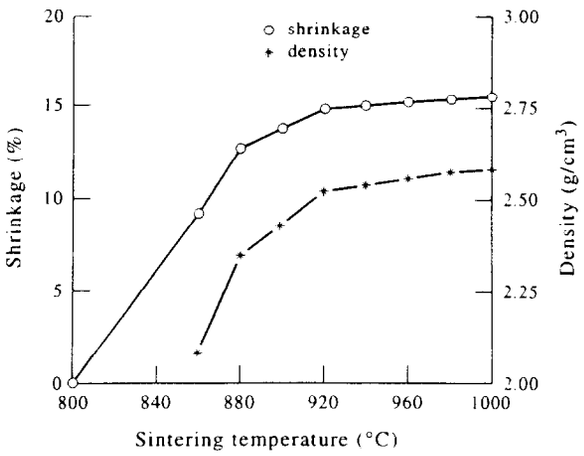

Fig. 2. Density and shrinkage versus sintering temperature relationship for the sintered MCAS composite glass.

40 min are shown in Fig. 3. Coalescence of glass particles resulting from viscous flow was observed and densification became more complete as the firing temperature was raised. After firing at 900°C for 40 min, as shown in Fig. 3(a), coalescence of glass particles via viscous flow was observed. As the sintering temperature increased to 940°C for 40 min, pore elimination and the enhancement of densification were promoted by the viscous flow of glass, as shown in Fig. 3(b). As for the specimens sintered at 1000°C for 40 min, unfilled void space was filled by the viscous flow of MCAS glass and few pores were recognized on the surface of the sintered specimens, as shown in Fig. 3(c).

X-ray diffraction patterns of specimens treated under varying sintering temperature and sintering time are shown in Fig. 4. It can be seen that the reaction to form cordierite phase proceeded readily at 900°C and above, as shown in Fig. 4(a) and (b). As Fig. 4(c) shows, the reaction to form anorthite phase proceeded readily at 940°C and above. When the sintering temperature was higher than 940°C, the presence of these two phases, cordierite and anorthite, was clearly detected by the X-ray diffraction patterns. Few unrecognized phases were also observed in the X-ray patterns. When following this reaction sequence by XRD, we observed that the first chemical reaction, which happens at about

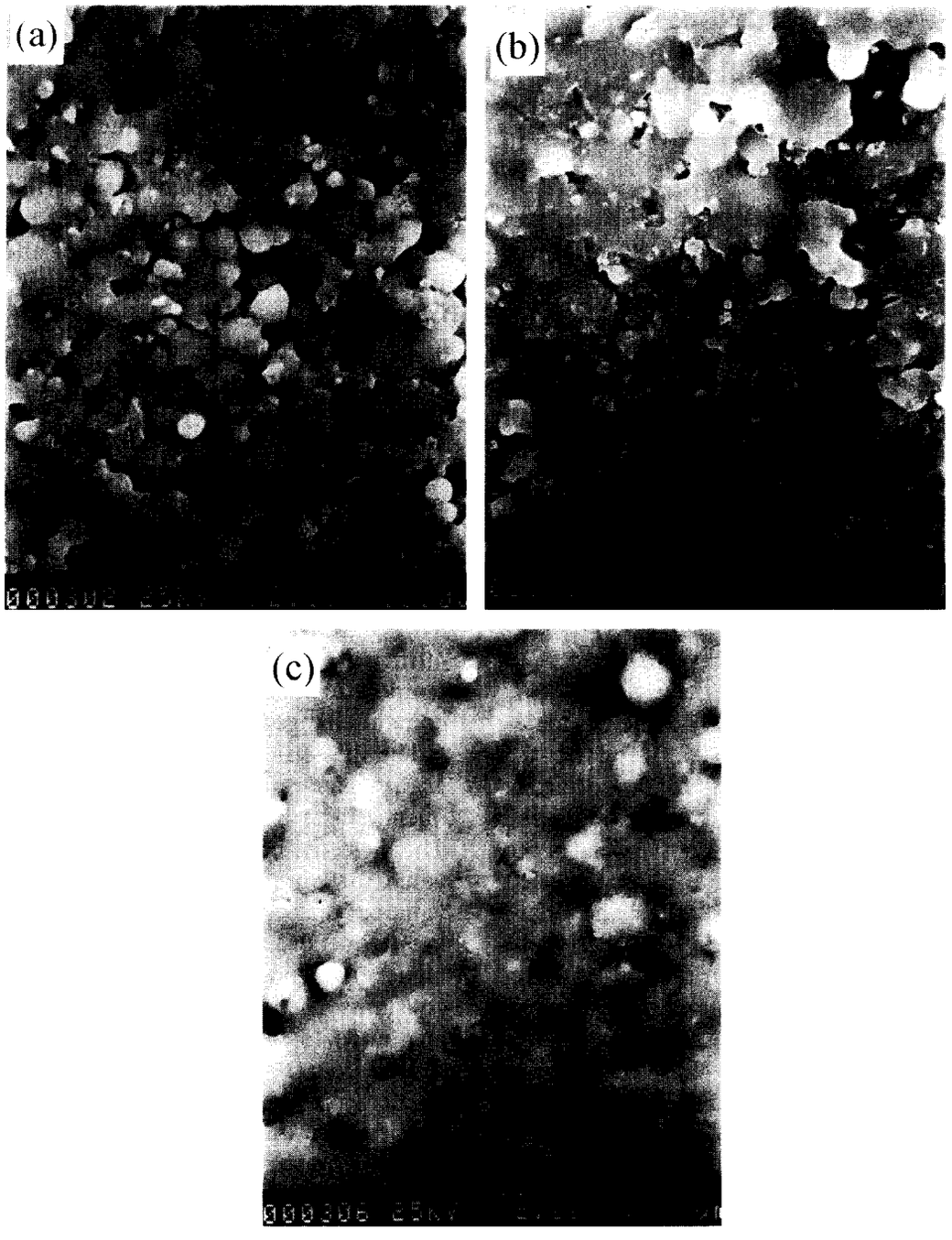

Fig. 3. Microstrucutres of MCAS specimens sintered at (a) 900°C, (b) 940°C and (c) 1000°C for 40 min.

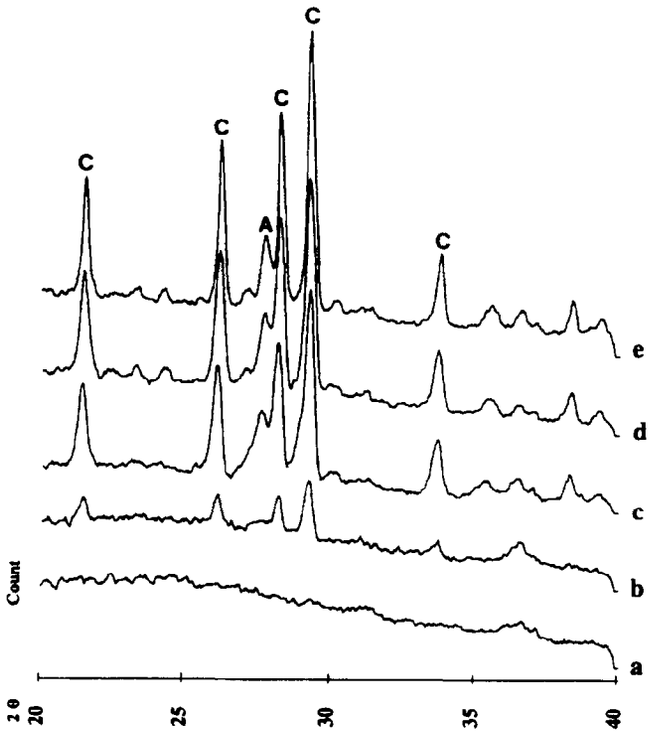

Fig. 4. X-ray diffraction patterns of MCAS composites glass sintered at (a) 800°C for 40 min, (b) 900°C for 40 min, (c) 940°C for 40 min, (d) 1000°C for 40 min and (e) 940°C for 360 min. (A: anorthite, C: cordierite).

900°C, is the conversion of magnesium oxide, aluminium oxide and silica to cordierite:

$$2MgO + 2Al_2O_3 + 5SiO_2 \rightarrow Mg_2Al_4Si_5O_{18}$$

The later reaction, which happens below 940°C, is the conversion of calcium oxide, aluminium oxide and silica to anorthite:

$$CaO + Al_2O_3 + 2SiO_2 \rightarrow CaAl_2Si_2O_8$$

By focusing attention on the (101) plane for metastable μ-cordierite phase ($2\theta = 25.8$) and on the (112), (202) and (211) planes for α-cordierite ($2\theta = 26.3°$, 28.5° and 29.5°, respectively), the metastable μ-cordierite phase did not appear in the sintered specimens. The cordierite phase revealed in Fig. 4 was the stable α-cordierite. The phase transformation procedure from μ-cordierite to α-cordierite did not happen during the sintering process of the MCAS system. Comparing Fig. 4(c), (d) and (e), the recrystallization rate of cordierite phase of specimens sintered at 940°C for 360 min was stronger than that of specimens sintered at 1000°C for 40 min. These results suggest that sintering time is a more important factor than sintering temperature to improve the recrystallization rate of the cordierite and anorthite phases, provided the sintering temperature is high enough.

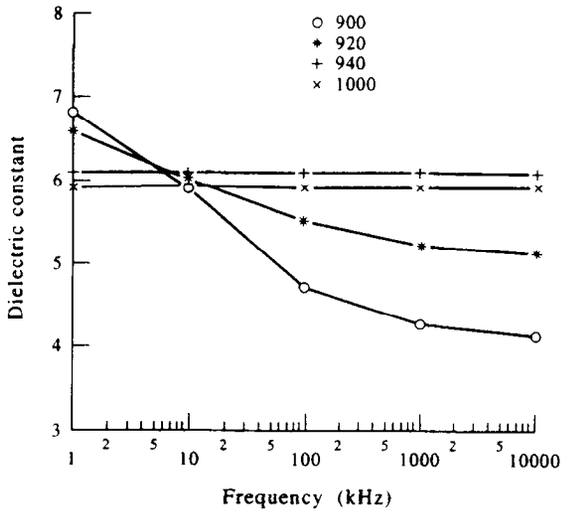

Fig. 5. Dielectric constant versus sintering temperature with a sintering time of 40 min.

The relative amounts of the anorthite phase were determined by the major integrated intensities of the main peak for cordierite phase (for 2θ at about 29.5°) and the main peak for anorthite phase (for 2θ at about 27.7°) from the XRD patterns of the sintered pellets. The percentage of anorthite phase formed was calculated by the following equation:[16]

$$\text{Anorthite content } (\%) = \frac{100 \times I_{ano}}{I_{cor} + I_{ano}} \qquad (1)$$

where I_{ano} and I_{cor} represent the intensities of XRD peaks for anorthite and cordierite phases, respectively. For specimens sintered at 940°C for 40 min, 41% anorthite phase was obtained. On increasing the sintering temperature from 940°C to 1000°C, the anorthite phase content changed from 41% to 31%. On increasing the sintering time from 40 min to 360 min, while keeping the sintering temperature constant at 940°C, the anorthite phase content changed to 27%.

The dielectric constant response of the sintered MCAS glasses was measured as a function of frequency. The measured data are shown in Fig. 5. The dielectric constant was slightly larger than the value for pure cordierite of 5.0. In general, the values of dielectric constant decreased with increasing frequency, and approached a stable value at higher frequency. The larger change in the dielectric constants of the specimens fired below 920°C is attributed to the incomplete densification, as evidenced from the relationship of density and sintering temperature shown in Fig. 2. When the sintering temperature was higher than 940°C, the sintered specimens reveal a stable dielectric-frequency curve.

The frequency dependency of the dielectric constant for the specimens sintered at 940°C with different time periods is shown in Fig. 6. Larger

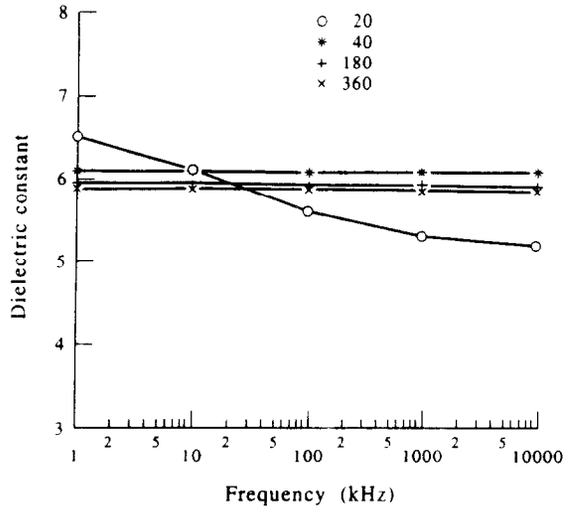

Fig. 6. Dielectric constant versus sintering time with a sintering temperature of 940°C.

decreases were observed for specimens sintered at 940°C for 20 min in the low frequency range. This result implies that for MCAS glasses sintered at 940°C, 20 min is not sufficient for densification. Except at a frequency lower than 10 kHz, the specimen sintered at 940°C for 40 min possesses the highest dielectric constant over a wide range of frequency. Since densification was almost complete after sintering at 940°C and 1000°C for 40 min, the α-cordierite phase will dominate the dielectric characteristics of the sintered specimens. The phenomenon of nearly constant frequency dependence maybe be attributed to the stable α-cordierite.

4 CONCLUSION

The following conclusions can be drawn from the experimental work described above:

1. In the sintered MCAS composite glass ceramics, cordierite and anorthite are the two main phases present.
2. The sintered density increases with temperature up to 1000°C, and the density of fully densified MCAS specimens is 2.580 g/cm^3.
3. For MgO-$CaAl_2O_3$-SiO_2 composite glass ceramics sintering time is a more important factor than sintering temperature to improve recrystallization, provided the temperature is high enough.
4. The dielectric constant of sintered MCAS composite glass will decrease with sintering temperature and time. MCAS composite glass ceramics sintered at 940°C for 40 min show stable dielectric-frequency curves, and the dielectric constant of about 6.1 is slightly larger than the value for pure cordierite of 5.0.

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