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The influence of crystallization on the flexural strength of $MgO–CaO–Al_2O_3–SiO_2$ composite glass

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Abstract

Glass with the composition of $MgO–CaO–Al_2O_3–SiO_2$ (MCAS) is prepared by sol–gel method. X-ray diffraction studies on specimens with a sintering temperature higher than 940°C show that cordierite and anorthite exist as two different phases. For sintered MCAS glass ceramics, both the average flexural strengths and the crystallization rates of anorthite and cordierite increase with sintering time (sintered at 940°C) and sintering temperature (sintered for 40 min). The average flexural strengths of porous MCAS glass ceramics is decreased in a way that is exponential with porosity: $\delta = \delta_o \exp(-np)$ Because of the crystallization of cordierite and anorthite, the dependence of flexural strength on both the pores fraction and the crystallization rates of cordierite can be expressed by the modified equation as follows: $\delta = \delta_o \exp(-\mathrm{np}) \times [1 + ax_i + b(x_i)^2]$ (a and b are constants, x_i is the crystallization rates for cordierite). © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

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1. Introduction

Cordierite ($2MgO–2Al_2O_3–5SiO_2$) [1–3] and cordierite-based [4–6] glass ceramics are promising materials for electronic packaging and offer lower dielectric constant (5.0 at 1 MHz) and thermal expansion in comparison to Al_2O_3. Recently, pure and crystallization cordierite and cordierite-based powders were prepared by the sol–gel method [7,8]. These powders could be sintered without any sintering aid, but no enhancement of mechanical properties was observed [9]. In the past, cordierite-based glass ceramics could also be prepared in the $MgO–CaO–Al_2O_3–SiO_2$ quaternary system [10]. In the present investigation, the glass with the composition of (in wt%) MgO 5%, CaO 19%, Al_2O_3 26%, and SiO_2 50% (with an approximate stoichiometry of MgO:CaO:Al_2O_3:SiO_2 = 6.5:14.5:27.5:51.5, abbreviated as MCAS) was prepared by the sol–gel method. The process for fabrication of MCAS glass powder and the sintering [11] and mechanical characteristics of MCAS glass ceramics were described.

Since fracture phenomena themselves are diverse and not clearly understood in all details, even for the simplest materials, it is apparent that no completely satisfactory and all-encompassing survey of the effects of microstructure is possible. The major effect of the structure in most ceramics is result of porosity. Experimentally, it is found that the average flexural strength of porous MCAS glass ceramics is decreased in a way that is nearly exponential with porosity. In this study, an empirical equation is suggested by analytical MCAS glass ceramics and shows the similarly analytical relationships with that of W.Duckworth [12]:

$$\delta = \delta_o \exp(-\mathrm{np}) \tag{1}$$

After the analysis on the flexural strength, it is found that the flexural strength of MCAS glass ceramics is not only accompanied by a significant increase with sintering temperature but also is accompanied by an increase with sintering time. As the sintering temperature is increased, the sintered surfaces reveal no apparent change in sintered surfaces, but the crystallization rates of cordierite and anorthite increase with the sintering time. In this study, we are tried to develop the differently modified exponential-type equation:

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$$\delta = \delta_o \exp(-\mathrm{np}) \times \left[1 + ax_i + b(x_i)^2\right] \quad (2)$$

which can be used to expand the relationships between the flexural strength and both the crystallization rates and the pores fraction of MCAS glass ceramics.

2. Experimental procedures

In a typical laboratory-scale synthesis using nitrates, colloidal silica was dispersed in 600 ml of deionized water and 12 ml of concentrated nitric acid. Magnesium nitrate hexahydrate, calcium nitrate hexahydrate, and aluminium nitrate hexahydrate was added into the solution. 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 resulting glass powder is termed as MCAS precursor. The powder was pressed to pellets or bars uniaxially in a steel die. Typical dimensions of circular pellet-shaped specimens were 15 mm in diameter and 1.5 mm in thickness. Typical dimensions of rectangular bar-shaped specimens were longer than 36 mm, 4.0 ± 0.1 mm in width, and 3.0 ± 0.1 mm in thickness. The pellets and bars were fired in air from room temperature at 5°C/min to a sintering temperature of 800 to 1000°C, followed by a 40 min hold at the sintering temperature.

Mechanical testing of sintered bar-typed specimens was performed in three-point flexural mode. The flexural strength test was performed at a crosshead speed of 0.5 mm/min. Three point flexural strength was tested by the MTS 310 system according to Japanese Industrial Standard R 1601 method. For every sintering condition, five sintered MCAS glass ceramics were used to carry out the flexural strength test and measure the average flexural strength. In order to examine the microstructure, scanning electron microscope (SEM) observations were conducted. X-ray diffraction patterns were taken at $2\theta = 4°$ per min using CuKα radiation. The sintered pellets were batched at 150°C for 24 h, then the weight of the sintered pellets was measured. In order to get the closed pores fraction, the sintered specimens were immersed in boiled deionized water for 12 h. Then the volume of immersed specimens was measured by the Archimedes method. After that, the weight of immersed specimens was measured again in order to calculate the density and pores fraction of sintered MCAS glass ceramics.

3. Results and discussion

SEM observations on the surfaces of sintered MCAS glass ceramics are shown in Fig. 1. After firing at 900°C for 40 min, as shown in Fig. 1(a), coalescence of glass particles resulting from viscous flow is observed. As Fig. 1(b) shows, as the sintering temperature was increased to 940°C, pores elimination was promoted by the decrease in viscosity flow of glass. For MCAS sintered at 940°C for 4 h is shown in Fig. 1(c). Owing to the beginning of crystallization (Fig. 2), as the sintering time is longer than 40 min, glass viscosity no longer decreases with the increase of sintering time. This, in turn, results in the saturation of pores fraction (Fig. 3). As when Fig. 1(b) and (c) are compared, the sintered surfaces of MCAS glass ceramics are almost unchanged as MCAS glass ceramics are sintered at 940°C with a sintering time longer than 40 min. When the specimens were sintered at 1000°C for 40 min, unfilled void space is filled by the viscous flow of MCAS glass and few unclear pores are left on the surfaces of sintered specimens as shown in Fig. 1(d). The observation of the fractured cross section of the sintered MCAS glass ceramics was also carried out, and in almost cases, no pores were left behind.

The strong dependence of crystallization rates on sintering temperature and sintering time were reflected in the X-ray diffraction patterns. As Fig. 2 shows, the MCAS glass ceramics starts crystallization at about 900°C. With a sintering time of 40 min, the reaction to form cordierite proceeded readily at 900°C and above [Fig. 2(b), (c), and (d)], and the reaction to form anorthite proceeded readily at 940°C and above [Fig. 2(c) and (d)]. The diffraction peak strengths of cordierite and anorthite increased with sintering temperature [Fig. 2(b), (c), and (d)]. Using 940°C as the sintering temperature, the diffraction peak strength of cordierite and anorthite also increased with sintering time [Fig. 2(c) and (e)].

There are many factors that can influence the flexural strength of porous ceramics. For example, the flexural strength of polycrystalline ceramics increases with decreasing grain size and pores fraction [13]. The variations of average flexural strengths and pores fraction of MCAS glass ceramics as a function of sintering temperature with a sintering time of 40 min was given in Fig. 3. The pores fraction decreased critically as the sintering temperature was lower than 920°C and decreased slightly as the sintering temperature was higher than 920°C. The specimens sintered at 1000°C showed a nearly complete densification. The lower average flexural strength for specimens sintered at 900°C and 920°C are attributed to the existence of porosity.

The average flexural strengths and pores fraction of MCAS glass ceramics sintered at 940°C as a function of sintering time were also given in Fig. 3. For the sintering time in the range of 10 and 40 min, the pores fraction decreased rapidly. A saturation value of 1.6% for pores fraction was reached at a sintering time of 40 min. The average flexural strengths of specimens sintered at

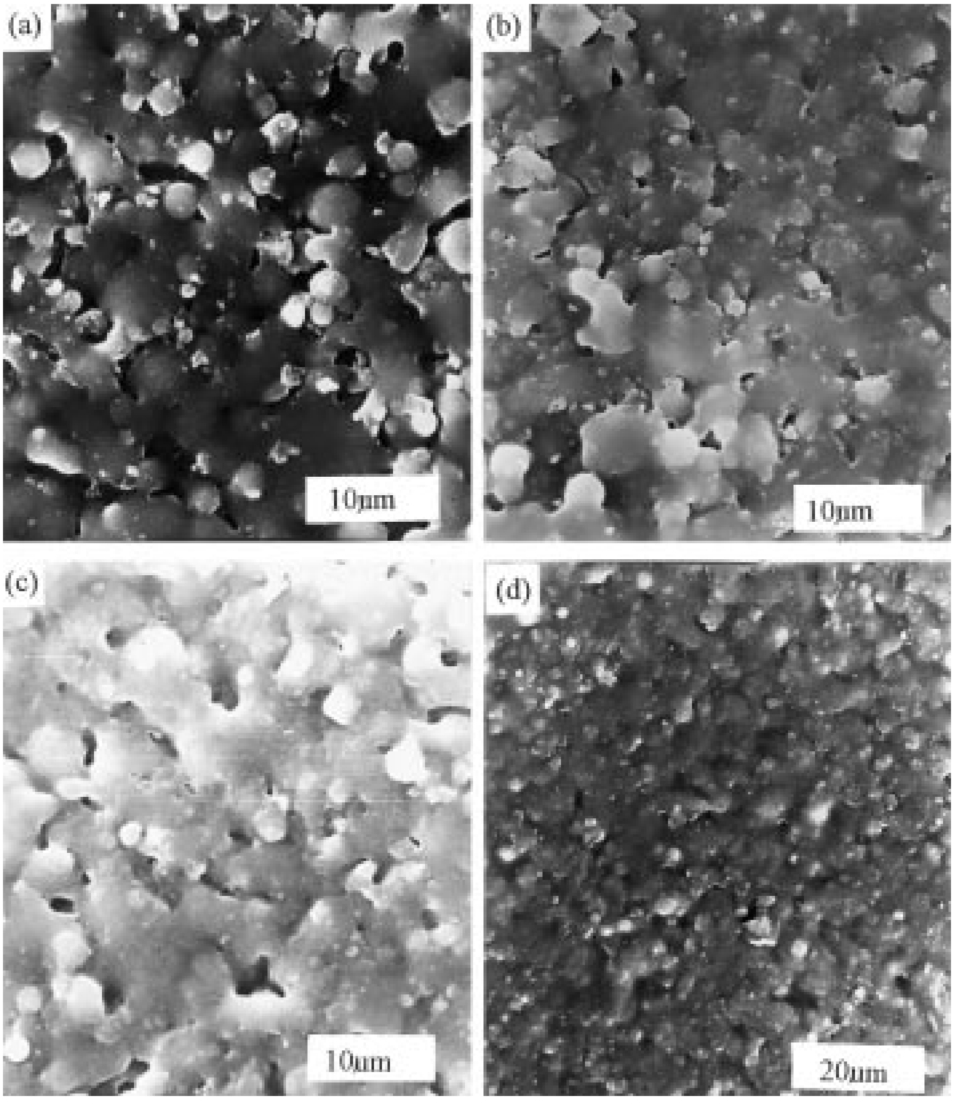

Fig. 1. The SEM observations of sintered MCAS glass ceramics: (a) 900°C, 40 min; (b) 940°C, 40 min; (c) 940°C, 4 h; and (d) 1000°C, 40 min.

940°C increased with the sintering time. For MCAS glass ceramics sintered at 940°C, the increase of average flexural strength with sintering time is not attributed to the decrease of pores fraction. As evidenced from Fig. 2 and Fig. 3, as the sintering time is longer than 40 min, the pores fraction of MCAS glass ceramics sintered at 940°C no longer decreases with sintering time. It is believed that there exist certain reasons, which are different from the porosity, that do influence the average flexural strength of MCAS glass ceramics.

Fig. 4 was a graphical presentation of the relationships between the pores fraction and the flexural strength of porous MCAS glass ceramics. Circles plotted on the Fig. 4 represented the average flexural strength of experimental values. The main reason for the increase in flexural strength is the strong dependence of densification rate on sintering temperature. This behaviour is reflected in the pores fraction vs sintering temperature curves. The average flexural strength increases critically with the decrease of pores fraction. Experimentally, it is found that the strength of porous ceramics is decreased in a way that is nearly exponential with porosity.

As Fig. 4 shows, three theoretical lines were calculated to extrapolate the flexural strength of nonporous MCAS glass ceramics, δ_o. The upper line was calculated from the experimental data of specimens sintered at 880°C (pores fraction = 10.1%), 900°C (6.2%), 920°C (2.1%), 940°C (1.6%), 960°C (0.9%), and 1000°C (0.0%). The expression for upper line is:

$$\delta = 215.257 \times \exp(-8.31856P) \tag{3}$$

where $\delta_o = 215.257$, $n = 8.31856$

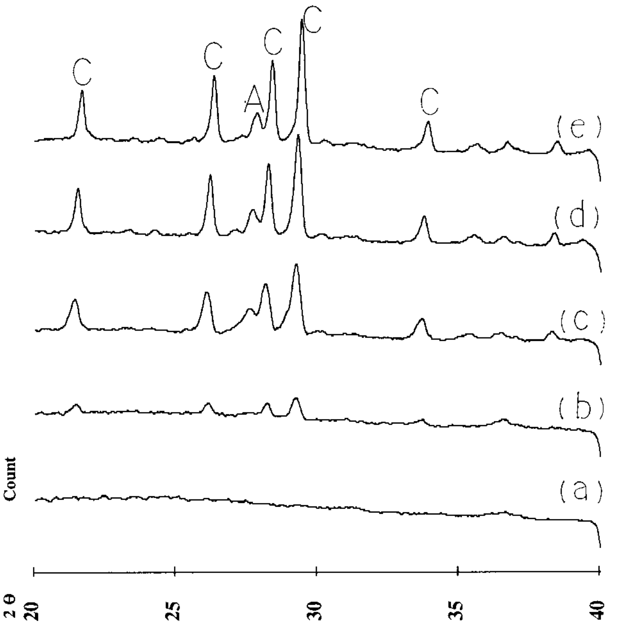

Fig. 2. X-ray diffraction patterns of MCAS glass ceramics for 40 min at (a) 800°C, (b) 900°C, (c) 940°C, (d) 1000°C, and (e) at 940°C for 4 h (A: anorthite, C: coriderite).

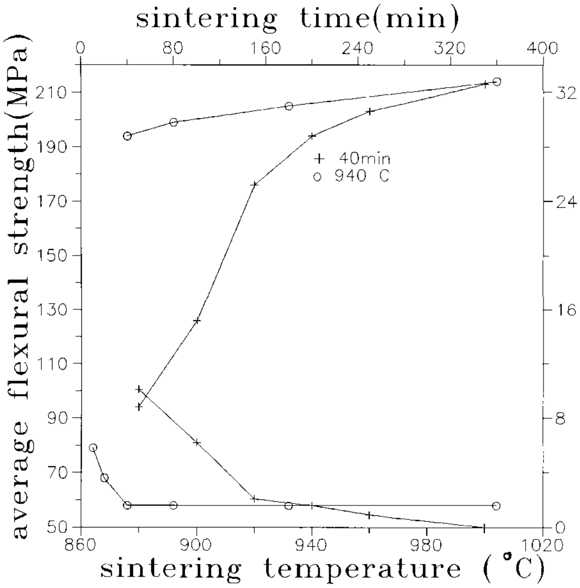

Fig. 3. The average flexural strengths and pores fraction of MCAS glass ceramics vs sintering temperature (sintered for 40 min) and sintering time (sintered at 940°C).

The middle line was calculated from the experimental data of the specimens sintered at 880, 900, 920, and 940°C, and yielded the following expression:

$$\delta = 214.436 \times \exp(-8.28929P) \qquad (4)$$

where $\delta_o = 214.436$, $n = 8.28929$

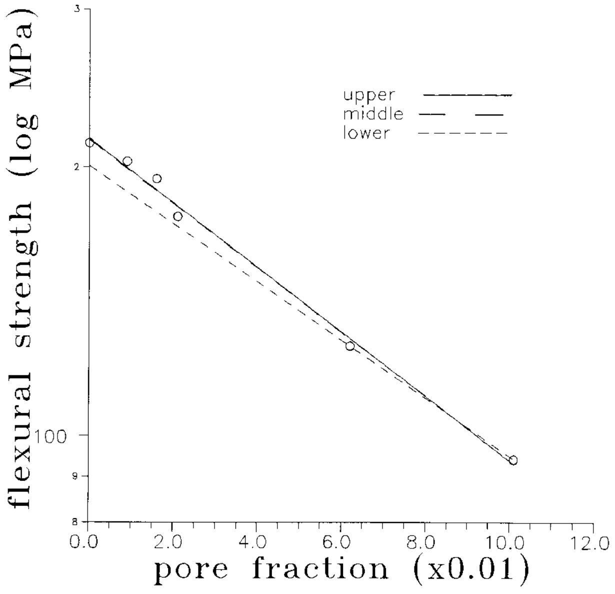

Fig. 4. The relationship between pores fraction and flexural strength with the calculated theoretical lines.

The lower line was calculated from the experimental data of the specimens sintered at 880 and 900°C and yielded the following expression:

$$\delta = 200.75 \times \exp(-7.51249P) \qquad (5)$$

where $\delta_o = 200.75$, $n = 7.51249$

As the results shown in Eqs. (3–5) are compared, the calculated flexural strength of nonporous MCAS glass ceramics increases as MCAS glass ceramics sinter at higher sintering temperature inductive data are used to extrapolate the flexural strength of nonporous MCAS glass ceramics. The crystallization of cordierite and anorthite phases almost did not happen in the specimens sintered below 900°C, and $\delta_o = 200.75$ in Eq. (5) is taken as the flexural strength of nonporous MCAS glass ceramics. The n value of 7.51249 is close to the experimental value of Ryshkewitch [12] (n is about 7), and the flexural strength value of nonporous specimens of 200.75 is also close to the experimental value of sintered cordierite (flexural strength of cordierite is about 190 MPa) [14]. As shown in Fig. 4, the average flexural strength of MCAS glass ceramics sintered at a temperature higher than 940°C will distort from the theoretical line extrapolated by Eq. (5) and show a higher value than that of the theoretical line. In addition to the decrease of porosity, the crystallization rates of cordierite and anorthite also show an increase with the sintering temperature. It is found that the diffraction peak strengths of cordierite and anorthite of MCAS glass ceramics are increased with sintering time [Fig. 2(c) and (e)]. For MCAS glass ceramics sintered at 940°C, the increase of average flexural strength with sintering time may be attributed to the increase of crystallization rates of anorthite and cordierite. The distortion of the experimental flexural strength from the theoretical values may be attributed to the increase of crystallization rates of cordierite and anorthite. The crystallization of cordierite and anorthite is therefore thought to have a beneficial effect on the flexural strength of MCAS glass ceramics.

Fig. 5 shows the relative intensity of the anorthite and cordierite peaks sintered at 940°C under various sintering times. Sintering at 940°C for 40 min resulted in the superstructure lines of anorthite and cordierite in the XRD pattern, and the superstructure lines intensity increased with the increase of sintering time. Because the crystallization of cordierite and anorthite will have certain influence on the flexural strength of MCAS glass ceramics, Eq. (1) is not enough to describe the relationships between the flexural strengths and both of crystallization rates and pores fraction. Therefore we tried to develop a modified equation in order to improve the shortcoming. In principle, the curves in Fig. 6 can be used to modify the flexural strength [Eq. (1)] of sintered glass as the function of pores fraction and crystallization rates. Because the diffraction peak strength of cordierite is higher than that of anorthite, the diffraction peak strength of (211) plane of cordierite is used to develop the modified equation. Because the strengths increases in a way that is nearly parabola shape with the sintering time, considering the following equation for such flexural strengths:

$$\delta_i = \delta_o \exp(-\mathrm{np}) \times \left[1 + ax_i + b(x_i)^2\right] \quad i = 1, 2, 3 \text{ and } 4 \tag{6}$$

where x_1, x_2, x_3, and x_4 are diffraction peak strengths of cordierite for MCAS glass ceramics sintered at 940°C for 40 min ($x_1 = 1310$), 80 min ($x_2 = 1720$), 180 min ($x_3 = 1940$), and 360 min ($x_4 = 2150$); δ_i are the flexural strength calculated by Eq. (6), and they are the functions of pores fraction (p) and crystallization rates (x_i) of cordierite; a and b are constant value. Using the specimens sintered at 40 min (194 MPa) and at 360 min (214 MPa), $a = 3.03255 \times 10^{-5}$ and $b = 2.88247 \times 10^{-8}$ can be obtained. The line obtained by Eq. (6) is good agreement to the flexural strengths of specimens. As the results showed, Eq. (6) can really be used as the modified equation to express the relationships between flexural strengths and both the pores fraction and the crystallization rate.

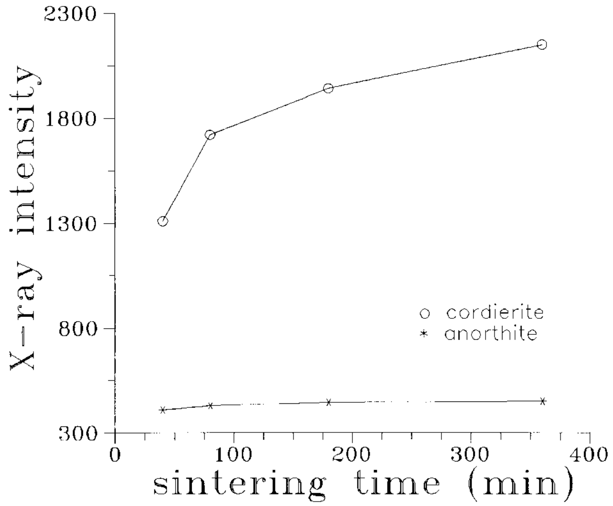

Fig. 5. The X-ray diffraction intensities of cordierite and anorthite.

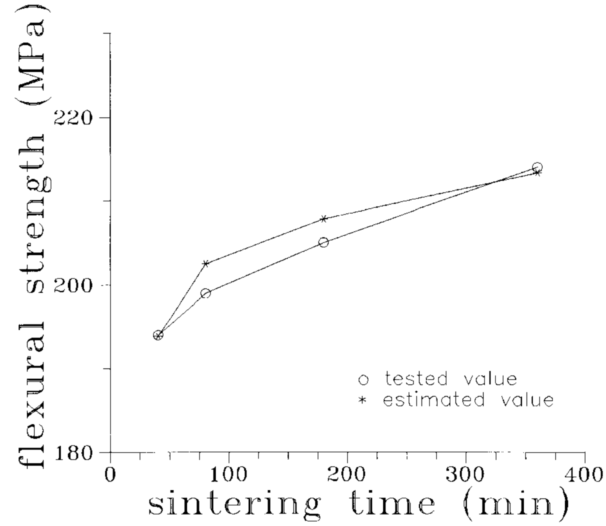

Fig. 6. The relationship between the tested flexural strength and the flexural strength estimated from the modified equations.

4. Conclusions

Cause time factors resulting in the inflection of flexural strength are potentially ambiguous, arising either out of the onset of crystallization rate or from complete densification. Equations such as shown in Eq. (6), $\delta_i = \delta_o \exp(-\mathrm{np}) \times \left[1 + ax_i + b(x_i)^2\right]$, may be used to obtain $\delta(p, x_i)$, but the equation may not be sufficient to fully describe $\delta(p, x_i)$ because of the deficiency of the exact a and b values. There may exist some degree of errors unavoidably because of the difficulty of detection of pores fraction of sintered MCAS glass ceramics and the lack of consideration of the crystallization rate of anorthite. Eq. (6) however, is capable of yielding comprehensive results to express the dependence of flexural strength on pores fraction and crystallization rates of sintered MCAS glass ceramics.

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