

Short communication

Characterization of α -cordierite glass-ceramics from fly ash

Yong He^{a,*}, Weimin Cheng^a, Hesheng Cai^b

^a Materials Science and Chemical Engineering College, China University of Geosciences, 430074 Wuhan, PR China

^b Engineering College, China University of Geosciences, 430074 Wuhan, PR China

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Abstract

Batches of α -cordierite glass-ceramics, designated as GC-I and GC-II, containing 68 and 64 wt.% fly ash, respectively, were crystallized in the temperature range of 1125–1320 °C. The XRD (X-ray powder diffractometer) of the glass-ceramics show that α -cordierite became the dominant phase in GC-I and GC-II at 1200 °C. GC-I and GC-II, whose solid parts contain 74 and 78 vol.% α -cordierite and whose compressive strengths are 35 and 50 MPa, respectively, have the respective linear thermal expansion coefficients of 1.51×10^{-6} and $1.43 \times 10^{-6}/^{\circ}\text{C}$. The fly ash α -cordierite glass-ceramics can be employed as kiln furniture, honeycomb substrates for catalysts, and heat exchangers.

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1. Introduction

Fly ash generated from thermal power plants has been still posing a heavy problem to the environment and economic growth throughout the world, since it is utilized much less today than generated [1–3]. Its chief consumer is still the construction industry, but its products including bricks, ceramics, cement and concrete are generally of low value [4–6]. Recently, increased attention has been focused on how fly ash is utilized in the high-valued products [7,8].

In this paper, the utilization of fly ash in the high-valued products like cordierite glass-ceramics is exemplified. The fly ash in this study, collected from a thermal power plant in Wuhan, China, was wet sieved through a series of four sieves with openings of 100 mesh (149 μm), 150 mesh (105 μm), 200 mesh (74 μm), and 325 mesh (44 μm). When dried, the fractions in weight of fly ash, in terms of +100 mesh, 100/150 mesh, 150/200 mesh, 200/325 mesh and –325 mesh, were calculated as 6.51, 9.34, 5.04, 17.32, and 61.79 wt.%, respectively. Consequently, only the portion of –325 mesh fly ash,

containing about 95 vol.% glassy powder, about 5 vol.% crystalline phases of quartz and mullite, and 7.1 wt.% free carbon volatile to be completely removed at 800 °C was utilized in the fabrication of cordierite glass-ceramics. Shown in Table 1 is the bulk composition of volatile-free fly ash.

Being isostructural with beryl [9], cordierite, $\text{Mg}_2\text{Al}_3[(\text{AlSi}_5)\text{O}_{18}]$, has coefficients of linear thermal expansion of 2.5×10^{-6} and $-0.9 \times 10^{-6}/^{\circ}\text{C}$ parallel to a_0 and c_0 axes [10], respectively, and accordingly a dense cordierite monolith has a linear thermal expansion coefficient, which ranges from -0.9×10^{-6} to $2.5 \times 10^{-6}/^{\circ}\text{C}$ with its batch ingredients and fabricating process [11,12]. At present, cordierite products, produced mainly from talc, kaolinite and alumina through solid reaction, are utilized as kiln furniture, honeycomb substrates for catalysts, and heat exchangers.

2. Experimental procedures

In the glass-ceramics, fly ash is the main ingredient and industrial alumina and basic magnesium carbonate powders are the other two ingredients added to introduce components

* Corresponding author.

E-mail address: heyongyu@263.net (Y. He).

Table 1
Bulk composition of volatile-free fly ash (wt.%)^a

SiO ₂	57.99
Al ₂ O ₃	28.98
Fe ₂ O ₃	4.33
TiO ₂	1.42
CaO	2.49
Na ₂ O	0.27
K ₂ O	1.31
Total	96.98

^a Analysis was carried out by Professor Yang on an X-ray fluorescence spectrometer.

Al₂O₃ and MgO. In the fabricating process the bulk powder of the fly ash, alumina, and basic magnesium carbonate were first mixed in a planetary ball mill for 4 h; then the batch was mixed again with methyl cellulose of 8 wt.% of the batch weight for another 2 h; then this well-mixed batch was granulated with water and pressed into disks with a diameter of 40 mm and a thickness of 1.8 mm under a pressure of 15 MPa; and finally, the disks were sintered at designated temperatures for 4 h before they were examined by an X-ray powder diffractometer (XRD; D/MAX-3B, Japan, Cu K α) for crystalline-phase determination and by an electron probe X-ray microanalyzer (Jxa-8800R, Japan), both for composition analyses of crystalline and glassy phases and for microstructure observation. To evaluate the volume fractions of the crystalline and glassy phases, the backscattering images of the sintered disks were analyzed by the imaging software, Image-Pro[®] Plus.

Based on the Archimedes principle, a procedure defined by ASTM C373 [13] was adopted to calculate the bulk density, apparent porosity, and water absorption in the cordierite glass-ceramics. The coefficients of the linear thermal expansion of the glass-ceramics were measured on a dilatometer (ZP-2, China). The compressive strength of the glass-ceramics in a cylindrical form was measured on a universal testing machine. The dielectric constants of the glass-ceramics were measured at 10 kHz at room temperature by using a low frequency impedance analyzer (HP 4192A). A silver paste was used for the electrodes.

The glass-ceramics were kept at 1200 °C for 15 min in a furnace, and then quenched in 28 °C water for one cycle, so that their thermal stability was evaluated by measuring the numbers of thermal shock cycles before they cracked.

3. Results and discussion

A cordierite glass-ceramic designated as GC-I, along with its batch components in Table 2, was sintered at 1300 °C for 4 h through a series of tests. To increase the quantity of the cordierite in the glass-ceramic, an improved cordierite glass-ceramic designated as GC-II, also along with its batch components in Table 2, was sintered at 1320 °C for 4 h.

To investigate the temperature range of the cordierite formation and the evolution of the crystalline and glassy phases

in the process of sintering, a series of green disks of GC-I were sintered in temperature range 900–1300 °C at an interval of 50 °C for 4 h before they were examined through the XRD technique. In order to determine the temperature at which the cordierite firstly occurred, another sample was sintered at 1125 °C for 4 h. In Fig. 1, there are XRD spectra of the –325 mesh fly ash, certain sintered disks and GC-II on the one hand, and (Fa) for the spectrum of the –325 mesh fly ash, (D) for the disk sintered at 1125 °C, (C) for the disk sintered at 1200 °C, (B) for the disk sintered at 1300 °C, i.e., GC-I, and (A) for GC-II on the other.

The XRD patterns of the spectra (A–C) fit in well with the XRD pattern of α -cordierite (JCPDS13-293) except for a few weak peaks of spinel with *d*-values of 0.244 and 0.203 nm (JCPDS No 21-540), hence the consistency of α -cordierite in the glass-ceramics with earlier researching results [14,15]. Fa spectrum in Fig. 1 shows that glass, next to which are quartz and mullite (JCPDS No 15-776), predominates in the –325 mesh fly ash, as observed under a polarizing microscope.

The XRD spectra in Fig. 1 show a clear phase transfer in our case. With the rise of sintering temperature from 900 °C, the quartz and mullite decreased in amount and disappeared completely at 1200 °C; and with the consumption of quartz and mullite the cordierite started to occur from 1125 °C and became the dominant phase in GC-I at 1200 °C with several weak diffraction peaks of phase spinel. However, our XRD data (not presented herein) show that the quartz and mullite, which originated in fly ash, had basically been used up at 1150 °C where the spinel appeared.

In Fig. 2, two backscattering images collected from GC-I and GC-II, respectively, on the electron probe X-ray microanalyzer show that the glass-ceramics consist mainly of four parts: the black areas referring to pores by P; the gray matrix to α -cordierite by C; the light area to glass by G; and the lighter areas to spinel by S. Shown in Table 3 are the compositions for α -cordierite, glass, spinel, and the inter-grain phase between spinel grains in GC-I and GC-II.

A comparison of the data in Table 3 shows that Si in the α -cordierites and Al in the spinels are less than those in their theoretical formulae, respectively; and that the α -cordierites in GC-II contain relatively more impurities than those in GC-I, whereas the spinels in GC-II seem purer than those in GC-I; and that the components CaO, FeO, TiO₂, Na₂O, and K₂O are concentrated in the glass phase which exists discretely in the α -cordierite matrix; and that the inter-grain phase between spinels in GC-I has a plagioclase composition while the corresponding phase in GC-II is not the plagioclase, but

Table 2
Batch components of fly ash cordierite glass-ceramics (wt.%)

Component	GC-I	GC-II
Fly ash (–325 mesh)	68	64
Al ₂ O ₃ powder (<0.08 mm)	10	10
Basic magnesium carbonate	22	26

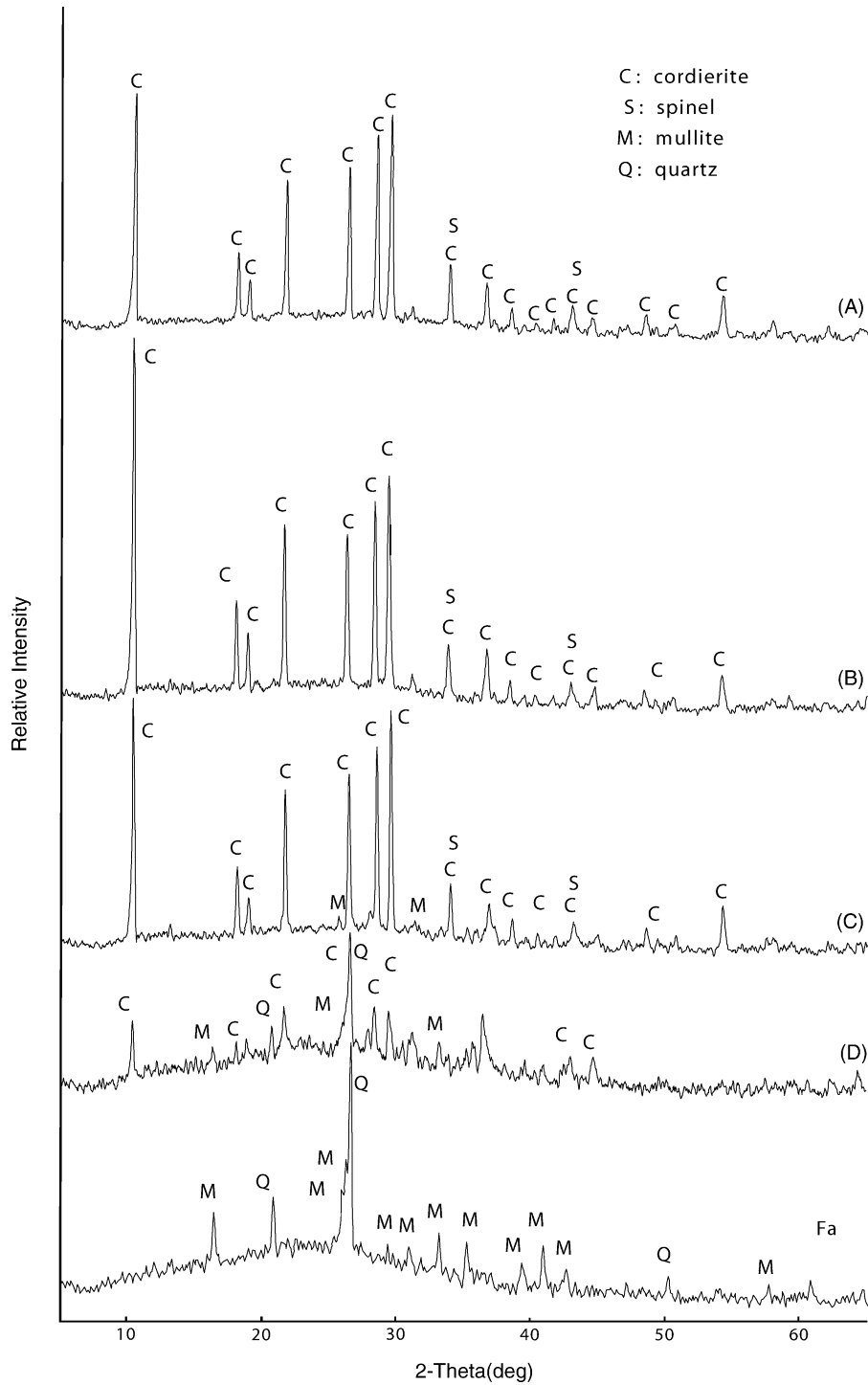


Fig. 1. XRD spectra of the –325 mesh fly ash and the cordierite glass-ceramics sintered from fly ash. (Fa) For the spectrum of the –325 mesh fly ash, (D) for the disk sintered at 1125 °C, (C) for the disk sintered at 1200 °C, (B) for the disk sintered at 1300 °C, i.e., GC-I, and (A) for GC-II. Four hours soaking time was for all samples.

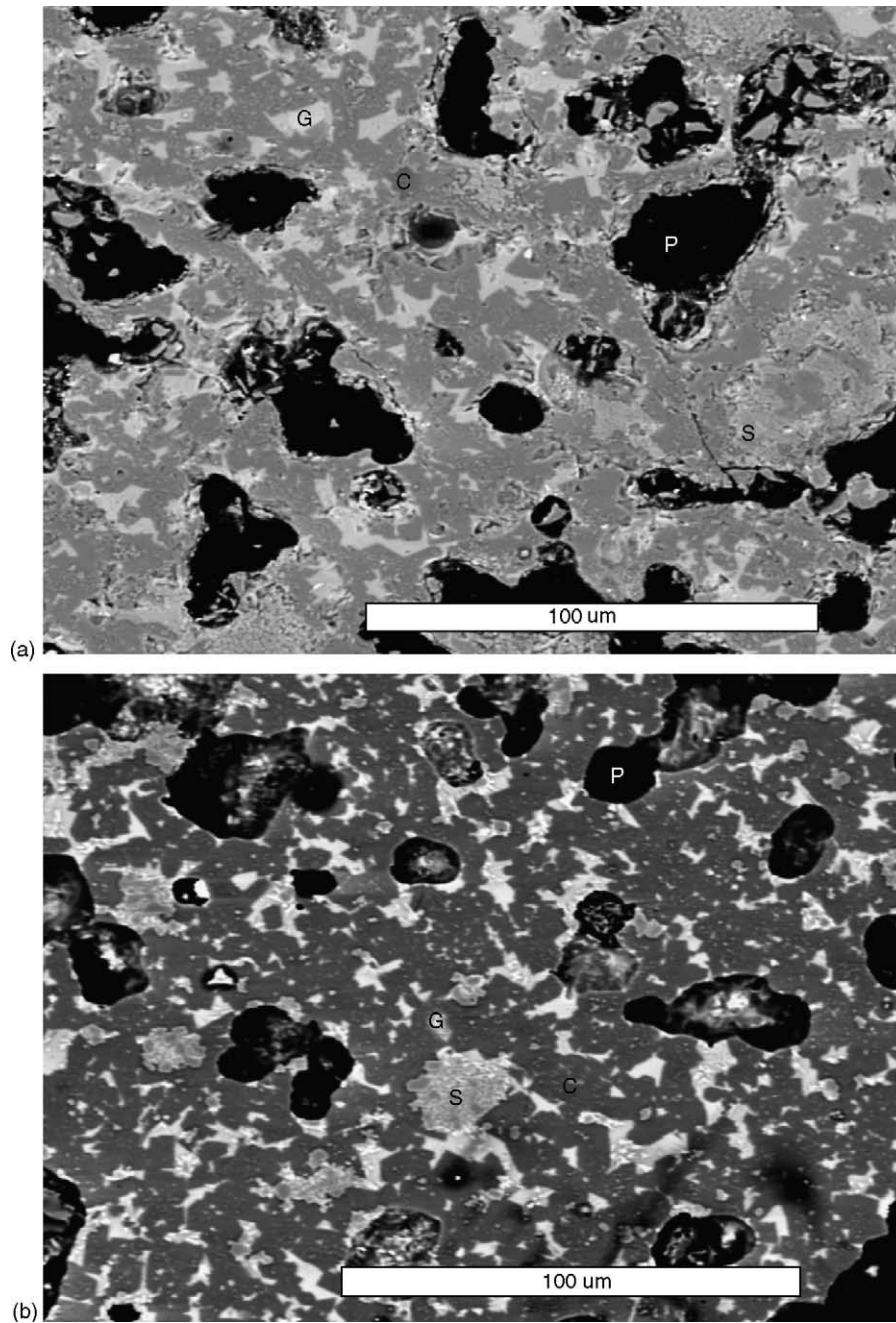


Fig. 2. Backscattering images of cordierite glass-ceramics, namely images (a and b) for GC-I and GC-II, respectively. The black areas referring to P as pores; the gray matrix to C as α -cordierite; the light irregular area to G as glass; and the lighter areas to S as spinel.

the glass with a bulk composition similar to that of the glass phases in the glass-ceramics.

Based on backscattering images of GC-I and GC-II, image analyses reveal that the α -cordierite, spinel, and glass phases make up 74.14, 6, and 19.86 vol.% of the solid part in GC-I, respectively, and similarly, the corresponding phases in GC-II are 78.69, 3, and 18.3 vol.%, respectively; and that GC-I has almost the same amount of glass as GC-II, but there is an increase of α -cordierite and a decrease of spinel in GC-II; and that both the sintering temperature and the proportion of main

components have an obvious effect on the microstructure of the glass-ceramics.

As shown in Table 4, certain properties of both GC-I and GC-II are stated, and the values of GC-I and GC-II in terms of bulk density, apparent porosity, and water absorption are calculated from the dry weight, the wet weight, and the weight in water of the testing glass-ceramics following the procedure defined by ASTM C373. The data in Table 4 show that GC-I has higher apparent porosity and thermal stability than GC-II though GC-I has a lower bulk density, and GC-I and GC-

Table 3
Bulk compositions of α -cordierite, glass, spinel and inter-grain phase between spinel in GC-I and GC-II (wt.%)

	GC-I ^a				GC-II			
	Cordierite	Glass	Spinel	Inter-grain phase	Cordierite	Glass	Spinel	Inter-grain phase
SiO ₂	48.53	57.39	nd	45.87	48.09	56.81	nd	54.00
Al ₂ O ₃	35.32	19.66	62.63	31.72	35.62	16.77	64.29	19.62
MgO	13.54	2.44	23.19	1.35	13.66	4.95	26.26	5.48
FeO	1.09	4.51	14.18	2.07	0.97	2.63	9.45	3.29
TiO ₂	0.20	3.28	nd	1.27	0.19	3.98	nd	3.44
CaO	0.77	8.83	nd	15.47	0.05	11.66	nd	9.81
Na ₂ O	0.18	1.34	nd	1.97	0.27	1.26	nd	1.85
K ₂ O	0.68	2.53	nd	0.29	1.15	1.64	nd	2.51

^a The average of three analysis results, with an associated error of ± 2 wt.%.

Table 4
Properties of fly ash α -cordierite glass-ceramics

	GC-I	GC-II
Bulk density (g/cm ³)	1.57	2.05
Apparent porosity (%)	41.32	24.11
Water absorption (%)	26.28	11.74
Compressive strength (MPa)	35	50
Linear thermal expansion coefficient ($\times 10^{-6}/^{\circ}\text{C}$)	1.56(25–800 $^{\circ}\text{C}$)	1.43 (25–1000 $^{\circ}\text{C}$)
Relative dielectric constant (10 kHz; in air)	9	9
Cycle number of thermal spalling (1200–28 $^{\circ}\text{C}$ water)	37	6

II have low thermal expansion coefficients, i.e., 1.51×10^{-6} and $1.43 \times 10^{-6}/^{\circ}\text{C}$, respectively. The reason why GC-II has poorer thermal stability may be due to higher degree of densification.

4. Conclusion

Cordierite glass-ceramics sintered from fly ash demonstrate several obtained attractive properties. For example its low linear thermal expansion coefficient and high compressive strength serve to take the place of industrial cordierite products like cordierite honeycombs, cordierite kiln furniture or heat exchanger. In addition, the utilization of fly ash in the cordierite glass-ceramics can effectively reduce the negative impact of this solid industrial waste on the environment; considerably decrease the production costs of relative industrial products, and efficiently save limited natural resources.

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