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Effect of silicon carbide additive on microstructure and properties of porcelain ceramics

Anze Shui *, Xiuan Xi, Yanmin Wang, Xiaosu Cheng

College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China

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Abstract

Porcelain green bodies with various silicon carbide contents (0–3 wt.%) were prepared from a porcelain tile powder as a major raw material and SiC particle as an additive, and were sintered at 1000–1240 °C. The samples were systematically characterized by the X-ray diffraction (XRD), scanning electron microscope (SEM) and metallurgical microscope. Effects of the SiC content and sintering temperature on the pore size, SiC particle size and sintered density were investigated in detail, and the correlative mechanism was also discussed. The SiC particle size decreased and the pore size augmented with increasing the sintering temperature. The sintered density decreased and the pore size enlarged with increasing the SiC content. The experimental results indicate that a small amount of SiC can cause porcelain ceramics to foam during sintering, and a foaming origin of the polishing porcelain waste during sintering could be attributed to the oxidation reaction of SiC particles under high temperature and alkaline molten salt conditions.

Keywords: Foaming; Sintering; Polishing porcelain waste; Silicon carbide

1. Introduction

Porcelain tile represents an advanced product developed in the sector of ceramic tiles [1–3]. Its low porosity is an essential feature, which provides the material with excellent mechanical and chemical properties, making it stain and frost resistant [2–6]. The porcelain tile is usually surface-polished to improve its aesthetic aspect and increase the competitiveness with the natural stones [5–7]. In recent years, there has been an increase in the polishing porcelain tile manufacture [1–3]. In China, the production of polishing porcelain tile has yearly achieved 3000 million m^2, and occupied more than a half of the total ceramic tile production.

But it is necessary that polish porcelain tile surface with polishing tool contained silicon carbide abrasive and magnesium oxychloride (MgO, $MgCl_2$) cement in the polishing porcelain tile production. In the polishing process, the porcelain material in a thickness range of 0.4–0.8 mm from the tile surface is commonly removed for obtaining the surface gloss level of 65–70%, resulting in a large amount of polishing porcelain waste generation [4–6], which usually contains approximately 1–5 wt.% of the silicon carbide abrasive and 2–6 wt.% of the magnesium oxychloride cement impurities derived from the polishing tool. In China, the output of polishing porcelain waste has reached 5 million - tons per year.

The large amount of polishing porcelain waste is currently disposed in landfill without any treatments, which causes serious environment pollution, increased mineral resource consumption and high production cost as well. Therefore, it is important to recycle the polishing waste in economic and environmental sustainabilities.

Some recent works reported recycling techniques of the polishing waste [8–12]. It is known that lightweight materials can be made from the polishing waste, because it easily makes the materials foaming or bloating during sintering.

However, the foaming mechanism of the polishing waste during sintering has not been understood well, the techniques cannot essentially solve the landfill problem from the large amount of polishing waste yet. It is very important to investigate first the foaming origin of the polishing waste during sintering for clarifying the foaming mechanism.

* Corresponding author. Tel.: +86 20 87110290; fax: +86 20 87110273.
E-mail address: shuianze@scut.edu.cn (A. Shui).

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Approximately 1–5 wt.% of the silicon carbide abrasive and 2–6 wt.% of the magnesium oxychloride cement impurities derived from polishing tool exist in the polishing waste [8–17], it seems that these impurities are the foaming origins during sintering. However, the silica protective layer generally forms on the silicon carbide particle surface due to the oxidation of silicon carbide in air atmosphere, which baffles the further oxidation. Besides, the magnesium oxychloride easily decomposes into MgO and HCl at 600–800 °C, the decomposition temperature is too low comparing with the general densification temperature of porcelain ceramics (about 1150–1200 °C). Furthermore, since there has been little work on the investigation of effects of silicon carbide or magnesium oxychloride on microstructure and properties of porcelain ceramics, the problems of polishing waste foaming origin during sintering are not understood yet.

The objectives of this paper are to carry out a detailed study on the effects of silicon carbide on microstructure and properties of porcelain ceramics, and to clarify the foaming origin of the polishing waste during sintering.

2. Experimental procedure

Porcelain tile powder, i.e. the powder of shattered porcelain tile (Newpearl Ceramics Group, Guangdong, China) was used as a major raw material. Table 1 shows the chemical compositions of the porcelain tile powder and polishing porcelain tile waste (i.e. the powder polished from porcelain tile surface).

Silicon carbide particle (Haixu abrasive Co., Ltd., Zhengzhou, China) was used as an additive, which is a typical abrasive used in the porcelain tile polishing process. The purity was more than 99.8 wt.%, and the nominal particle size was 38.3 μm from the manufacturer. Distilled water and 0.5 wt.% of polyethylene glycol (PEG-400 binder, Guangzhou Taiqi Chemical Technology Co., Ltd., China) were added into a mixture of the porcelain tile powder and SiC particle (the SiC content: 0–3 wt.%) to make slurries (water: mixture = 0.8:1 in a mass ratio). The slurries were planetary-milled for 30 min. The raw material powders with various SiC contents were prepared by drying the slurries, granulating and sieving (in a sieve with 30 mesh, i.e. 550 μm). Porcelain green bodies of pellet shape were fabricated by dry-pressing moulding the raw material powders at 10 MPa, which were 35 mm in diameter and 5 mm in thickness. The green bodies were sintered in an electric furnace at 1000–1240 °C in air atmosphere, at a heating rate of 5 °C/min and holding time of 20 min.

The samples were characterized by X-ray diffraction (XRD, Philips PW-1710 model X-ray diffractometer, the Netherlands) using Cu Kα, a scanning electron microscope (SEM, Philips L30FEG, The Netherlands), a metallurgical microscope (L20-4, Guangzhou Mingmei Technology Co., Ltd., China) and a laser particle size analyzer (BT-9300S, Dandong Bettersize Instruments Ltd., China).

The image analysis software (Image-Pro Plus6.0, Media Cybernetics, USA) was used to determine the SiC particle size and pore size from their micrographs. The sintered densities were measured with the Archimedes method for the samples.

Table 1
Chemical compositions of the porcelain tile powder and the polishing porcelain tile waste (wt.%).

	IL[a]	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
Porcelain tile powder	0.6	69.01	22.29	0.44	0.17	0.54	0.48	1.35	4.93
Polishing porcelain tile waste	3.14	67.27	19.21	0.37	0.15	0.62	2.94	1.19	5.17

[a] IL: ignition loss.

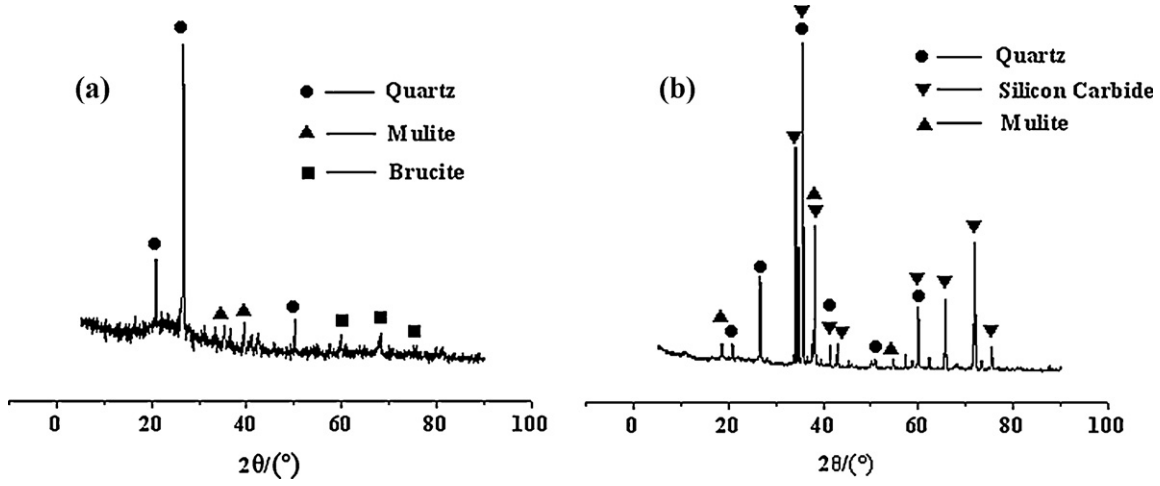

Fig. 1. XRD patterns of (a) the porcelain tile powder and (b) the polishing porcelain tile waste.

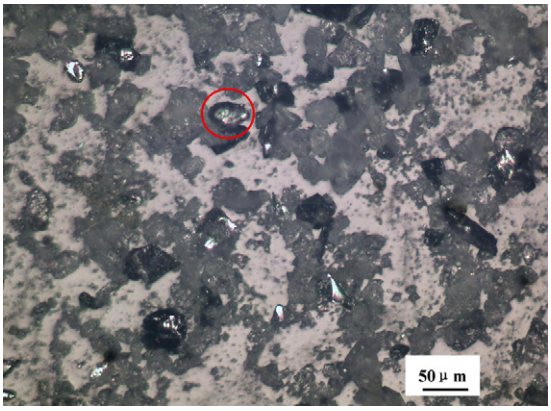

Fig. 2. Metallurgical microscope micrograph of the porcelain green body with 2.0 wt.% SiC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).

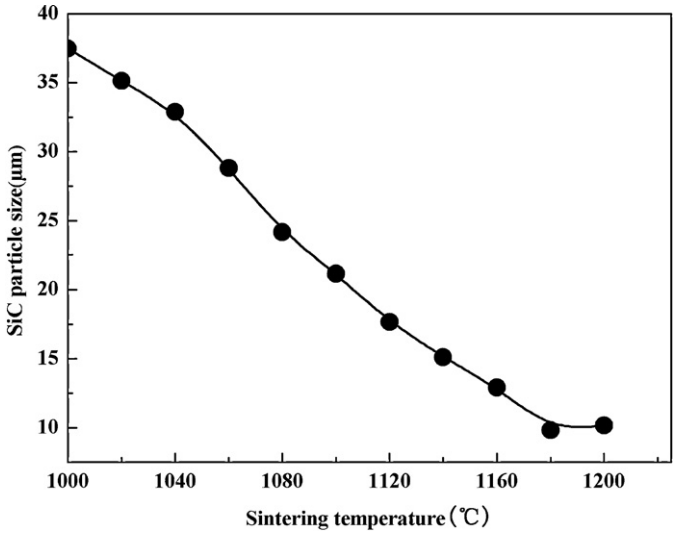

Fig. 3. Effect of sintering temperature on the SiC particle size in the samples with 2.0 wt.% SiC.

3. Results and discussion

3.1. Effect of sintering temperature on the foaming

Fig. 1 shows the XRD patterns of porcelain tile powder and polishing porcelain tile waste. There was not the SiC crystalline phase in the porcelain tile powder, but it existed in the polishing porcelain tile waste, which was derived from the SiC abrasive in the polishing tool.

Fig. 2 shows the metallurgical microscope micrograph of the porcelain green body with 2.0 wt.% SiC. The SiC particles can be clearly observed as shown in the circle in this micrograph.

Fig. 3 shows effect of sintering temperature on the SiC particle size in the samples with 2.0 wt.% SiC. The SiC particle

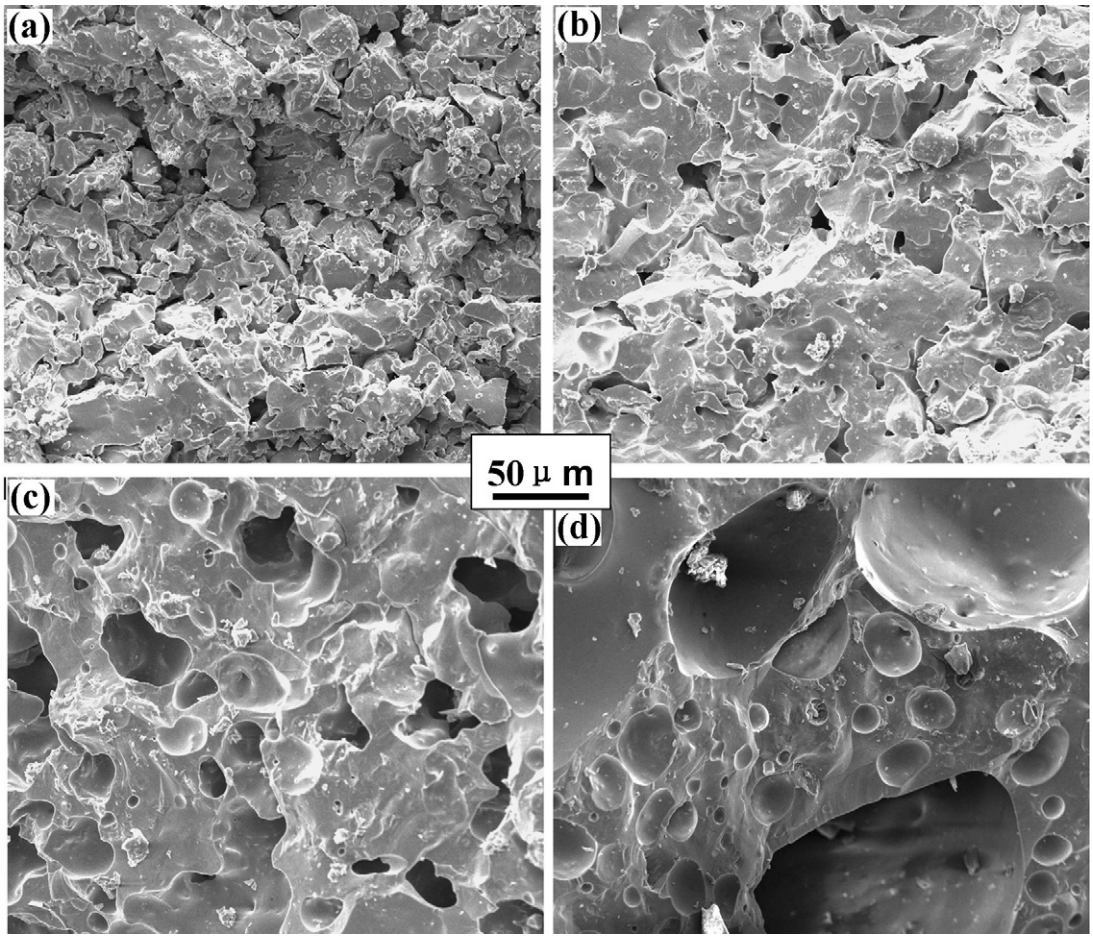

Fig. 4. SEM micrographs of the sintered samples with 2.0 wt.% SiC at sintering temperature (a) 1050 °C, (b) 1100 °C, (c) 1150 °C, (d) 1200 °C.

size decreased with increasing the sintering temperature from 1000 °C until 1180 °C, the average particle size decreased from 37.5 μm at 1000 °C to 10.2 μm at 1180 °C. However, it no longer continued to decrease at >1180 °C.

Fig. 4 shows the SEM micrographs of the sintered samples with 2.0 wt.% SiC at sintering temperatures of 1050 °C, 1100 °C, 1150 °C and 1200 °C, respectively. Clearly, the higher the sintering temperature, the greater the densification, and the more and the larger the closed pores can be. When the samples sintered at 1050 °C and 1100 °C were in a loose state, there were not the closed pores in these samples. However, when the samples sintered at 1150 °C and 1200 °C were in a dense state, the more and the larger the closed pores existed in these samples.

Fig. 5 shows effect of sintering temperature on the pore size of the sintered samples with 2.0 wt.% SiC. The pore size increased with increasing the sintering temperature. The average pore size increased from 21.5 μm at 1150 °C to 291.0 μm at 1240 °C.

The silica protective layer forms on the SiC particle surface due to the oxidation in air atmosphere, which are responsible for the oxidation resistance of SiC, because the oxygen diffusion rate through the silica protective layer is rather slow (10^{-14}–10^{-15} cm^2/s in vitreous silica) [18–20]. However, the silica protective layer reacts with the alkaline molten salt to form silicate liquid under high temperature and alkaline molten salt conditions, causing the corrosion or broken of the protective layer and the rapidly oxygen diffusion through the protective layer. This leads to a substantial increase in the chemical reaction of SiC with oxygen to generate a large amount of CO_2 and CO gas. The product gas is not timely discharged outward to remain in the liquid, resulting in the closed pore generation. The higher the sintering temperature, the stronger the protective layer corrosion, the more intense the oxidation reaction of SiC particle, and the more and the larger the closed pores generated can appear.

Also, the exorbitant sintering temperature causes a large amount of liquid phase generation and the densification acceleration, resulting in the inward diffusion of oxygen in air blocking and the further oxidation reaction of SiC particle stagnation [21–27]. Therefore, the particle size of SiC could no longer continue to decrease at >1180 °C (see Fig. 3).

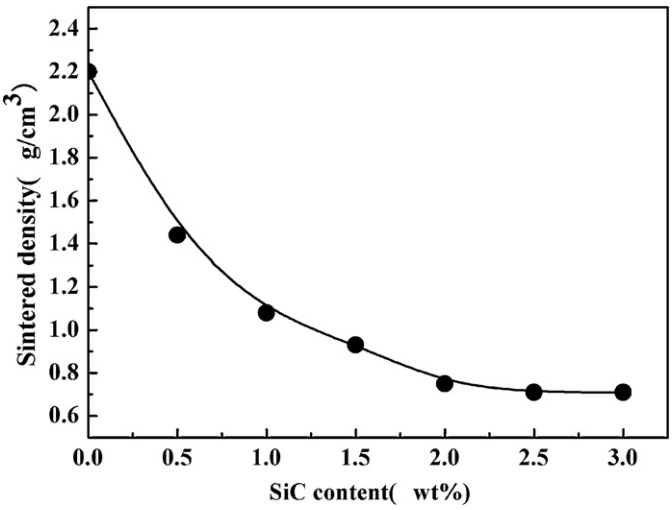

Fig. 6. Effect of SiC content on the sintered density of the samples sintered at 1200 °C for 20 min.

The loose state of samples sintered at 1050 °C and 1100 °C is conducive to the inward diffusion of oxygen in air and the outward diffusion of product CO_2 and CO gas (see Fig. 4). When the SiC oxidation reaction occurs, the product gas discharges outward. Otherwise, at >1150 °C, the SiC oxidation reaction intensifies, the liquid phase generation and the densification accelerate, the product gas becomes difficult to discharge outward, causing the generation of the more and the larger closed pores in the samples. Therefore, the most and the largest closed pores existed in the samples sintered at 1200 °C.

It is reasonable that the pore size increases with increasing the sintering temperature (see Fig. 5), because the product gas in the closed pore linearly bloats with increasing temperature (see Figs. 3 and 4).

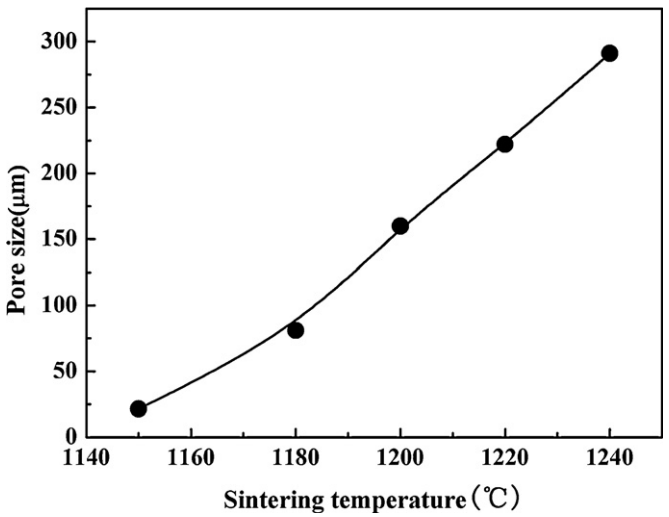

Fig. 5. Effect of sintering temperature on the pore size of the sintered samples with 2.0 wt.% SiC.

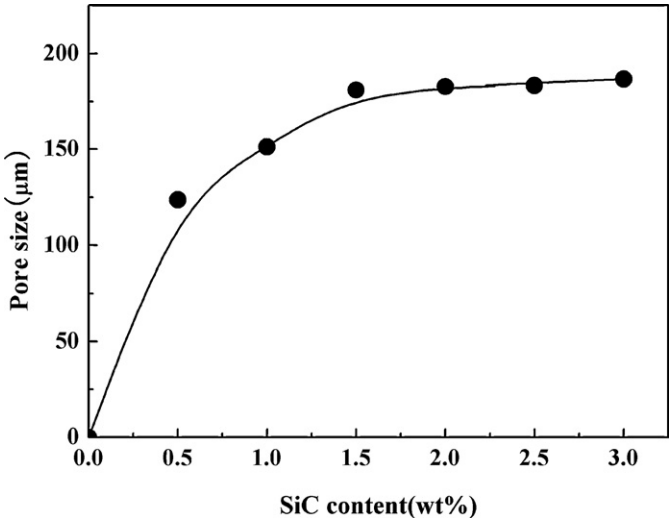

Fig. 7. Effect of SiC content on the pore size of the samples sintered at 1200 °C for 20 min.

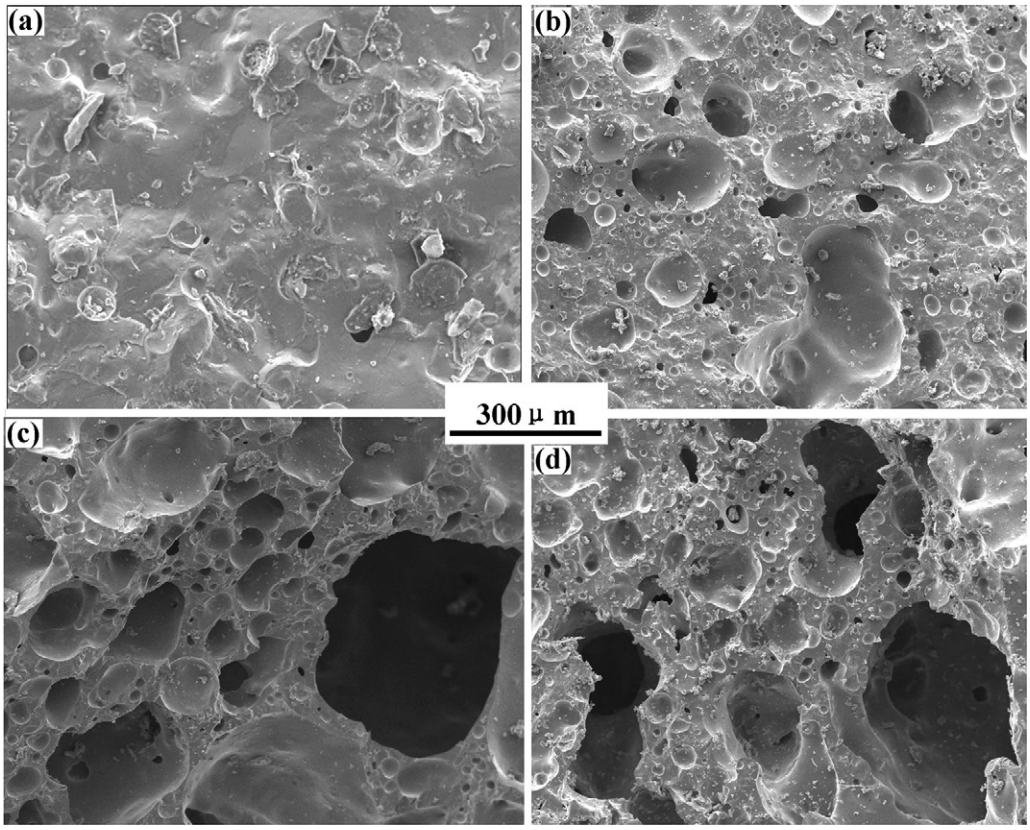

Fig. 8. SEM micrographs of the samples with (a) 0.0 wt.%, (b) 0.5 wt.%, (c) 1.5 wt.%, (d) 3.0 wt.% SiC sintered at 1200 °C for 20 min.

3.2. Effect of SiC content on the foaming

Fig. 6 shows effect of SiC content on the sintered density of the samples sintered at 1200 °C for 20 min. The sintered density significantly decreased with increasing the SiC content. However, the decreasing tendency in the sintered density became insignificant, when the SiC content was >2.0 wt.%. The sintered density decreased from 2.20 g/cm^3 at 0.0 wt.% SiC (without SiC) to 0.71 g/cm^3 at 3.0 wt.% SiC.

Fig. 7 shows effect of SiC content on the pore size of the samples sintered at 1200 °C for 20 min. The pore size sharply increased with increasing the SiC content. However, the increasing tendency in the pore size became unremarkable when the SiC content was >2.0 wt.%.

Fig. 8 shows the SEM micrographs of the samples with various SiC contents sintered at 1200 °C for 20 min. Clearly, there were not the pores in the sintered sample without any SiC, but the pores existed in the sintered samples with 0.5–3.0 wt.% SiC.

With increasing the SiC content, the oxidation reaction of SiC particle intensified to generate the more CO_2 and CO gas, which produced the more pores, and the pores were easily connected together to form the larger pores in the samples. Also, when the liquid phase was increased and the densification was accelerated at 1200 °C, the inward diffusion of oxygen in air was blocked, and the further oxidation reaction of SiC particle was restrained. This illustrates that the excessive SiC (>2.0 wt.%) did not play an important role in the foaming. Therefore, the decreasing tendency in the sintered density and the increasing tendency in the pore size became unconspicuous when the SiC content was >2.0 wt.%.

It should be emphasized that this study does not exclude the importance of magnesium oxychloride (MgO, $MgCl_2$) on the foaming of porcelain ceramics during sintering. In the next study, it was found that porcelain ceramics with both magnesium oxychloride and SiC remarkably foam during sintering, but the porcelain ceramics with only magnesium oxychloride (without SiC) almost do not foam during sintering.

4. Conclusions

Porcelain green bodies with various SiC contents were prepared and sintered. Effects of SiC content and sintering temperature on the pore size, SiC particle size and sintered density were investigated in detail.

The SiC particle size decreased and the pore size increased with increasing the sintering temperature, however, the decreasing tendency in the SiC particle size became insignificant at >1180 °C. The sintered density decreased and the pore size increased with increasing the SiC content, but the variation tendencies became unconspicuous at >2.0 wt.% of SiC content.

A small amount of SiC can cause porcelain ceramics to foam during sintering. A foaming origin of the polishing porcelain waste during sintering could be attributed to the oxidation reaction of SiC particles under high temperature and alkaline molten salt conditions.

This work carried out a quantitative study on effect of silicon carbide on microstructure and properties of porcelain ceramics in detail, and discussed the foaming origin of polishing porcelain tile waste during sintering and the related mechanism. It is believed that this work will have a significant contribution to recycling a large amount of the polishing porcelain waste in the world.

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