Foaming Mechanism of SiC in Steel Slag Foamed Ceramics

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Steel slag discharged from steel-making process is a kind of huge secondary resources and hard to be reused. Foamed ceramics are building materials used in the wall insulation and could be a potential goal product for huge amount and high value-added utilization of solid waste. In this paper, foamed ceramics containing 30 wt.% steel slag and using SiC as foaming agent were prepared. The effects of SiC content and sintering temperature on its properties were studied, and the difference of foaming mechanism between in steel slag ceramics and in traditional clay ceramics was discussed. The results showed that the foamed ceramics sintered at 1 160°C had a qualified properties with density of 0.50 g/cm³ and flexural strength of 2.6 MPa, and only 0.1 wt.% SiC was added into it, which is an order of magnitude lower than 1–3 wt.% SiC added in traditional clay foamed ceramic. SiO₂ formed from oxidation of SiC had reacted with CaO and Fe₂O₃ component derived from steel slag to generate new minerals, augite and anorthite. The reactions not only significantly promoted reaction rate of oxidation of SiC from 4.9% to 73.5%, but also widened temperature range of the oxidation reaction, contributing to foaming process of ceramics and thereby substantial saving of SiC.

KEY WORDS: foamed ceramics; steel slag; foaming mechanism; CaO; Fe₂O₃.

1. Introduction

Steel slag is a kind of huge secondary resources with the amount of above 200 million tonnes in 2019 discharged with output of 1.87 billion crude steel in the world.¹⁾ It is difficult to reuse due to its low cementitious reactivity and instability of free-CaO and MgO. In areas gathering many steel-making factories, utilization of steel slag is worse with most of slag dumped. Steel slags at present was mainly reused in concrete, road pavement and artificial reefs areas. Many new value-added methods were researched in recent years,²⁾ such as converting it into glass ceramics,³⁾ building ceramics,^{4,5)} backfill materials,⁶⁾ carbonation materials⁷⁾ or fertilizes⁸⁾ and recovery of phosphorus.⁹⁾ In order to improve utilization level of steel slag, exploring new value-added materials with huge application market became important.

Foamed ceramics are widely used in the insulation of building walls. a large amount of closed gas inside the closed hole of the foamed ceramic can effectively prevent the heat exchange on both sides of the wall, and the heat insulation effect can be achieved. Compared with other inorganic thermal insulation material, such as a foamed concrete and mineral wool board, foamed ceramics not only have the advantages in corrosion resistance and high temperature resistance, but also have low thermal conductivity, fireproof, high strength and good durability. As energy-saving build-

ing was paid more attention, the foamed ceramics will have huge market in the fields of wall insulation, fire insulation isolation and sound insulation areas.^{10–12)}

The preparation of traditional foaming ceramics is mostly based on the research of foaming process on silica-alumina based ceramics with raw materials, such as cordierite, clay, kaolin and so on, whose compositions were rich in alumina and silica. Researches on the silica-alumina ceramics is relatively mature, and most of foamed ceramics had silica or silica-alumina based reaction phases, such as quartz, mullite and so on.^{13–15)} After studying a large amount of clay and shale, C.M. Riley¹⁶⁾ believed that the suitable chemical composition for foaming was in the range of 53 wt.% to 79 wt.% SiO₂, 10 wt.% to 25 wt.% Al₂O₃, and the 13 wt.% to 26 wt.% solvent including Fe₂O₃, CaO, MgO, Na₂O and so on.

Steel slag however is characterized by a large content of CaO and Fe₂O₃ with a typical composition of 45 wt.% CaO, 18 wt.% SiO₂, 22 wt.% Fe₂O₃ (all the element Fe shown in the form of Fe₂O₃ and detected by XRF), and 6 wt.% MgO.¹⁷⁾ The characteristics makes steel slag difficult to be added with high proportion into traditional silica-alumina based ceramics. In order to mixing more slag with high CaO and Fe₂O₃ content into ceramics, a new SiO₂–CaO–MgO–Al₂O₃–Fe₂O₃ system ceramics with main crystals of pyroxene and anorthite were researched in recent years. L H Zhao *et al.*⁴⁾ studied the steel slag ceramic and found that when the proportion of steel slag in ceramics reached 40 wt.%, the ceramic sample with about 12 wt.% CaO and

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8 wt.% Fe_2O_3 prepared at 1 210°C had the maximum bending strength of 143 MPa. A. V. Gorokhovskiy, *et al.*¹⁸⁾ also added 33–50 wt.% slag to synthesis ceramic with bending strength of 203 MPa and the ceramics contained perovskite, hollandite, pyrophanite-ilmenite, leucite and pyroxene-like crystalline phases. E. Karamanova *et al.*¹⁹⁾ prepared ceramics with 30 wt.%, 50 wt.% and 70 wt.% steel slag in the temperature at 1 200–1 220°C with an elevated crystallinity and formation of anorthite solid solutions and pyroxenes. X B Ai, *et al.*²⁰⁾ prepared steel slag-based ceramics with crystal phases of pyroxenes including augite and diopside at 34 wt.% addition of steel slag.

As the ceramic from steel slag has its high good mechanical property, preparing foamed ceramics from steel slag is suitable to improve its mechanical properties under a certain porosity. For steel slag based ceramics system contains high CaO and Fe_2O_3 content, its liquid phase will be more easily formed,²¹⁾ which is beneficial to the expansion of the ceramic under the action of gas. However, as the content of CaO and Fe_2O_3 increases, the viscosity of the liquid phase at a high temperature decreases, which is adverse to the residence of the gas inside the sample.²²⁾ Therefore, it is essential for preparation of a high-quality foamed ceramics that the temperature of gas generating for a foaming agent matches the temperature of forming a liquid phase with a suitable viscosity in the steel slag ceramics.

SiC is a suitable foaming agent and widely applied into practices. It was found²³⁾ that SiC can continue to oxidize and release gas in a wide temperature range from 570°C to even above 1 200°C. The wide temperature range provides a wide adaptability for different ceramics. Foaming mechanism of SiC as a foaming agent have been researched in recent years. C C Jiang *et al.*²⁴⁾ prepared foamed ceramics containing uniform closed pores from granite scraps and minor clay tailings as the main raw materials with the addition of 1.0 wt.% SiC. It was mentioned that SiC effectively acted as foaming agent due to the oxidation reactions and then the formed CO_2 and CO gas stayed in the melt with equilibrium. Yonglin Zhang²⁵⁾ studied the effect of different amount of SiC addition on the foaming performance. Its results showed that SiC produced CO_2 by self-oxidation with high efficiency to play a role in foaming process. But SiC would form a dense and collectively bonded SiO_2 film on the surface under high temperature, which made it difficult for oxygen to diffuse into the interior of SiC and resulted a large proportion of unreacted SiC in foamed ceramics even at a high sintering temperature of over 1 200°C.²⁶⁾ For improving oxidation of SiC to release more gas, increasing fineness of SiC from 200-mesh sieve to 500-mesh or even 1 000-mesh sieve for obtaining an huge superficial areas to react with oxygen was traditionally applied into practices but its cost was significantly increased as well. Another method was mixing CaO with SiC to promote its oxidation. Researcher on foamed ceramics from porcelain tile powder revealed that the addition of a small amount of CaO accelerated foaming properties of ceramics, while its foaming rate was notably inhibited by an increasing formation of anorthite.²⁷⁾

The above researches all focused on traditional silica-alumina system ceramics, but the slag based ceramics has a composition of CaO + Fe_2O_3 larger than 20 wt.%, and the

high proportion of CaO and Fe_2O_3 component could have significantly effect on oxidation and gas releasing process of SiC. Research on the foamed mechanism of ceramics was thereby important for preparation of foamed ceramics from CaO and Fe_2O_3 rich slag.

In the paper, the effects of the amount of SiC addition from 0 to 0.3% and the sintering temperature on the steel slag foamed ceramics from 1 110°C to 1 160°C were studied. And the foaming mechanism in this process were discussed. The innovation aspect of the work was to reveal that reactions between CaO (or Fe_2O_3) and SiC promote oxidations and gas releasing of SiC, which would significantly reduce addition of SiC by an order of magnitude lower than that in traditional silica-alumina foamed ceramic. The objective was to provide a theoretical basis for reducing the amount of SiC addition and optimizing of the foam process. XRD and TG-DSC analysis was the main means used in the study. The change of the mass of the samples and the temperature of the main reaction, especially for oxidization reaction of $\text{SiC(s)} + 2\text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{s}) + \text{CO}_2(\text{g})$ can be obtained by the TG-DSC curve. Then the results of XRD were combined to ensure the different reaction process related to SiC between in slag ceramics and in clay ceramics. The foaming mechanism of SiC in steel slag foamed ceramics was further discussed.

2. Experiments

2.1. Raw Materials

The raw materials used in the study were Laiwu Steel Slag, talc and two clays. Clay 1 was from Zhangqiu and clay 2 was from Laiyang. The raw materials were crushed and ground until they could be passed through a 200-mesh sieve, then dried in a drying oven at 105°C. Their compositions were examined by X-ray fluorescence spectrometer (XRF-1800). The results are shown in **Table 1**. Chemical analysis was further employed for steel slag to detect compositions containing different iron valence in according to Chinese national standard.^{28–30)}

As can be seen from Table 1, the main characteristics of the steel slag are that it contains a large amount of CaO and iron oxide but less SiO_2 and Al_2O_3 . The results by chemical analysis shows that Fe in steel slag existed in the form of 17.8 wt.% TFe, 0.8 wt.% MFe, 12.7 wt.% FeO, 10.2 wt.% Fe_2O_3 .^{28–30)} The two clays are added as a supplement to SiO_2 and Al_2O_3 . The talc mainly provides MgO for the ceramic, which is beneficial for generating augite. And augite can increase the strength of the ceramic samples.

Table 1. The chemistry composition of raw materials and ceramics S0 (wt.%).

wt.%	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	K_2O
Steel slags	19.6	2.9	42.9	4.1	23.1	–	0.1
Talc	37.0	13.8	2.6	26.0	4.2	0.3	0.9
Clay 1	60.9	22.7	1.8	0.8	7.9	0.2	4.0
Clay 2	70.4	15.9	4.1	4.3	2.2	0.3	2.3
S0	48.7	15.3	14.5	3.6	11.4	0.1	2.4

2.2. Preparation of Samples

Composition of steel slag ceramic was shown in Table 1 and proportion of its raw materials was shown in Table 2, numbered S0. On the basis of it, 0.1 wt.%, and 0.3 wt.% of SiC were added, and respectively numbered S1 and S3. Each batch of raw materials were mixed and wet ground in a pot mill for 20 min to obtain homogenization. After being screened by 200-mesh sieve and dried at 110°C for 10 h, the raw materials were granulated to small particles with 6–8 wt.% moisture. The green body having a size of 50 mm × 5 mm × 5 mm was prepared under a pressure of 15–20 MPa. The dried green body was fired at different sintering temperature in an electrically operated laboratory furnace, heated at a heating rate of 5°C/min to a sintering temperature and maintained for 1 h, followed by natural cooling in the furnace to ambient temperature.

Only steel slag and SiC were mixed to further study the mechanism of the reaction. Theoretically, the complete consumption of Al₂O₃, CaO, MgO and Fe₂O₃ by 100 g steel slag required a total of 1.705 mol SiO₂, 100 g steel slag contains 0.7 mol SiO₂. 1.005 mol SiO₂ thereby needs to be added through SiC, 40.2 g of SiO₂ produced by the complete reaction of SiC, and the mass ratio with steel slag is thereby 5:2. The sample that steel slag to SiC of 5:2 were mixed firstly and then sintered at 1 200°C. It was denoted as S-MS. At the same time, steel slag and SiC were sintered at 1 200°C separately, then mixed in the same ratio as a reference. This sample was denoted as S-SM. Similarly, clay was studied as a kind of typical silica-alumina material with 54.3 wt.% SiO₂, 32.9 wt.% Al₂O₃, 2.2 wt.% CaO and 3.9 wt.% Fe₂O₃. The sample in the same ratio was mixed firstly and then sintered, the sintered sample was denoted as C-MS, and the sample which was sintered separately and then mixed was denoted as C-SM. In order to ensure the effects of typical components in steel slag on the foaming process of SiC, CaO (chemically pure) and Fe₂O₃(chemically pure) were mixed with SiC separately. Due to obtain the same molar ratio of 1:1 between Ca:Si and Fe:Si in respectively mixtures, the mass ratio of CaO to SiC was 7:5 and Fe₂O₃ to SiC was 2:1.

2.3. Material Characterization Techniques

Thermal gravimetric-differential scanning calorimeter analysis (TG-DSC; USA) was used to study the temperature of the phase change and the thermal reaction. The test condition of temperature range was from ambient temperature to 1 300°C with a heating rate of 10°C/min in air atmosphere. The particle diameter distribution of SiC was determined by laser particle size distribution analyzer (SEISHIN, Inc., Japan). Crushed powder samples were flattened and scanned by an X-ray diffraction instrument (XRD; M21X, MAC Science Co., Ltd., Japan) to test the composition of the sample. Surface morphology of the sample was observed by using an optical microscope (Leica Microsystems CMS GmbH, Germany).

Table 2. The weight ratio of S0 (wt.%).

Sample	Steel slag	Talc	Clay 1	Clay 2
S	30	5	50	15

Then, several formulas were used to calculate some parameters. Flexural strength of the sintered samples was calculated by Eq. (1).

$$R = \frac{3 \times F \times L}{2 \times b \times h^2} \dots\dots\dots (1)$$

where R is the flexural strength (MPa); F is the load (N) tested by a ceramic tile flex; L is the fulcrum spacing (mm), b is the width (mm) and h is the height (mm) tested by a digital vernier caliper.

The bulk density was calculated by Eq. (2).

$$D_V = \frac{m_1}{m_2 - m_3} \dots\dots\dots (2)$$

where D_V is the bulk density (kg/m³); m_1 is the dry weight of the sample (kg); m_2 is the weight of the saturated sample in the air (kg); m_3 is the weight of the saturated sample in water (kg).

For preparing the saturated sample, CXX-A type ceramic water absorption vacuum device (Ningxia Machinery Co., Ltd) was used.

3. Results

3.1. Thermal Analyses of Raw Materials

The results of particle diameter distribution of SiC were shown in Fig. 1. The particle diameter was distributed from 1.29 μm to 32.78 μm, where diameter of 50% particle of SiC was below 6.923 μm. And its specific surface area was 1.386 m²/cm³.

In order to obtain the characterization of raw materials, the thermal analyses of SiC and steel slag from ambient temperature to 1 300°C in air atmosphere had been measured by TG-DSC method. The results are shown in Fig. 2.

The theoretical reaction of SiC under sufficient O₂ conditions is

Oxidation of SiC results in 50 wt.% mass gained after SiO₂ formed and CO₂ escaped according to the calculation from Eq. (3). Actually, it can be seen from Fig. 2 that the mass increased only 2.2 wt.% until 1 300°C. Meanwhile, SiC was relatively stable before 1 016°C, and increased its

Fig. 1. The particle diameter distribution of SiC. (Online version in color.)

Fig. 2. The TG-DSC result of (a) SiC, (b) steel slag and (c) clay. (Online version in color.)

mass rapidly after 1 016°C with an obvious reaction peak. After 1 200°C, the mass was still increased, but the reaction rate had been slowed down. Therefore, it was chosen to sinter SiC at 1 200°C and the XRD results were shown in Fig. 3. It can be proved from Fig. 3 that a large amount of SiC remained unreacted with little amount of SiO₂ produced.

3.2. Properties of the Foamed Ceramics

The shrinkage, water absorption and flexural strength of S0 sintered at different temperatures were shown in Fig. 4. It can be seen that the temperature range of 1 100–1 130°C was the densification stage of the ceramic and its liquid phase appeared after 1 120°C due to dramatic changes of its water absorption and flexural strength and become excess

Fig. 3. The XRD result of untreated SiC and SiC sintered at 1 200°C and the special red number meant the strongest or/and characteristic peak of a crystal phase. (Online version in color.)

Fig. 4. Water absorption and flexural strength of S0 sintered at different temperatures. (Online version in color.)

after 1 130°C for decrease of its flexural strength. The temperature range was just fallen into the temperature range of oxidation of SiC. It was beneficial for the foaming process.

As shown in Fig. 5, S1 and S3 had flexural strength of near 50 MPa higher than that of S0 at 1 110°C, but had significant lower flexural strength than S0 when they were fired at and above 1 120°C. Oxidation of SiC started at 1 016°C which was indicated in Fig. 2. Moreover, ceramics fell into a liquid sintering process above 1 120°C as shown in Fig. 4. Gas releasing thereby occurred simultaneous with liquid sintering process for S1 and S3 after 1 120°C, which was contributed to the decrease of strength of S1 and S3 fired at above 1 120°C.

The bulk density is an important part of the properties of foamed ceramics. It can be seen from Fig. 6 that S1 and S3 were slightly smaller than S0 during firing temperature below 1 130°C, and they decreased rapidly under the temperature above 1 130°C. Formation of a large quantity of liquid in ceramics promoted foaming process of S1 and S3, which was contributed to the rapid decrease in density. The

Fig. 5. The flexural strength of S1 and S3 sintered at different temperature. (Online version in color.)

Fig. 6. The bulk density and the view of three batches of samples at the same scale. (Online version in color.)

bulk density was reduced under 1 g/cm^3 at 1150°C for S1 and at 1140°C for S3. The presence of pores caused to the decrease of the strength especially after 1130°C , as was shown in Fig. 5, which was in consistency with the trend of density reduction in Fig. 6.

The foamed ceramic S1 had high flexural strength of 6.0 Mpa , density of 0.83 g/cm^3 and specific strength of $7229 \text{ N}\cdot\text{m/kg}$ at firing temperature of 1150°C , and its density, flexural strength and specific strength decreased to 0.50 g/cm^3 , 2.60 Mpa and $5200 \text{ N}\cdot\text{m/kg}$ when it was sintered at 1160°C . S3 fired at 1150°C had a similar density, flexural strength and specific strength of 0.31 g/cm^3 , 1.11 Mpa and $3581 \text{ N}\cdot\text{m/kg}$. The density of foaming ceramic insulation board in the external wall insulation system is generally $\leq 0.28 \text{ g/cm}^3$, flexural strength is $\geq 0.6 \text{ mpa}$, specific strength is greater than $2100 \text{ N}\cdot\text{m/kg}$. All the samples can meet the strength requirements of foaming ceramic insulation board. It is induced that larger amount of SiC in ceramics decreased the firing temperature for obtaining similar properties. Moreover, it is interesting that the addition of SiC into it was only $0.1\text{--}0.3 \text{ wt.}\%$, which is an order of magnitude lower than $1\text{--}3 \text{ wt.}\%$ addition of SiC in traditional

Fig. 7. The XRD results of (a) S1 sintered at 1140°C , 1150°C , 1160°C , (b) S0, S1, S3 sintered at 1150°C , and the special red number meant the strongest or/and characteristic peak of a crystal phase.

silica-alumina foamed ceramic.^{24–27)}

Figures 7(a) and 7(b) showed the XRD results of S1 sintered at 1140°C , 1150°C , 1160°C and S0, S1, S3 sintered at 1150°C . It can be seen from Fig. 7(a) that a large amount of SiO_2 generated in ceramic sintered at 1140°C . With the increase of temperature, the characteristic peaks of quartz and rankinite decreased and that of anorthite and augite increased accordingly. The results of S1 and S3 were similar in Fig. 7(b). Compared with S0, the characteristic peaks of quartz and rankinite decreased as well. It was difficult to find the existence of SiC in the XRD results due to the extremely small amount addition. But it can be inferred from the decrease of quartz and rankinite and the increase of anorthite and augite that CaO and SiO_2 were more converted in the S1 and S3 to be converted into anorthite and augite. It was indicated that CaO played a crucial role in promoting the reaction of SiC.

Microstructure of S1 was studied and shown in Fig. 8. It can be seen that the pores didn't formed at 1130°C and then became larger and larger with the increasing temperature. The shape of the pores at 1140°C was not very regular, and pore walls hadn't been formed obviously. Starting from

Fig. 8. The microstructure of S1 sintered at (a) 1 130°C, (b) 1 140°C, (c) 1 150°C and (d) 1 160°C.

1 150°C, the shape and size of the main pores tended to be regular, and the pore walls could be distinguished obviously. At the same time, there were also some small holes in the pore walls, and smaller pores were distributed around the pore wall. At 1 160°C, the size of the main pores was further increased and the size of the pores on the pore wall was simultaneously increased. It was also observed that the pores in the pore walls had a tendency to merge toward the main pores. Such large and inhomogeneous pores would be adverse to its mechanical but be beneficial to its heat-insulation and bulk density properties.

These features indicated that the generation of gas was a continuous process. The gas generated firstly stayed inside the body to form pores, afterwards moved slowly in the body with a certain viscosity and finally synthesized large pores. During the cooling process, the small pores that did not synthesize large pores stayed in the solidified body. Since the viscosity of the body lowered under the raising temperature, the diffusion of the pores became higher and the pores were easier to merge into large pores.

4. Discussion

4.1. Comparison of Foaming Mechanism between Slag Ceramic and Clay Ceramic

Low reaction rate for SiC was considered to be formation of the SiO₂ film which is coated on the outer surface of SiC particles to prevent its further reaction. In order to promote the reaction rate of SiC, it is necessary to destroy the surface of SiO₂ film for continuous reaction between the internal SiC and O₂. Steel slag with high content of CaO and Fe₂O₃ is a cheaper additive for reaction with SiO₂. For further study of the reaction between slag and SiC, TG-DSC and XRD of samples were conducted, and samples related to clay and SiC as a reference were conducted as well.

TG-DSC curves of mixture of steel slag and SiC were shown in Fig. 9. Compared with respective curves of SiC

Fig. 9. The TG-DSC result of mixture of steel slag and SiC with mass ratio of 5:2. (Online version in color.)

and steel slag in Figs. 2(a) and 2(b), it was found that the curves of mixture were not their simple superimposition. An exothermic peak appeared obviously from firing temperature of 1 130°C to 1 220°C, corresponding to mass gain of about 10.5 wt.%, which was significantly different from the curves of both steel slag and SiC.

Compared with TG-DSC curves of SiC and clay in Figs. 2(a) and 2(c), curves of mixture of clay and SiC (in Fig. 10) however were almost the superposition of curves of clay and SiC with feature of a mass lost from 400°C to 600°C due to high volatile content of clay and a mass gain above 1 016°C due to oxidization of SiC. An exothermic peak appeared from firing temperature of 1 041°C to 1 300°C, corresponding to mass gain of 0.7 wt.%, which was almost resulted from oxidization of SiC. As oxidization of SiC causes 2.2 wt.% gain in mass, the mixture with 2/7 SiC would theoretically be 0.63 wt.%, approaching the mass gain of 0.7 wt.%.

The same results as TG-DSC curves took place on XRD patterns. As shown in Figs. 11 and 12, S-MS (mixture of raw steel slag and SiC) was sintered at 1 200°C, and it

Fig. 10. The TG-DSC result of mixture of clay and SiC with mass ratio of 5:2. (Online version in color.)

Fig. 11. The XRD result of S-MS, S-SM, slag and SiC sintered at 1200°C, and the special red number meant the strongest or/and characteristic peak of a crystal phase. (Online version in color.)

Fig. 12. The XRD result of C-MS, C-SM, clay and SiC sintered at 1200°C, and the special red number meant the strongest or/and characteristic peak of a crystal phase. (Online version in color.)

had significantly different XRD pattern with that of S-SM (mixture of sintered steel slag and sintered SiC at 1200°C), which was the simple superimposition of patterns of sintered steel slag and sintered SiC. While C-MS (mixture of raw clay and SiC) was sintered at 1200°C had a similar XRD pattern with that of C-SM (mixture of sintered clay and sintered SiC at 1200°C).

The above results proved that there was a different foamed mechanism in steel slag ceramics with traditional clay ceramics, and a new chemical reaction between slag and SiC occurred during the temperature range of 1130–1220°C.

At 1200°C in Fig. 11, new phases of augite $\text{Ca}(\text{Mg,Fe,Al})(\text{Si,Al})_2\text{O}_6$ and wollastonite CaSiO_3 generated in S-MS due to reactions between SiO_2 and $\text{CaO}/\text{Fe}_2\text{O}_3$ components. However, simple mixture of sintered steel slag and SiC had the unreacted Ca_2SiO_4 , Fe_3O_4 (slag-1200°C) and SiO_2 (SiC-1200°C). It also proved that the new reactions between slag and SiC were formation of augite and wollastonite, which contributed to the different TG-DSC curves in Fig. 9.

Reaction rate (RT) is defined as mass ratio for mass gain due to oxidation of SiC into SiO_2 to the maximum mass gain due to whole conversion of SiC to SiO_2 . Conversion of SiC to SiO_2 results into 50 wt.% mass gain of raw SiC under both CO or/and CO_2 releasing condition. RT is thereby calculated by Eq. (4).

$$RT_{T_1-T_2} = \Delta m / (0.5 \times m) \dots\dots\dots (4)$$

where $RT_{T_1-T_2}$ is the reaction rate (%) of SiC during temperature range from T_1 to T_2 , and Δm is mass gain (kg) during the temperature due to oxidation of SiC according to Eq. (3) and m is the mass (kg) of SiC.

The exothermal process of the mixture, steel slag with SiC completed during a relative narrow temperature range from 1130–1220°C in Fig. 9, and the mass gained was 10.5 wt.%, which is obviously about 4 times higher than 2.2 wt.% mass gain of pure SiC from 1016–1300°C in Fig. 2(a). For only 2/7 mass of mixture was SiC, $RT_{1130-1220^\circ\text{C}}$ of mixture was 73.5%, an order of magnitude higher not only than $RT_{1016-1300^\circ\text{C}}$ of single SiC (4.4%), but also $RT_{1041-1300^\circ\text{C}}$ of mixture between clay and SiC (4.9%). It can be seen that the addition of steel slag can promote the reaction of SiO_2 on the surface of SiC to expose the internally unreacted SiC to the air for further reaction with O_2 to release CO_2 or CO.

Meanwhile, The TG-DSC result of SiC indicate that the reaction of SiC begin to produce SiO_2 at 1016°C. Figure 7 showed the XRD results, and it can be inferred that quartz and rankinite were converted into anorthite and augite.

Al_2O_3 - CaO - SiO_2 -10wt.%FeO phase diagram was shown in Fig. 13 As 1) most Fe in steel slag exists in Fe^{2+} , and 2) SiC in sintering process play a reduction role, Fe for composition of 11.4 wt.% Fe_2O_3 derived from XRF test is referred to be Fe^{2+} in ceramic S0. The red circle in Fig. 13 is the position of composition of sample S0 with 48.7 wt.% SiO_2 , 15.3 wt.% Al_2O_3 , 12.5 wt.% FeO and 18.1 wt.% CaO (Mass ratio of MgO was counted into mass ratio of CaO). It shows that S0 fell into initial crystallization zone and located on position with eutectic temperature of 1300°C, much lower than melting point of SiO_2 (1600–1700°C). Therefore, when SiO_2 layer formed on the surface of SiC particle, the

Fig. 13. Al_2O_3 - CaO - SiO_2 -10wt.% FeO phase diagram, red circle is the position of composition of sample S0. (Online version in color.)

layer would be dissolved in liquid phase due to its eutectic composition between SiO_2 and surrounding oxides.

As shown in Fig. 7, anorthite formed sintered at and above 1 140°C, which proved by initial crystallization zone of S0. The lower crystallization temperature of anorthite in ceramics than in Fig. 13 meant that more impurity ions including Na^+ and K^+ in ceramics had further decreased its crystallization temperature and liquidus temperature.

Meanwhile, the steel slag ceramics entered into densification stage at and above 1 120°C as shown in Fig. 4. When sintering at and above 1 130°C, the liquid phase in ceramics increased, which provided one necessary condition for foaming of ceramics. A large quantity of gas releasing during the liquid formation stage was another necessary condition for foaming. The relative narrow exothermal peaks of mixture of SiC and steel slag was from 1 130°C to 1 220°C, overlapping with the temperature stage of the liquid phase sintering. The overlap made the foaming process more effectively due to largely formation of pores from the gas and liquid phase, avoiding ineffective gas releasing at lower temperature without formation of liquid phase. Bulk density of the foamed ceramics thereby decreased rapidly with pore formation from 1 130°C as shown in Fig. 6. The formation of pores was thereby consistent with the gas releasing behavior and its changes of properties.

4.2. The Effect of CaO and Fe_2O_3 in Steel Slag on the Foaming Process

As steel slag contains a 42.9 wt. CaO and 23.1 wt.% Fe_2O_3 , both CaO and Fe_2O_3 had significant effect on foaming process of steel slag ceramics. The above study confirmed that reactions between steel slag and SiC occurred above 1 130°C which was benefit to the foaming process. However, the difference of effect between CaO and Fe_2O_3 on SiC need to be distinguished. CaO and Fe_2O_3 were thereby mixed with SiC in the molar ratio of $\text{Ca}:\text{Si}$ or $\text{Fe}:\text{Si} = 1:1$ to study the role of them in the foaming process. The results of TG-DSC and XRD were shown in Figs. 14–17.

It was shown in Fig. 14 that the addition of CaO decreased the oxidation temperature of SiC mass by 40°C, and the

Fig. 14. The TG-DSC result of mixture of CaO and SiC with molar ratio of 1:1. (Online version in color.)

Fig. 15. The XRD result of the mixture of CaO and SiC with molar ratio of 1:1. (Online version in color.)

mass gain of SiC increased from 2.2 wt.% to 6.8 wt.%. $RT_{959-1\,300^\circ\text{C}}$ of the mixture was 32.6%, so there was still a large amount of SiC left even if the reaction rate increased. Figure 15 showed that Ca_2SiO_4 and SiO_2 are formed and the formation of Ca_2SiO_4 requires the participation of calcium and silicon, so the advance of the temperature and the increase of the reaction rate can also prove that CaO can effectively destroy the oxide layer on the SiC surface and promote the SiC reaction.

As shown in Fig. 16, the reaction temperature of SiC and Fe_2O_3 was much higher than that of SiC and CaO . But the reaction was obviously concentrated in a narrow interval and completed almost within 1 min. After that, the TG curve tended to be gentle and the final mass gain was 11 wt.% and $RT_{1\,258-1\,279^\circ\text{C}}$ of the mixture was 65.9%, which was equivalent to the reaction rate of SiC.

It was noticed in Fig. 16 that during range of the exothermal reaction peak of the DSC curve from 1 258–1 279°C, a decline of temperature occurred, resulting curves of both TG and DSC near 1 270°C decreased to lower temperature and then increased continuously. The decline of temperature likely resulted from endothermic reaction of reduction of Fe_3O_4 (shown in sample slag-1 200°C in Fig. 11) to FeO . As

Fig. 16. The TG-DSC result of mixture of Fe_2O_3 and SiC with molar ratio of 1:1 (a) firing from 0°C to 1300°C (b) firing from 1200°C to 1300°C. (Online version in color.)

Fig. 17. The XRD result of the mixture of Fe_2O_3 and SiC with molar ratio of 1:1. (Online version in color.)

shown in Fig. 11, most iron in the form of Fe^{2+} enter into augite $\text{Ca}(\text{Mg}, \text{Fe}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$ in mixture (S-MS-1 200°C) after steel slag reacted with SiC. Iron may carry oxygen as Fe^{3+} from the outer of reaction areas mostly during heating process and can react with SiC and be reduce to Fe^{2+} by releasing O to form CO or/ and CO_2 , resulting with a sharp weight loss at about 1263°C. The reduced Fe^{2+} and O_2 in air can further react with residual Si to form fayalite,

which contributed to the greatly accelerated reactions during 1258–1279°C. The XRD results in Fig. 17 showed that fayalite and magnetite were produced after sintering at 1300°C. But there was still much SiO_2 left in the product, indicating that Fe_2O_3 didn't destroy the surface oxide layer in the process of promoting the SiC reaction, but reacted with SiC quickly in a short time to avoid to forming oxide layer, so as to greatly promoting the reaction rate of SiC.

It was shown from the results that CaO can easily react with SiO_2 on the surface of SiC, which made the internal SiC contact with air in advance. While Fe_2O_3 promoted a full oxidation of SiC in a high and narrow temperature range. The disadvantage of the narrow temperature was that reaction was going fast and need to be sophisticatedly controlled. Combination of the two process could make the whole reaction proceed controllable in increasing the amount of releasing gas, the initial temperature and the temperature range of foaming reaction. As previously discussed, when the results applied to the material containing a large amount of CaO and Fe_2O_3 such as steel slag, 0.1 wt.% of SiC can achieve a desired effect, which was at least an order of magnitude lower than the amount of pure SiC added in the ceramics.

5. Conclusions

Steel slag can be used to prepare foamed ceramics. The prepared samples with 30 wt.% steel slag sintering at 1160°C had a density of 0.50 g/cm³ and flexural strength of 2.6 MPa. Furthermore only 0.1 wt.% SiC added in the foamed ceramic is an order of magnitude lower than 1–3 wt.% of the amount of SiC in traditional clay foamed ceramic.

SiO_2 formed from oxidation of SiC had reacted with CaO and Fe_2O_3 component derived from steel slag to generate new minerals, augite and anorthite.

Compared with the traditional foamed ceramic, reaction rate of SiC mixing with steel slag from 1130°C to 1220°C significantly increased to 73.5%, which is an order of magnitude higher than 4.9% of reaction rate of SiC mixing with clay from 1016–1300°C. Temperature range of oxidation reaction of SiC was concentrated into 1130–1220°C from 1016°C to above 1300°C and overlapped with the range of the liquid phase sintering of ceramics, resulting in a more effectively foaming process to generate more pores from the concurrence between gas and liquid phase.

Addition of steel slag into SiC has a great application prospect in preparation of low cost foamed ceramics.

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