EFFECT OF THE Si POWDER ADDITIONS ON THE PROPERTIES OF SiC COMPOSITES

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By means of transient plastic phase process, the SiC silicon carbide kiln furniture materials were produced through adding Si powder to SiC materials. At the condition of the same additions of SiO_2 powder, the effect of the Si powder additions on properties of silicon carbide materials after sintered at 1450°C for 3 h in air atmosphere was studied by means of SEM and other analysis methods. The results showed that silicon powder contributes to both sintering by liquid state and plastic phase combination to improve the strength of samples. When the Si powder additions is lower than 3.5 %, the density and strength of samples increase and porosity decrease with increasing Si powder additions. However when the Si powder additions is higher than 3.5 %, the density and strength of samples decrease and porosity increase with increasing Si powder additions. With increasing of Si additions, the residual strength of sample after thermal shocked increased and linear change rate decreased, and get to boundary value when Si additions is 4.5 %. The results also indicated that at the same sintering temperature, the sample with 3.5 % silicon powder has maximum strength.

INTRODUCTION

Silicon carbide (SiC) is one of the most widely used non-oxide ceramics. Its good high temperature properties, strength retention and resistance to oxidation and thermal shock, high thermal conduction and low distensibility make it useful as kiln furniture. It satisfies the needs of quick firing technology, lower energy consumption in great range and increase throughput of kiln. But SiC has low sintering driving force because it is a covalent bond compound with low self-diffusion coefficient, bulk diffusion and grain boundary diffusion speed which is necessary for densification. However its ratio of grain boundary energy to powder surface energy is much higher than ionic compound and metal. For these reasons, pure SiC is difficult to sinter densification only by solid phase sintering. It is necessary to add some sinter accessory ingredient to accelerate sintering by producing liquid phase at high temperature [1-3].

Metal plastic phase combination is a new method for materials preparation, which is widely studied at home and abroad. Si compound Al_2O_3–SiC, Fe compound Si_3N_4–MgO and Si–Al transition phase compound sialon have been produced and widely used by this method [4-6]. In the sintering process, metal liquid plays an important role in wetting other compositions and filling in the interspace by capillary force to increase its properties. SiC kiln furniture bonded ultrafine SiO_2 (uf-SiO_2) are widely used in. Uf-SiO_2 powder has an ability to improve the wetting property of liquid metal with SiC phase, and fill with the interspace of raw materials, and the author have discussed that the with the increase of the addition amount of uf-SiO_2, the result show that the addition of uf-SiO_2 has an effect of effectively inhibiting the reaction between liquid Si and oxygen and preventing the infiltration of liquid Si, and the sample with addition amount of 3.5 % uf-SiO_2 shows excellent physical properties [7]. The main purpose of the present study is to discuss the effect of the different Si powder additions on the properties of SiC composites with 3.5 % uf-SiO_2 powder, and then determine the best additions of Si powder.

EXPERIMENTAL

The main raw materials are acid washed SiC, 971 superfine SiO_2 powder (Elkem Company), 325 mesh Si powder. In order to obtain reasonable ratio of different particle grain size, different granularities of SiC were used: 8~10, 16~20, 36~46, 70~80, 240 and 325 meshes. Table 1 shows the chemical composition of raw materials and table 2 shows the starting mixture compositions. 4 % dextrine liquor with 20 % concentration was added to ensure excellent molding properties in pressing process.
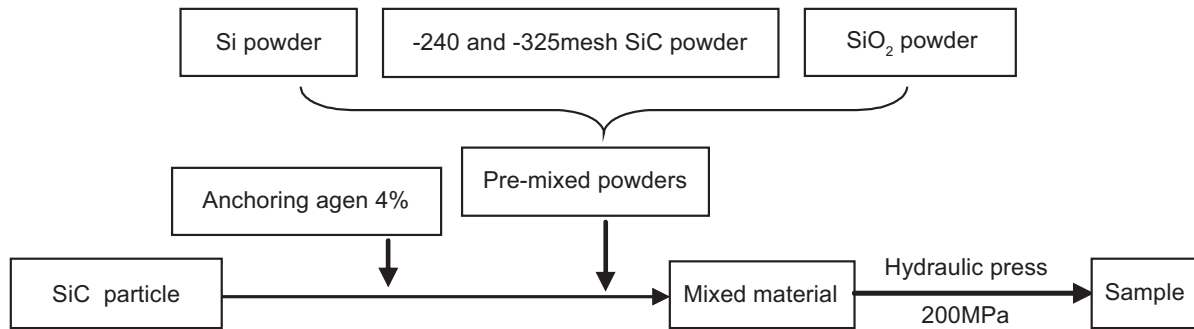
Figure 1. Flow chart of preparing sample.

Table 1. Chemical composition of raw materials (mass %).

materials	SiO_2	Fe_2O_3	SiC	C	Si	IL
SiC	0.53	0.4	98.54	0.5		0.53
Si					99.18	0.12
SiO_2	97.1	0.2		0.5		1

Table 2. Starting mixture composition (mass %).

materials		1	2	3	4	5	6
	>240 mesh	67					
SiC	-240 mesh	13					
	-325 mesh	16	15	14	13	12	11
uf-SiO_2	<1µ	3.5					
Si	-325	0.5	1.5	2.5	3.5	4.5	5.5

The samples were prepared according to the process chart of Figure 1. The powders were pre-mixed and ball milled with stainless steel pot in air at room temperature for 2 h. The samples with dimension of 125×25×25 mm and Φ50×30 mm were soured at room temperature for 24 h and dried for 24 h at 110°C in cabinet drier, and then sintered at 1450°C for 3 h in air atmosphere.

The sintered samples were characterized by carrying out by Chinese State Standard bulk density and apparent porosity, phase compositions, cold module of rapture (CMOR), cold compressive strength (CCS) in room temperature, heat module of rapture (HMOR) in high temperature, microstructure analyses and thermal shock resistance. The bulk density and apparent porosity were measured by immersion method in water under vacuum using Archimedes' principle. The microstructure was observed by scanning electron microscopy (SEM) equipped with energy dispersive X-ray analyzer (EDX). The cold flexural strength was tested according to ASTM C133-94 (Standard Test Methods for Cold Crushing Strength and Modulus of Rupture of Refractories) using a Mayer SMT50 universal testing machine in three-point bend configuration with a support roller span of 100 mm, at 25°C with crosshead speed of 1 mm.min^{-1}. The speci-

mens for hot modulus of rupture measurements were heated at a rate of 10°C.min^{-1} from ambient temperature to 1000°C, and, for tests at higher temperatures, further on at a rate of 5°C.min^{-1} from 1000 to 1250°C and 3°C.min^{-1} from 1250°C up to 1450°C. The specimens were held at 1450°C for 30 min before measurement at temperature was made. Strength at temperature was determined using a three-point bending method. The span and loading rate used in measuring the strength were 100 mm and 0.49 MPa·s^{-1}. The thermal shock resistance was evaluated by quenching the samples in water with room temperature for 5 min after heating at 1100°C for 15min, and this test was recycled three times. Then test the retained strength and calculate the residual strength conservation ratio. Residual strength conservation ratio= (residual strength after thermal shocked / cold strength of sample sintered at 1450°C) ×100 %. The sintered Φ50×30 mm samples were heated at 1100°C for 10 h and 20 h respectively, and the resistance to oxidation of the samples with different additions of Si powder was determined by the weight gain. The experimental data obtained are three sample average values.

RESULTS AND DISCUSSION

Effects of additive on properties
of the sintered specimens

Figure 2 shows the effects of Si powder additions on properties of the sintered specimens at 1450°C for 3 hours. It is obviously showed that with increasing of Si powder additions the apparent porosity decrease and get minimum value when additions is 3.5 wt. % and the value increase with Si additions of further increase. The variation of bulk density showed an opposite trend.

Figure 3 clearly show that CMOR and CCS of the specimens in room temperature after firing at 1450°C for 3 hours in oxidizing atmosphere with various Si additions. It is clearly seen that with increasing of Si additions the CCS and CMOR of specimens increase until Si additionss is 3.5 % and value decreases with further Si additions. When the additions of Si is less than 4.5 %, the rupture of specimens is stress edge rupturing,

and no crush breaks; when the additions of Si is more than 3.5 %, compression sample shows flake break, with obviously intergranular fracture characteristic.

Figure 4 show the effects of Si powder additions on HMOR of sintered specimens.. It is clearly seen that with increasing of Si additions the HMOR of specimens increase and the maximum HMOR of specimen with 3.5 wt. % Si additions is 16.8 MPa, then the value decreases when Si additions more than 3.5 wt. %.

Figure 5 shows the variation of permanent linear change of the specimens fired at 1450°C for 3 h with various Si additions. It is clearly seen that the all specimens expanded after heated at 1450°C for 3 h, but the value are less than 0.1 %, and with increasing of Si additions the linear change rate decrease and the minimum expansion are obtained with 4.5 wt. % additions.

The melting point of Si is 1412°C. When the specimens were heated at 1450°C for 3 h, Si become into melt and fill in the gaps between particles. Finally, using the interfacial tension role will particles tightly together, making material of porosity drops, bulk density rise. With the increase of the additions of silicon, this kind of help burn function is more and more obvious and the properties of specimens get better. But too much Si

powder addition amount may lead to enormous Si melt get together in an area during sintering process, and this area became the weak part samples, then the properties of materials performance deteriorated.

Effects of additive on resistance to oxidation of the sintered specimens

The sintered samples of dimension Φ50×30 mm were heated from 25°C to 1100°C during 3.5 hours, and holding temperate at 1100°C for 10 h and 20 h respectively, and the resistance to oxidation of the samples with different additions of Si powder was determined by the weight gain. The mass gain rates (η) were calculated by followed formula:

$$\eta = (M_2 - M_1)/S$$

where M_1 is the weight of sintered specimens (g), M_2 is the weight of sintered specimens after oxidized (g) and S the surface area of sintered specimens (cm^2).

Figure 4. Effect of Si additions on the heat module of rapture of sintered specimens at 1450°C for 30 min.
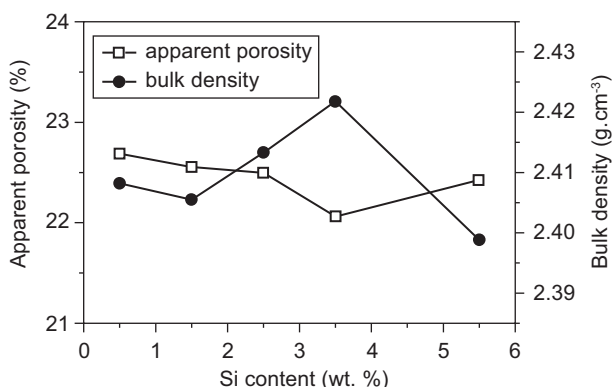

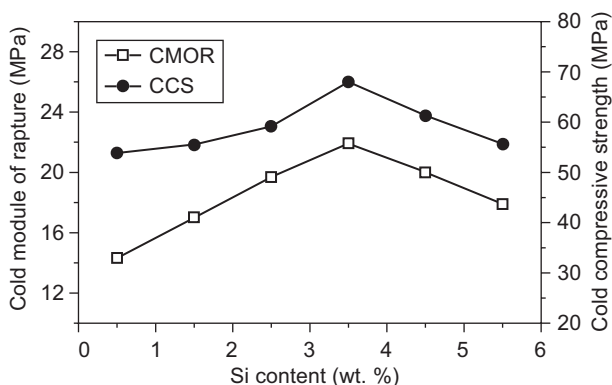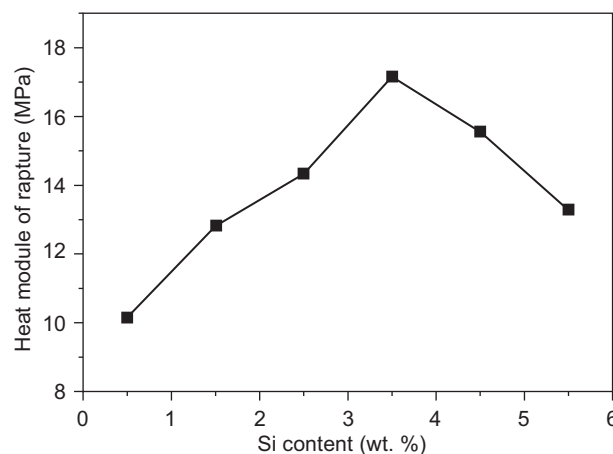Figure 2. Effect of Si additions on bulk density and apparent porosity of sintered specimens.

Figure 3. Effect of Si additions on mechanical properties of sintered specimens in room temperature.
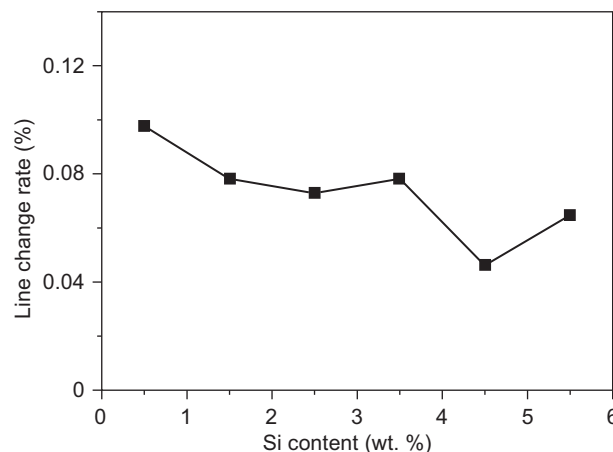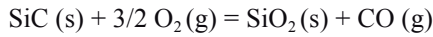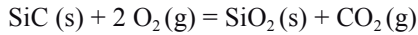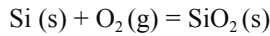

Figure 5. Effect of Si powder additions on line change rate of sintered specimens.

The oxidation curves of samples are shown in Figure 6. At the beginning of oxidation, a dense oxide layer of SiO_2 is formed on the easily oxidized part of the specimen. The involved reactions are as follows:

$$Si\,(s) + O_2\,(g) = SiO_2\,(s)$$

$$SiC\,(s) + 2\,O_2\,(g) = SiO_2\,(s) + CO_2\,(g)$$

$$SiC\,(s) + 3/2\,O_2\,(g) = SiO_2\,(s) + CO\,(g)$$

After the oxidation layer formed the following oxidation of Si and SiC only can be performed by the diffusing of oxygen (O_2) through SiO_2, i.e. this oxidation step is dominated by the diffusion of O_2. Because of the low diffusion speed of O_2 in SiC (self-diffusion coefficient is 1.3×10^{-18}), with the increase thickness of oxidation layers, the formation rate of SiO_2 decrease. Therefore there is a tendency of oxidation increase of the specimen. With oxidizing time prolonging, the mass gain rates increase. And with various of Si additions, the mass gain rates of specimens with oxidized for 10 hours is maximum with Si additions is 3.5 wt. %, followed 2.5 wt. % and the value is minimum with 1.5 wt. % Si additions; the mass gain rates of specimens with oxidized for 20 hours is maximum with Si additions is 3.5 wt. %, followed 4.5 wt. % and the value is minimum with 1.5 wt. % Si additions.
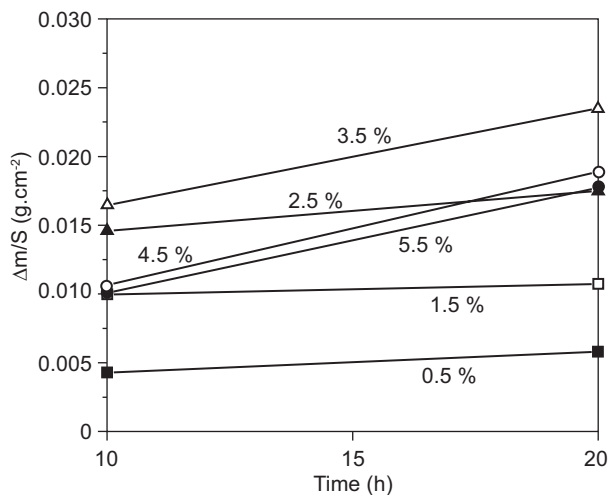

Figure 6. Oxidation time versus mass gain rate of specimen.

Effects of additive on resistance to thermal shock of the sintered specimens

Residual strength value and strength conservation ratio of sample after thermal shocked one times and three times as a function of additions of Si powder is shown in Figure 7 and Figure 8. It can be seen that in all the cases the residual strength value of specimens after thermal shocked are lower than those of sintered specimens, and thermal shock test times to strength retention influence is not obvious. The specimen with 4.5 wt. % Si additions get to maximum residual strength value after thermal

shocked for one times and 3 times. It can also be seen that in all the cases there is residual strength conservation ratio with increasing the additions of Si powder gradually decreased until 3.5 wt. % and get to minimum, and then gradually increased. This is because that Si powder can become melting during heated process and accelerate to sintering, and then the combination of compositions become more tightly, these samples were damaged more than other after thermal shock test. Thermal shock testing can crated little microcrack in specimens. This microcrack provides channels for O_2 diffusing, and Si or SiC were oxidized by these O_2 and formed SiO_2, and then the strength of sample will increase during heat treatment at 1100°C for 15 min.
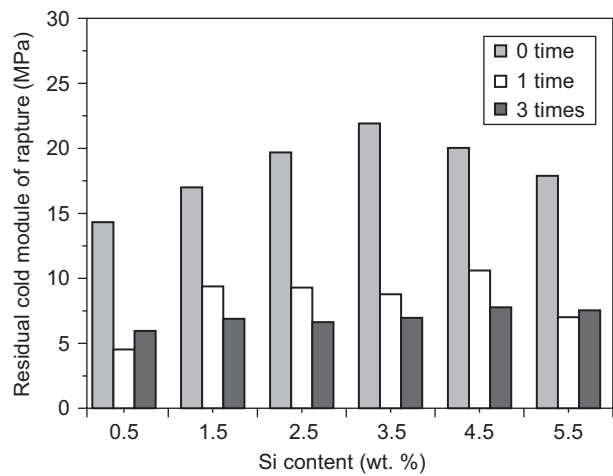

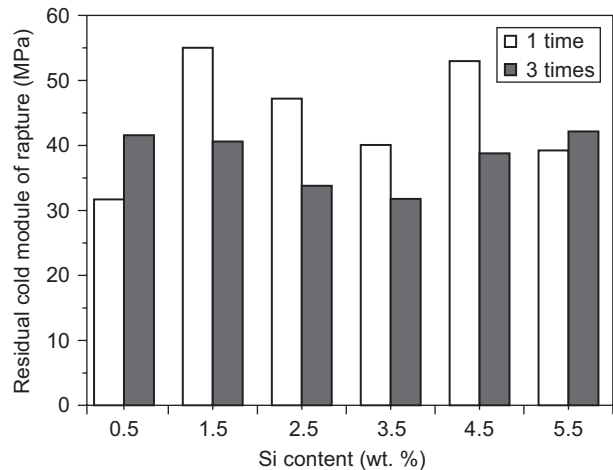Figure 7. Effect of Si powder additions on residual strength of specimens.

Figure 8. Effect of Si powder additions on residual strength conservation ratio of specimens.

Microstructure

The microstructure of specimens' inside were observed by SEM were shown in Figure 9. With increasing the additions of Si addition, the specimens become more compact. Silicon powder contributes to both sintering by

liquid state and plastic phase combination to improve the strength of samples. The specimens existed free Si which oxidized by oxygen were during sintering process, these Si will occurred following reaction when Si additions is 3.5 and more.
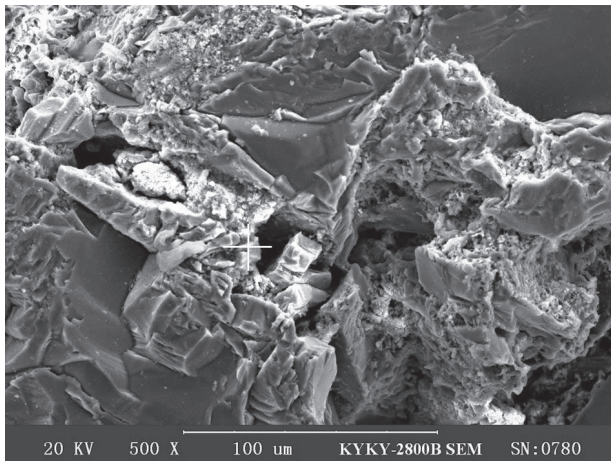
$$3\,Si\,(s) + 2\,N_2\,(g) = Si_3N_4\,(s)$$
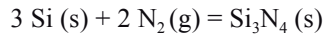
In Figure 10 we can see that the oxygen and nitrogen element is distributed uniformly in the edge of the SiC particles, which means Si plays an important role in the binder of SiC particles. Silicon powder contributes to both sintering by liquid state and plastic phase combination to improve the strength of samples.
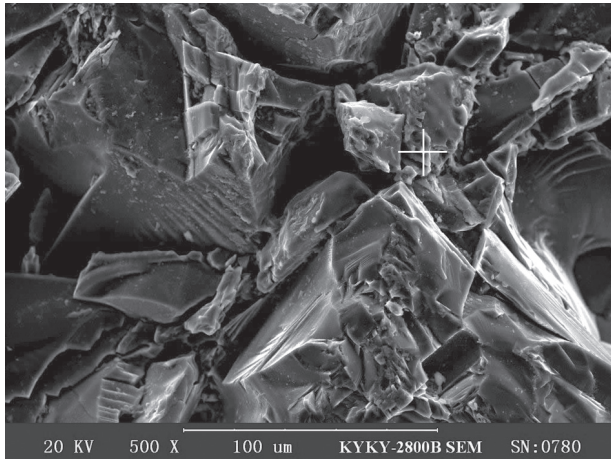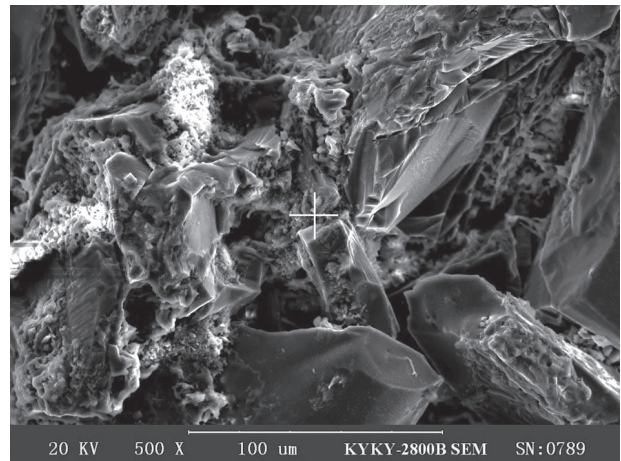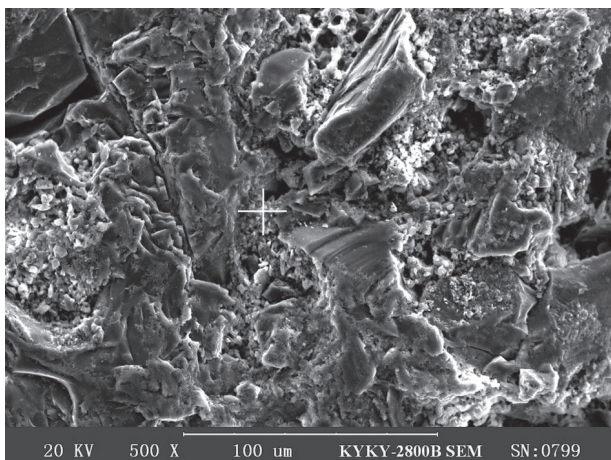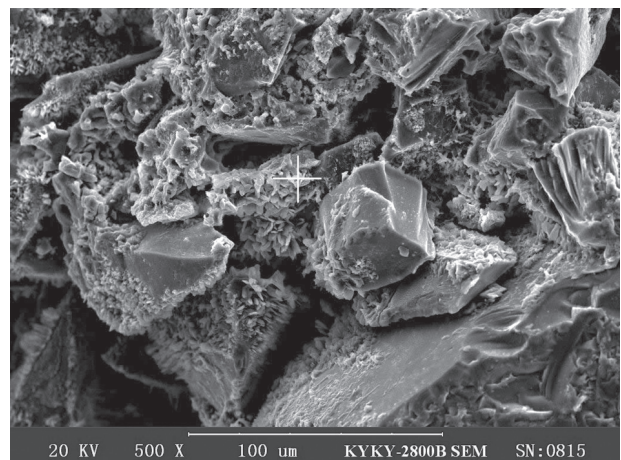
a) Si - 0.5 %
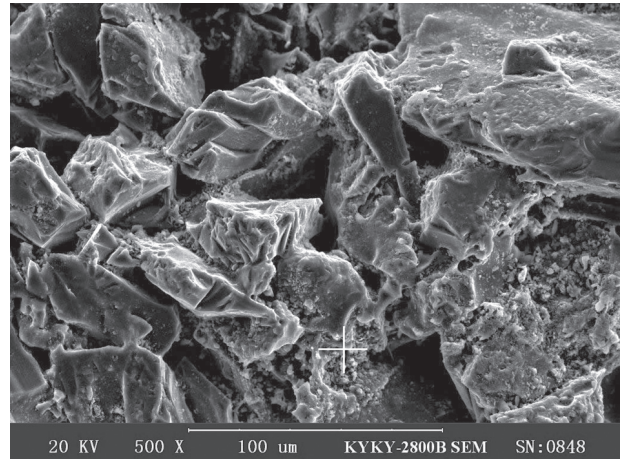
b) Si - 1.5 %

c) Si - 2.5 %

d) Si - 3.5 %

e) Si - 4.5 %

f) Si - 5.5 %

Figure 9. Secondary electron image of micrographs of sintered specimens' inside with various Si additions.

CONCLUSION

According to transient plastic phase process, the present work studied the effect of Si powder addition on sintering and properties of SiC composites. Based on the results above, it could be concluded as following:

1) With the increasing of the addition amount of Si powders, the density and strength of samples increase and porosity decrease until Si powder additions is 3.5 wt. %, however when the Si powder additions is more than 3.5 %, the density and strength of samples decrease and porosity increase with prolonging increase Si powder additions. And the HMOR of specimens increase and the maximum HMOR of specimen with 3.5 wt. % Si additions is 16.8 MPa, then the value decreases when Si additions more than 3.5 wt. %. The addition of Si contributes to both sintering by liquid state and plastic phase combination to improve the strength of samples.

2) In all the cases there is cold strength and residual strength conservation ratio enhancement with increasing the additions of Si powder. And the specimen with 4.5 wt. % Si additions get to maximum residual strength value after thermal shocked for one times and 3 times, followed with 3.5 wt. %, and get to minimum with 1.5 wt. %. The results also indicated that at the same sintering temperature, the sample with 3.5 % silicon powder has maximum strength.

3) The specimens existed free Si which oxidized by oxygen were during sintering process, these Si will occurred reaction into Si_3N_4 when Si additions is 3.5 and more.
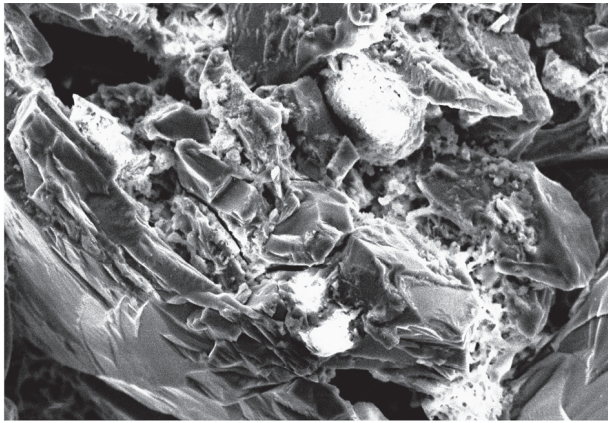
60μm   Mixed
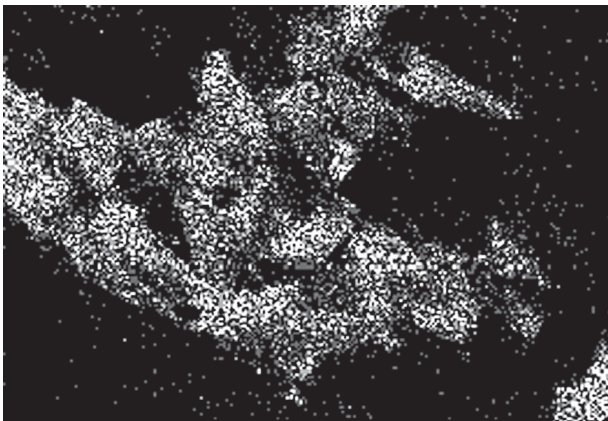
60μm   Silicon Ka1

60μm   Carbon Ka1_2

60μm   Oxygen Ka1

60μm   Nitrogen Ka1_2

Figure 10. Element maps photograph of specimens' edge with 3.5 %-Si additions.

Acknowledgements

References

1. Zheng N., Tian Y., Sun J., et al.: China Ceramics *5*, 24 (2006).
2. Lomello F., Bonnefont G., Leconte Y., et al.: Journal of the European Ceramic Society *32*, 633 (2012).
3. Amirthan G., Udaya A., Balasubramanian M.: Ceramics International *37*, 423 (2011).
4. Brodkin D., Kalidindi S., Barsoum M., et al.: Journal of the American Ceramic Society *79*, 1945 (1996).
5. Barsoum M., Zavaliangos A., Kalidindi S., et al: JOM *11*, 52 (1995).
6. Liu X., Yin H., Ren Y.: Naihuo Cailiao *42*, 47 (2008).
7. Ruan G., Meng F., Cheng, Z., et al.: Naihuo Cailiao *41*, 263 (2007).
8. Ruan G., Zhang Z., Chen Y. : Materials Science Forum. *610-613*, 262 (2009).