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The effects of transition metals on carbothermal synthesis of β-SiC powder

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Abstract

Several transition metals were added in the carbothermal syntheses of β-SiC powder from silica and phenolic resin at temperatures ≤1500 °C. The effects of the transition metals on the yields of SiC and powder morphology were investigated. The results showed that by adding 1 wt.% of Fe, Co or Ni in the silica/phenolic resin mixtures, the synthesizing temperature of SiC decreased and the yields of SiC increased. But adding Mn, Pd or Cu has no favorable effects on the syntheses of β-SiC powder. After reaction at 1400 °C, the highest yield was obtained by adding 1 wt.% Fe, which reaches 77%. Adding Co could result in 73% yield and adding Ni could only have 30% yield. The SiC powder obtained from mixtures with 1 wt.% Fe was agglomerated, while that from mixtures with 1 wt.% Co was mostly un-agglomerated particles of 100–300 nm in size. The positive effects of transition metals in SiC powder synthesis at temperatures <1500 °C seems to be in the enhancement of $SiO_{(g)}$ formation.

Keywords: Combinatorial synthesis; Ceramic; Additives; Morphology; Powder

1. Introduction

Silicon carbide (SiC) powder is an excellent reinforcement for ceramic composites because of its high hardness, high strength, chemical inertness and oxidation resistance. It has been exploited in various ceramic composites to improve their structural properties [1–10]. There are several common synthesizing methods for silicon carbide, including direct carbonization of Si metals [11], CVD from silane [12,13], sol–gel [14] and carbothermal reduction of silicon dioxide [15,16]. These methods have their own advantages and disadvantages. For example, the silicon carbide powder made from chemical vapor deposition and sol–gel method has high purity and narrow particle size distribution. But the reactants are unstable and toxic and the production cost is high. Direct carbonization method is simple and cheap, but it will leave significant amounts of unreacted silicon and impurities. So far, the carbothermal reduction method is the most prevailing method for SiC powder synthesis [15–20]. It not only gives high purity β-SiC powder but also involves inexpensive starting materials (e.g., silicon dioxide, rice husk, graphite and charcoal).

Although the carbothermal reduction method only requires cheap reactants and could have good products, it is usually performed at 1600 °C or above in order to have high yield of β-SiC [15]. At higher temperature (1600 °C or higher), the reaction is believed to be a $SiO_{(g)}$–$CO_{(g)}$ gas–gas reaction, favoring whisker formation [17,21]. Transition metals (especially Fe, Co, Ni) have been shown to act as catalysts in the gas–gas reaction to form whisker via VLS (vapor–liquid–solid) mechanism [17]. At lower temperatures (1500 °C or lower), the reaction is attributed to the $SiO_{(g)}$–$C_{(s)}$ gas–solid reaction, favoring powder formation. Because of low temperatures, the yield of SiC is usually low. Whether or not the transition metals have similar effects in the lower-temperature carbothermal synthesis of SiC powder appears to be relatively unclear.

In this research, we surveyed a number of transition metal additives in terms of their effects on the synthesis of SiC powder at lower temperatures (1500 °C or lower), where gas–solid reaction dominates. The yields of SiC and the morphology of products were studied.

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2. Experiment

Ludox®[1] (colloidal silica, 40 wt.% suspension in water, particle size 20–24 nm) and phenolic-resin[2] (resol type in methanol, 78% solid content, 50% in solid (carbon) content after carbonization) were used as the silica and carbon sources, respectively. Both chemicals were mixed in ethanol (95%) with a weight ratio of C/SiO_2 equaled to 5/3 (corresponded to C/SiO_2 molar ratio equaled 3/1) after carbonization of phenolic resin. Salts of transition metals were then added into the solution and mixing with a stirrer for 1 h. After mixing, the mixtures were dried under IR lamps. The dried cakes were then ground into powder for subsequent heat treatments. The transition metal salts used were $PdCl_2{\cdot}6H_2O$, $Mn(CH_3COO)_2{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and $CuSO_4{\cdot}5H_2O$. The amounts of these additives were such that after high temperature reduction, the transition metals were 0.5, 1 and 3 wt.% of the solid (carbonized carbon + silica) mixtures.

Carbothermal synthesis of β-SiC powders was performed with two-step heat treatments in flowing Ar (100 ml/min) in alumina crucibles. The heat treatment was first to maintain at 1000 °C for 2 h (with 10 °C/min heating rate) to carbonize the phenolic resin [22], and then heated to 1300, 1400 or 1500 °C and soaked for 4 h.

The products were analyzed with X-ray diffractometry (XRD) for phase identification (D-5000, Siemens, Karlsruhe, Germany; Cu Kα radiation). Quantitative analyses of the powder were performed using weight loss and XRD internal standard method [23] with CaF_2 as the internal standard. The product powder was first heated in air at 650 °C for 1 h to remove the residual (unreacted) carbon. The weight loss after this treatment is the amount of residual carbon in the product. Then, the powders were analyzed with XRD internal standard method to obtain the weight percentage of SiC in the powders after carbon removal. The balance would be the amount of cristobalite/silica (SiO_2). The morphology of the powder products was observed in a scanning electron microscope (JSM 5600, JEOL, Tokyo, Japan).

3. Results

Fig. 1 is the X-ray diffraction patterns of SiO_2/resin mixtures without additives after reaction between 1300 and 1500 °C. The patterns reveal that no β-SiC was produced after reaction at 1300 °C. This sample contained only amorphous carbon and silica, as indicated by the hump near two-theta equals ~22°. As the reaction temperatures increased to 1400 °C, β-SiC started to appear. The β-SiC became the major crystalline phase after reaction at 1500 °C.

Fig. 2 shows the diffraction patterns of SiO_2/resin mixtures with 1 wt.% transition metal additives and reacted at 1300 °C for 4 h. Peaks of β-SiC are present in the patterns for samples with Fe, Co, Ni or Cu additions. The XRD patterns for samples

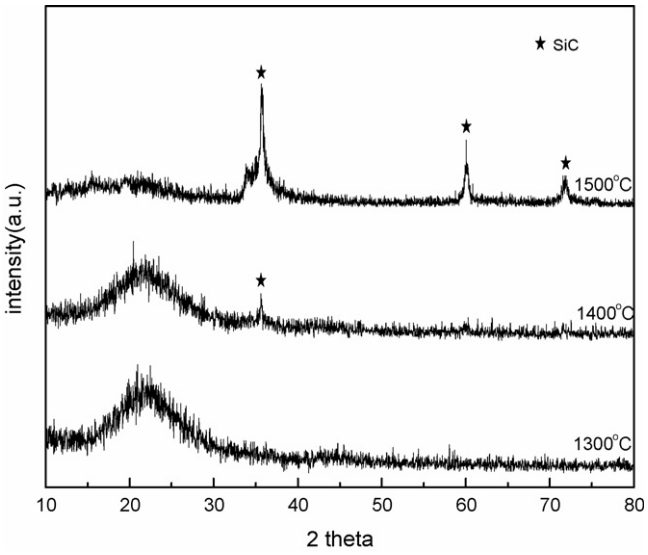

Fig. 1. X-ray diffraction patterns of the SiO_2/resin mixture, without additives, after reaction at different temperatures in Ar.

with Pd or Mn additions show no crystalline phases. Consequently, the addition of Pd and Mn has no effects in promoting SiC formation at 1300 °C while the addition of Fe, Co, Ni or Cu lowers the formation temperature of SiC. It is also noted that cristobalite peaks are present in the patterns for the samples with Ni or Cu addition, indicating Ni or Cu also enhances the crystallization of cristobalite (from silica).

The effectiveness of Fe, Co, Ni, and Cu addition in the promotion of SiC formation can be also confirmed by the weight loss after reaction. The gas–solid reaction of SiC formation proceeds in two steps [15,20,24]:

$$C_{(s)} + SiO_{2(s)} \rightarrow SiO_{(g)} + CO_{(g)} \quad (1.1)$$

$$2C_{(s)} + SiO_{(g)} \rightarrow SiC_{(s)} + CO_{(g)} \quad (1.2)$$

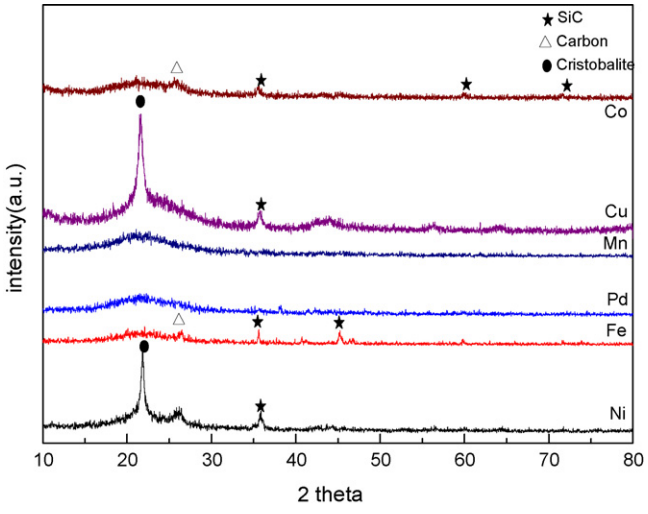

Fig. 2. X-ray diffraction patterns of the SiO_2/resin mixture, with 1 wt.% of different transitional metal additives, after reaction at 1300 °C for 4 h in Ar.

[1] AS 40, Dupont, Wilmington, DE, USA.
[2] PF-650 Chung-chun Plastic Co. Ltd., Hsinchu, Taiwan.

According to Eqs. (1.1) and (1.2), the SiO_2 needs to be reduced to gaseous $SiO_{(g)}$ in order to react with C to form SiC. Carbon monoxide (CO) is a by-product in both equations and will dissipate so that the reactions can continue. Therefore, the weight loss could indicate that the reactions take place. More weight loss implies higher degree of reaction. If the additives had no effects in the reaction, the weight loss after reaction at each temperature would be the same as that from synthesizing mixtures without additives. On the other hand, if the additives promote one or both steps of the reactions, the weight loss would be more than that from mixtures without additives under the same conditions. Hence, the weight loss could be used as an indicator of the proceeding of the reactions and the effectiveness of the additives.

Fig. 3 is the weight loss of the SiO_2/resin mixtures with 1 wt.% of different additives after reaction between 1300 and 1500 °C. Without additives, significant difference in weight loss occurred between 1400 and 1500 °C, which is consistent with the temperature range of SiC formation revealed in XRD (see Fig. 1). In contrast, the differences in weight losses are equally important between 1300 and 1400 °C and between 1400 and 1500 °C in samples with Fe, Co, Ni additives. This implies that in samples without additives, the reaction to form SiC is important only above 1400 °C, while in samples with Fe, Co, Ni, significant reaction starts from 1300 °C.

It is noted in Fig. 3 that the sample with Cu addition showed different weight loss behavior. Although at 1300 °C, the weight loss was significant, between 1300 and 1500 °C it was not as high as shown by other additives in the same temperature range. This indicates that the reactions started at low temperature (<1300 °C), but did not proceed in the same way as for the other samples at higher temperature. As seen further in Fig. 4, the samples with Cu have much lower SiC yield than the samples with Fe, Co or Ni additives.

To investigate the yields of SiC after reaction at 1400 °C, quantitative analyses were performed. Fig. 4 compares the weight percentages of each component (SiC, residual carbon and SiO_2) in the products with additives after reaction at 1400 °C. The compositions of the products of reaction from mixture without additives are also included for comparison. From this figure, it appears that the addition of 1 wt.% of Fe and Co resulted in a dramatic increase in SiC yields after reaction at 1400 °C. Without additives, the samples had 19% of SiC at 1400 °C and 32% of SiC at 1500 °C. When 1 wt.% of Fe or Co were used, the yields of SiC at 1400 °C reached 77 and 73%, respectively. These yields were much higher than the yield obtained from mixture without additives. In contrast, the addition of Ni had only moderate increase in the SiC yield at 1400 °C (30%). More noticeably, the addition of Cu had adverse effect on the yield of SiC formation (7% from sample with 1 wt.% Cu versus 19% from sample without additives) even though it lowered the formation temperature of SiC (see

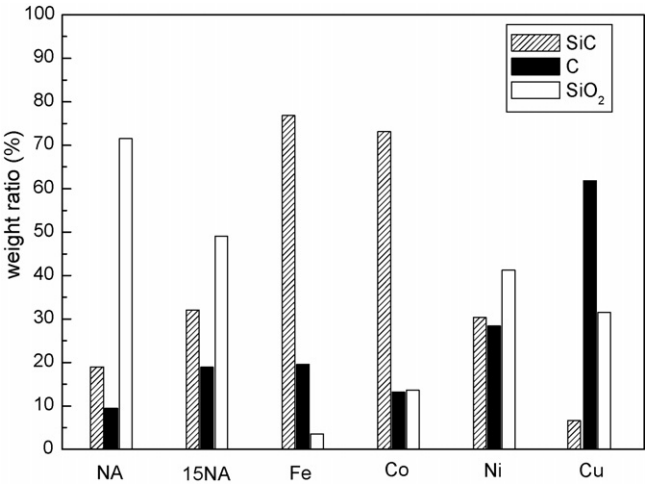

Fig. 4. Weight percentages of SiC, residual carbon and SiO_2 in the reaction products with 1 wt.% additives reaction at 1400 °C. Also included were samples without additives. NA, no additives, reaction at 1400 °C; 15NA, no additives, reaction at 1500 °C.

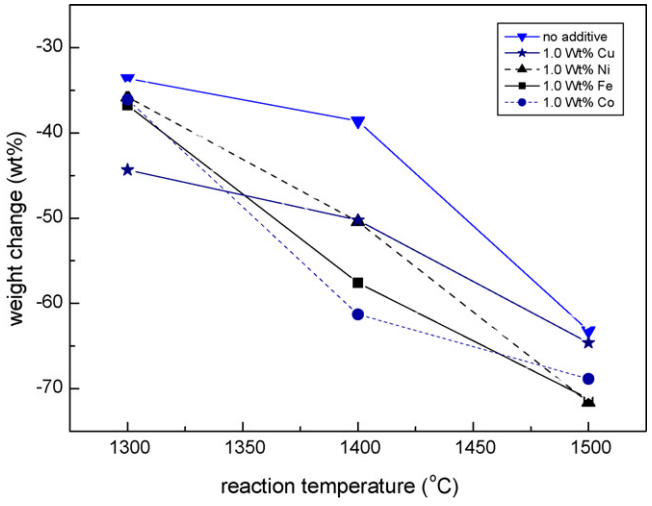

Fig. 3. Weight changes of the SiO_2/resin mixtures with 1 wt.% of different additives after reaction between 1300 and 1500 °C, for 4 h, in Ar.

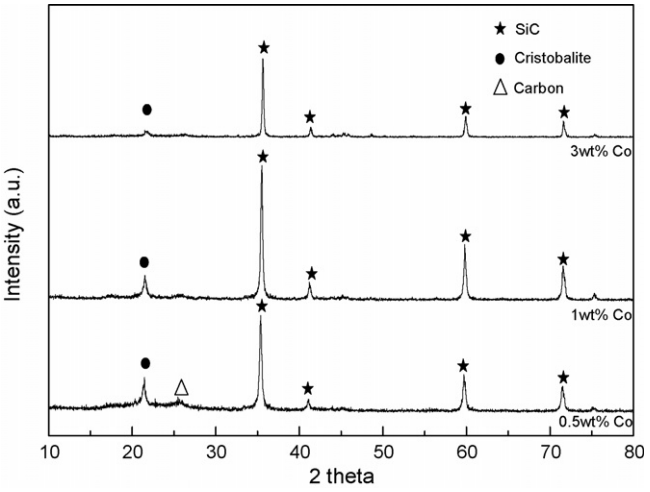

Fig. 5. X-ray diffraction patterns of the SiO_2/resin mixtures with 0.5–3 wt.% Co, after reaction at 1400 °C for 4 h in Ar.

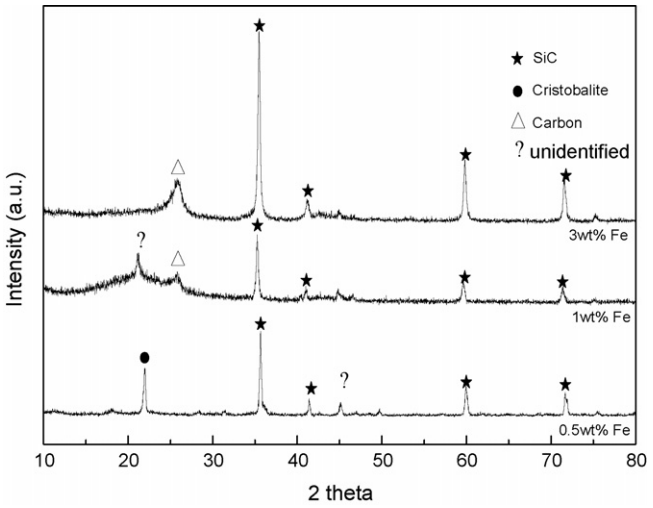

Fig. 6. X-ray diffraction patterns of the SiO_2/resin mixtures with 0.5–3 wt.% Fe, after reaction at 1400 °C for 4 h in Ar.

Fig. 2). The low SiC yield in the Cu-added sample was also confirmed by the low weight loss between 1300 and 1500 °C. Figs. 5 and 6 show XRD patterns of samples with different amounts (0.5–3 wt.%) of Co and Fe additions, respectively. The results reveal that increasing amounts of both additives could decrease the amount of cristobalite in the reaction products.

The additives also affect the morphology of the reaction products. Samples with Fe or Cu agglomerated during thermal treatment, while samples with Co or Ni remained loose powders. Fig. 7a is the SEM micrograph of the powder sample without additives and reacted at 1500 °C, while Fig. 7b–d are SEM micrographs of the powder samples with different transitional metal additions and reacted at 1400 °C. These powders consisted basically of particulates of about 100–300 nm. The sample with Ni addition contained notable whiskers/fibers. In contrast, the samples with Fe and Co had few whisker/fiber. Furthermore, spherical particles, which are likely fused metal balls were also found in these two samples, see Fig. 7b and c. It implies that at 1400 °C, even with metal balls of Fe or Co to enhance whisker formation via VLS mechanism, there were little amounts of whiskers in these two samples. Consequently, $SiO_{(g)}$–$CO_{(g)}$ gas–gas reaction could be considered insignificant at this temperature. The synthesis of SiC at 1400 °C should be via $SiO_{(g)}$–$C_{(s)}$ gas–solid reaction.

Unlike the samples with Fe, Co, the sample with Ni showed whiskers/fibers formation. Nevertheless, the sample with Ni addition had relatively low SiC yield and high concentration of SiO_2 (cristobalite) compared to the samples with Fe or Co additions. Therefore, it is supposed that these whiskers/fibers are mostly of SiO_2 fibers.

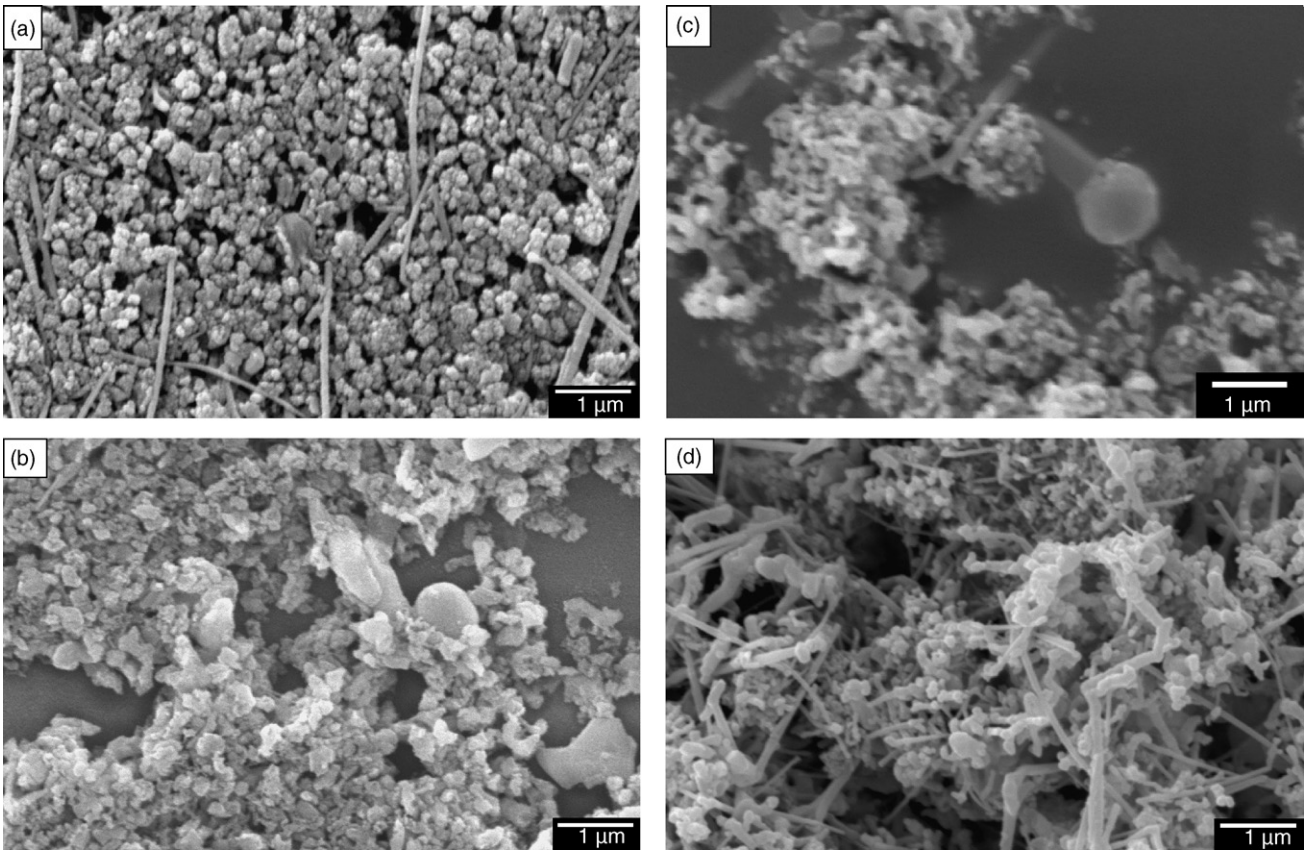

Fig. 7. SEM micrographs of the SiO_2/resin mixtures after reaction for 4 h: (a) 1500 °C without additives; (b–d) 1400 °C with 1 wt.% of Fe, Co, and Ni, respectively. Note the spherical metal particles in (b) and (c).

4. Discussion

The favorable effects of transition metals on SiC whisker formation (at high temperature) is to provide preferred reaction sites for $SiO_{(g)}$ and $CO_{(g)}$ via VLS mechanism [25]. In contrast, the positive effect of transition metals in solid–gas reaction for SiC powder formation seems to be in the enhancement of $SiO_{(g)}$ formation in the first step Eq. (1.1) of the SiC formation. When the concentration of $SiO_{(g)}$ increases, the second step of the gas–solid reaction Eq. (1.2) proceeds readily to the right, lowering the (apparent) synthesizing temperature and increasing the yield of SiC. However, if the additives melt and cause the carbon agglomeration at relatively low temperature (where SiC formation is unlikely to occur or at a very slow reaction rate), the decrease of carbon surface area (therefore, the contact of SiO and C) would decrease the subsequent reaction between $SiO_{(g)}$ and $C_{(s)}$. This would decrease the yield of SiC.

Consequently, the additives can be divided into three categories according to their effects at temperatures lower than 1500 °C: (1) no effects on the SiO and SiC formation. This category of additives showed no effects in any observable aspects; (2) enhancing SiO formation and agglomeration (or sintering) of the reactants. Samples with additives of this category will result in low to moderate yields of SiC powder depending on the competition between SiC formation (from SiO and C) and agglomeration of reactant and/or the reaction product powders. If the agglomeration occurs early or rapidly in the synthesis, carbon would not be able to react to form SiC; and (3) enhancing SiO formation without agglomeration or the agglomeration occurs slowly such that SiC formation could be nearly completed. In such case, SiC forms with high yield. Among the additives investigated in this research, Pd seems to fall in the first category while Mn, Cu and Ni in the second category, with decreasing tendency of agglomeration. The Fe and Co are in the third category.

5. Conclusions

Powders of β-SiC could be synthesized carbothermally from mixtures of silica and phenolic resin. The addition of Fe, Co or Ni was effective in decreasing the reaction temperatures and increasing the yields, while the addition of Mn, Pd or Cu had no favorable effects. The enhancement of yields was pronounced when 1 wt.% of Fe or Co were added and reacted at 1400 °C. After reaction at 1400 °C, the highest yield (77%) was obtained by adding 1 wt.% Fe. Adding Co would result in 73% yield and adding Ni could only give 30% yield, which was close to the yield (32%) of silica/resin mixtures without additives and reacted at 1500 °C. The SiC powder obtained from mixtures with 1 wt.% Fe was found to be agglomerated, while that from mixtures with 1 wt.% Co consisted mostly of un-agglomerated particles of 100–300 nm in size and with few whiskers. The positive effects of the transition metals on the SiC powder synthesis at temperatures lower than 1500 °C appeared to be in enhancing the $SiO_{(g)}$ formation.

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