Synthesis of SiC-TiC composite powders by carbothermal reduction and their sintering behavior

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SiC-TiC composite powders were synthesized in Ar at 1300 ~ 1700 °C by carbothermal reduction using TiO₂, carbon black and silica sol as the starting materials. The synthesized products were characterized by XRD and SEM. The ignition loss was calculated to determine the degree of the carbothermal reaction. The results show that the SiC-TiC composite powders synthesized at 1600 °C for 1 h are composed of round-like and plate-like particles and a small amount of whiskers with a size of 50 ~ 100 nm. The influence of a AlN-Y₂O₃ additive on the sintering behavior of the SiC-TiC composite powders was investigated by microstructural observation and Rockwell hardness testing. The SiC-TiC composites with 10 vol% AlN-Y₂O₃ hot pressed at 1900 °C under 25 MPa possess a relative density of 98.9% and Rockwell hardness of 93.2HRA.

Key words: SiC, TiC, Powder, Carbothermal reduction, Synthesis, Sintering.

Introduction

Silicon carbide (SiC) possesses an excellent combination of mechanical, physical and chemical properties, such as high temperature strength, high hardness, good oxidation resistance, low electrical resistivity and good chemical stability [1-2]. It is widely used in structural and functional parts, e.g. thermal exchangers, metal working parts, armor plates, cutting tools and nozzles. However, the application fields of SiC ceramics is limited by its low room-temperature strength, poor fracture toughness and high flaw sensitivity.

An effective method to solve the problems is to introduce a transition metal boride or carbide as a dispersed phase into the SiC matrix. A boride or carbide has been recognized as a candidate for advanced structural applications due to their exceptional hardness and stability at high temperature. Titanium carbide (TiC) is a promising structural material which has a high Young's modulus (410-450 GPa), high melting point (> 3000 °C), high Vickers hardness (28-35 GPa), good electrical conductivity and excellent chemical stability. These characteristics make TiC and TiC-based composites attractive materials for cutting tools, wear-resistant parts, bullet-proof armor, aircraft components etc [3-4]. There have been many reports about other materials reinforced with TiC such as silicon nitride [5-6], MoSi₂ [7-8] and Al [9-10]. Meanwhile, there exist a number of reports concerning the effect of TiC particles dispersed in a SiC matrix [11-18].

Generally, SiC-TiC composites are fabricated by hot-pressing or spark plasma sintering using SiC and TiC powders as the starting materials. Nevertheless, mechanical mixing of the powders introduces inhomogeneity in the composite. Because the particle size and mixed uniformity of SiC-TiC composite powders have a great effect on the properties of SiC-TiC composites, preparation of well-mixed unagglomerated composite powders can be an important stage for making SiC-TiC composites with excellent properties. Among the synthetic methods available, carbothermal reduction is the most commonly chosen route to produce SiC and TiC. Unfortunately, there are limited reports of the synthesis of SiC-TiC composite powders by the carbothermal reduction method. In this paper, SiC-20 mol%TiC composite powders are synthesized by carbothermal reduction using silica sol, carbon black and titania powder as the starting materials. The effects of the reaction temperature on the phase composition and morphology of SiC-TiC composite powders are discussed in detail. Densification is carried out by hot pressing and the sintering behavior is investigated.

Experimental

Silica sol (SiO₂, 28 wt%), carbon black (ash content: < 0.1 wt%, particle size: < 40 nm) and TiO₂ (purity: ≥ 99.0%, D_{50} = 1.7 μm) were taken as the starting materials for the preparation of SiC-TiC composite powders. Ar gas (purity: ≥ 99.99%) was used as a protective gas to prevent oxidation of graphite die and samples. The experimental procedure is shown in Fig. 1. All the starting materials were accurately weighed according to reactions (1) [19] and (2) [20], and the percentage of the TiC content was designed as 20 mol%.

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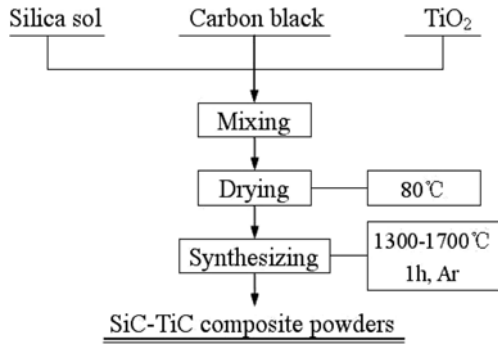
Fig. 1. Procedure for the preparation of SiC-TiC composite powders.

These ingredients were uniformly mixed in a planetary ball mill in ethanol for 0.5 h using SiC balls as the grinding body. The well-mixed starting materials were dried at 80 °C, then put into a graphite crucible and placed in Φ100-1 multi-functional hot press furnace. Heating was performed at 20 K min^{-1} from room temperature to 1300-1700 °C in an argon atmosphere. The holding time at the desired temperature was 1h. Subsequently the furnace was cooled naturally and the composite powders were obtained. The final products were characterized by X-ray diffractometry(XRD, Rigaku D/max-2200PC, Cu K$_\alpha$ radiation) and field-emission scanning electron microscopy(FE-SEM, JEOL JSM-6700F).

$$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g) \tag{1}$$

$$TiO_2(s) + 3C(s) \rightarrow TiC(s) + 2CO(g) \tag{2}$$
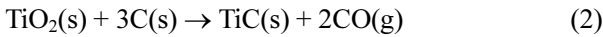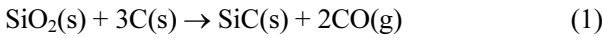
AlN (purity: $\geq$ 99.9%) and Y$_2$O$_3$ (purity: $\geq$ 99.9%) were used as sintering aids with a molar ratio of 3:2, and the total amount of sintering aids was 5, 10, 15 and 20 vol.%. All the powders were milled in ethanol for 4 h, using SiC grinding balls. The milled slurry was dried at 80 °C, sieved through a 60-mesh screen and subsequently hot-pressed at 1900 °C for 1 h, under a pressure of 25 MPa, in a nitrogen atmosphere. The density of the sintered products were measured by the Archimedes method. The theoretical densities of the specimens were calculated based on the densities of SiC (3.21 g cm^{-3}), TiC (4.93 g cm^{-3}), AlN (3.26 g cm^{-3}) and Y$_2$O$_3$ (5.01 g cm^{-3}) according to the rule of mixtures. The Rockwell hardness of the hot-pressed samples polished was also determined. The microstructures of the sintered samples were observed by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F).
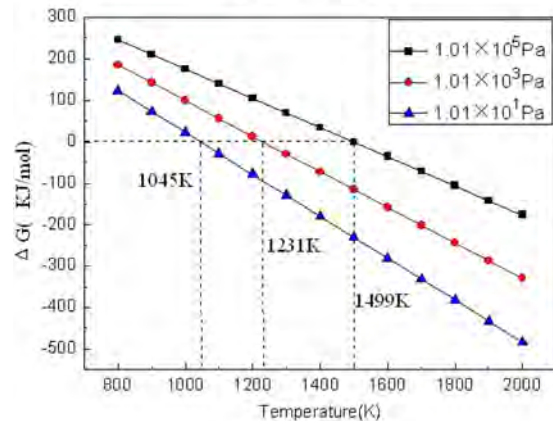
Results and Discussion

Thermodynamic analysis

In order to determine the synthesis temperature of the SiC-TiC composite powders, a thermodynamic analysis is carried out. Based on reaction (1) and (2), ΔG values can be calculated using the following equations:
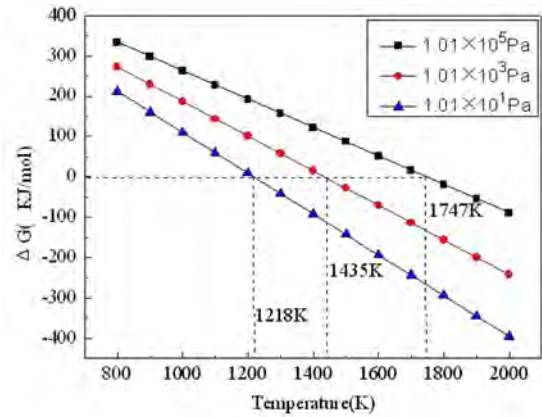
(a)   reaction (1)

(b)   reaction (2)

Fig. 2. Relationship between Gibbs' free energy (ΔG) and temperature (T) under different CO pressure conditions for carbothermal reduction. (a) for reaction (1) and (b) for reaction (2).

$$\Delta G = \Delta G^\theta + RT\ln K_p \tag{3}$$

$$\Delta G = \Delta G^\theta + RT\ln(P_{CO}/P^\theta) \tag{4}$$

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta \tag{5}$$

where ΔG^θ is the standard Gibbs free energy, R is the gas constant, K_p is the equilibrium constant, T is the thermodynamic temperature, P^θ is the standard atmospheric pressure and P_{CO} is the CO gas partial pressure.

According to the relative thermodynamics data taken from NIST-JANAF [21], the ΔG expressions can be obtained from the above equations:

$$\Delta G_1 = 616560 - 353.04T + 2 \times 8.314 \times T\ln(P_{CO}/P^\theta) \tag{6}$$

$$\Delta G_2 = 527850 - 352.19T + 2 \times 8.314 \times T\ln(P_{CO}/P^\theta) \tag{7}$$

where expressions (6) and (7) correspond to reaction (1) and (2), respectively.

Taking P_{CO} as 1.01×10^5 Pa, 1.01×10^3 Pa, 1.01×10^1 Pa, and P^θ as 1.01×10^5 Pa, respectively, according to the expressions (6) and (7), the relationship curves between Gibbs free energy (ΔG) and temperature (T) are shown

in Fig. 2. It can be seen from the figure that the ΔG value decreases remarkably with increasing temperature and decreasing of the CO gas partial pressure. This result means that the temperature and CO gas partial pressure have a significant effect on the synthesis of both SiC and TiC. It can be also found that the smaller CO gas partial pressure, the bigger the slope of $\Delta G \sim T$ straight line. Therefore, reducing the CO gas partial pressure during the reaction is an effective method for promoting the synthesis of SiC and TiC. It can be inferred from the above analysis that choosing vacuum conditions will help to decrease the synthesis temperature or promote the reaction for preparing SiC and TiC.

The objective of this study is to synthesize SiC-TiC composite powders by the carbothermal reduction method under atmospheric conditions. The CO gas partial pressure will increase gradually with the synthesis of SiC and TiC going on. From Fig. 2, ΔG values in the expressions (6) and (7) are both 0 under a CO gas partial pressure of 1.01×10^5 Pa when the treatment temperature is at 1747 K and 1499 K, respectively. This means that, when the temperature is higher than the above two values, reaction (1) and (2) can theoretically take place to generate SiC and TiC.

Effect of treatment temperature on the crystal phases of the products

The XRD patterns of reaction products of SiC-20 mol%TiC composite powders are shown in Fig. 3. It can be learnt that, the treatment temperature has a great effect on the phase composition of the products. There exist peaks indexed as from SiO_2, TiO_2, Ti_3O_5 and TiC in the pattern of the product treated at 1300 °C, which indicates that the carbothermal reduction of the mixture of TiO_2 and carbon black powders begins at 1300 °C. When the treatment temperature rises to 1400 °C, there exist peaks indexed as from SiO_2 and TiC while the peaks of TiO_2 and Ti_3O_5 disappear. Accompanied by a rise of treatment temperature, the peaks become intense.
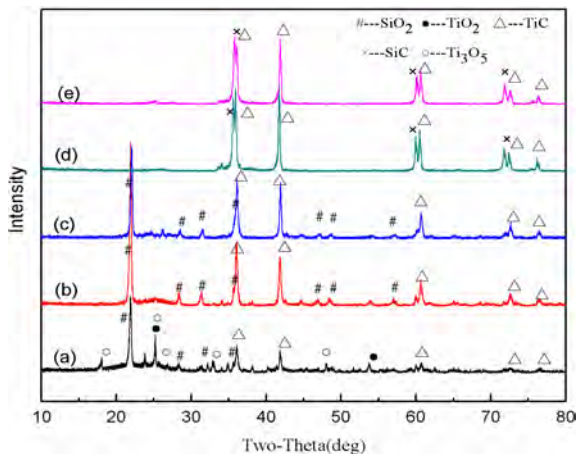
A weak peak of SiC besides the ones of SiO_2 and TiC can be observed at 1500 °C, which shows that the carbothermal reduction of the mixture of SiO_2 and carbon black powders begins at this temperature. When treated at 1600 °C, the product is composed of SiC and TiC, and no other phase can be found in the XRD patterns. Under this condition, therefore, the carbothermal reduction of the mixture may reach completion at approximately 1600 °C. When the treatment temperature rises further to 1700 °C, there are no significant changes in the XRD pattern, only the diffraction peaks of SiC and TiC become more intense. This indicate that, in comparison with the product obtained at 1600 °C, the composite powder obtained at 1700 °C has an increase of crystallinity.

The degree of the synthesis reaction

The relationship between reaction temperature and ignition loss for the products is shown in Fig. 4 (the holding times are all 1 h). Because carbon monoxide (CO) is a by-product in the carbothermal reduction process and will dissipate so that the reactions can continue, the ignition loss can indicate that the reactions take place. A greater ignition loss implies a higher degree of the reaction. Hence, the ignition loss can be used as an indicator of the proceeding of the reactions. It can be seen from the figure that the ignition loss increases when the treatment temperature is increased. When the treatment temperature is at 1300 °C and 1400 °C, the ignition loss is 11.60% and 28.04% respectively, which is far lower than the theoretically calculated value of 55.99%. The ignition loss rises to 38.08% with temperature up to 1500 °C. At 1600 °C, the ignition loss reaches 58.68%, which is higher than the theoretically calculated value. When the treatment temperature continues to go up to 1700 °C, the ignition loss is 59.85%, which is close to the value of the procuct obtained at 1600 °C. Through the above analyses, this research is of the opinion that the carbothermal reduction can reach completion at 1600 °C. This is in accord with the results of the XRD analysis. The reason
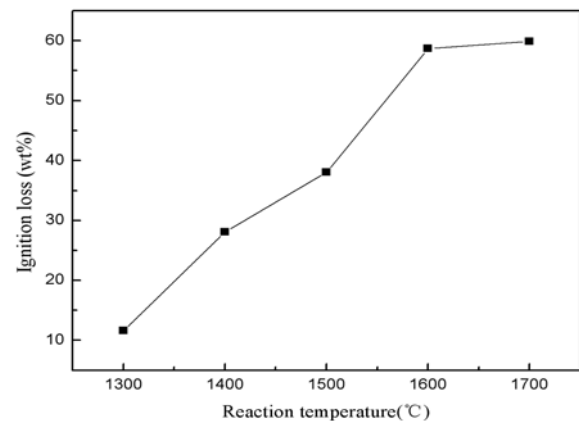

Fig. 3. XRD patterns of SiC-20 mol%TiC composite powders synthesized at different temperatures in an Ar flow for 1 h. (a) 1300 °C, (b) 1400 °C, (c) 1500 °C, (d) 1600 °C, and (e) 1700 °C.
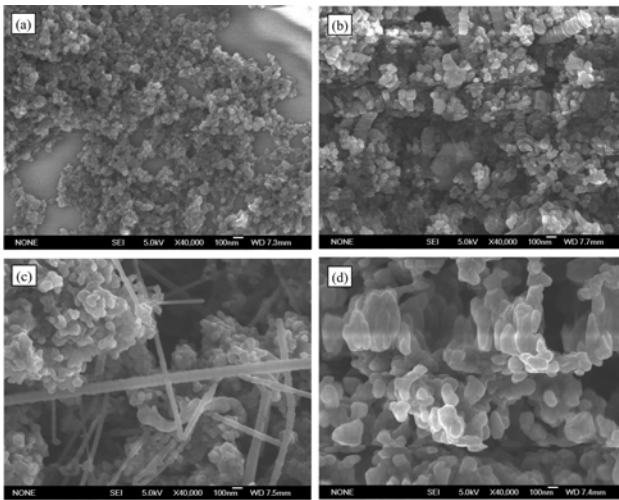

Fig. 4. Relationship between reaction temperature and ignition loss for the products.

that the ignition loss is higher than the theoretically calculated value when the treatment temperature is above 1600 °C is as follows [19]: Since gaseous SiO is generated in the reaction process at high temperatures it does not get completely changed into SiC and a very small quantity with the CO gas is taken away by the flowing argon. This causes the actual ignition loss to be higher than the theoretically calculated value.

Effect of treatment temperature on the morphologies of the products

The morphologies of the samples synthesized at different temperatures for 1 h are shown in Fig. 5. As can be seen from Fig. 5a, when the treatment temperature is at 1400 °C, the powders synthesized are mainly composed of fine round-like particles. According to the XRD and ignition loss analysis above, it can be inferred that these round-like particles are mainly newly-formed TiC as well as SiO_2 and carbon black in the starting materials. Compared with the products synthesized at 1400 °C, the morphologies of the products synthesized at 1500 °C have changed slightly (Fig. 5b). The products consist basically of round-, plate- and short rod-like particles because TiC generated at a lower temperature grows to a certain extent and a small quantity of SiC begins to form at 1500 °C. Fig. 5c shows the morphology of the samples synthesized at 1600 °C for 1 h. It is easy to see that the composite powders are chiefly composed of round-like and plate-like particles with a small amount of whiskers with a size of 50 ~ 100 nm. It can be seen easily from Fig. 5d that the product is mainly composed of a few round-like particles and a great deal of plate-like particles. Also the particle size of the product is 100-200 nm. This suggests that the whisker growth of SiC in the composite powders is inhibited and the particle size increases apparently when the treatment temperature goes up to 1700 °C.

Sintering behavior of synthesized powders

The powders synthesized at 1600 °C were hot-pressed at 1900 °C in a 0.2 MPa nitrogen atmosphere to investigate their sintering behavior, using AlN and Y_2O_3 as sintering agents. The density and hardness of the sintered bodies are displayed in Table 1. It can be observed that the relative density increases with an increased AlN-Y_2O_3 content and reaches a maximum value of 98.9% with 10 vol% of AlN-Y_2O_3, but it decreases when the amount of AlN-Y_2O_3 added is higher than 15 vol%. It is noted that the change of hardness has a similar pattern with the relative density with an increasing amount of AlN-Y_2O_3. The Rockwell hardness of the samples increase with an increase of the AlN-Y_2O_3 content, reach a maximum at 10 vol% AlN-Y_2O_3, and become lowered gradually for the samples with 15 and 20 vol% AlN-Y_2O_3. The major reason why the hardness of the sintered bodies with 15 and 20 vol% AlN-Y_2O_3 are lower than the one with 10 vol% AlN-Y_2O_3 is that both AlN and Y_2O_3 have theoretically lower hardnesses than SiC and TiC. SEM morphologies of HPed bodies with AlN-Y_2O_3 contents of 5 vol% and 10 vol% respectively are shown in Fig. 6a and b. There are many pores in the sample with AlN-Y_2O_3 content of 5 vol%, and the sintered body seems to be not too dense. However, a more densified and homogeneous microstructure can be observed in the sample with an AlN-Y_2O_3 content of 10 vol%. As mentioned above, the SiC-TiC sintered body with 10 vol% AlN-Y_2O_3 possess a high densification, superior Rockwell hardness and a densified microstructure, its relative density and Rockwell hardness are 98.9% and 93.2HRA, respectively. This implies that the powders synthesized at 1600 °C for 1 h have a very good sinterability.

Table 1. The relative density and Rockwell hardness of HPed bodies containing different amounts of AlN-Y_2O_3 additive

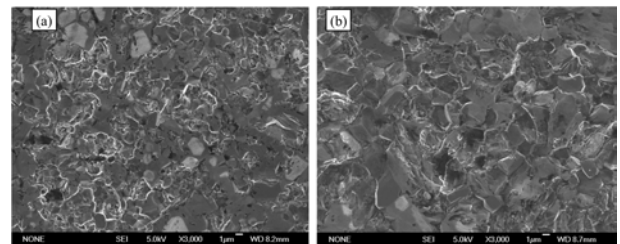| Sample	SiC-20 mol%TiC (vol%)	AlN-Y_2O_3 (vol%)	Relative density (%)	Hardness (HRA)
AY-5	95	5	95.1	91.4
AY-10	90	10	98.9	93.2
AY-15	85	15	98.6	91.8
AY-20	80	20	98.1	90.1

Fig. 5. SEM morphologies of SiC-20 mol%TiC composite powders synthesized at different temperatures in an Ar flow for 1h. (a) 1400 °C, (b) 1500 °C, (c) 1600 °C, and (d) 1700 °C.

Fig. 6. SEM morphologies of HPed bodies containing different AlN-Y_2O_3 contents. (a) 5 vol% and (b) 10 vol%.

Conclusions

SiC-TiC composite powders were successfully synthesized by carbothermal reduction processing. The treatment temperature and CO gas partial pressure have significant effects on the synthesis of both SiC and TiC. Reducing the CO partial pressure during the reaction is an effective method for promoting the synthesis of SiC and TiC. Theoretically, reactions (1) and (2) can take place to generate SiC and TiC when the temperature is higher than 1747 K and 1499 K, respectively.

In the formation of composite powders, the reaction temperature plays a very important role. In the carbothermal reduction process, the formation of TiC occurs before SiC. When treated at 1600 °C, the product is composed of SiC and TiC, and no other phase can be found in the XRD patterns. The ignition loss was higher than the theoretically calculated value when the treatment temperature was above 1600 °C owing to the escape of gaseous SiO generated in the reaction process. The composite powders synthesized at 1600 °C for 1 h are mainly composed of round-like particles, plate-like particles and a certain amount of whiskers. When the treatment temperature goes up to 1700 °C, whiskers are inhibited and the particle size increases apparently.

Synthesized SiC-TiC powders show good sinterability when the amount of AlN-Y$_2$O$_3$ added is 10 vol%. The sample with an AlN-Y$_2$O$_3$ content of 10 vol%, which was hot-pressed at 1900 °C for 1 h under 25MPa, has a relative density of 98.9% and Rockwell hardness of 93.2 HRA.

Acknowledgements

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