



# SYNTHESIS AND MECHANISM OF SiC–ZrC COMPOSITE POWDERS BY CARBOTHERMAL REDUCTION METHOD

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SiC–ZrC composite powders were synthesised by the carbothermal reduction method using starch as the carbon source, zirconium dioxide as the zirconium source, and silica sol as the silicon source. The effects of the reaction temperature on the phase composition and microstructure of the SiC–ZrC composite powders were investigated. The reaction process was thermodynamically analysed and calculated, and the synthesis mechanism of the SiC–ZrC composite powder was analysed. The synthesised powder samples were characterised and analysed by X-ray diffraction, scanning electron microscopy, and other testing methods. The results show that the optimum reaction condition for the synthesis of SiC–ZrC composite powders is at 1550 °C–1600 °C for 1.5 h. A high temperature and a low pressure are beneficial in conducting the synthesis reaction. The SiC–ZrC composite powders synthesised by calcining at 1550 °C and holding for 1.5 h are mainly composed of a certain amount of whiskers, spherical particles, floc particles, and other structures. Moreover, their grain size is small (100–200 nm). The powder samples synthesised at 1600 °C produced a larger number of whiskers. The length of the whiskers was mostly 10  $\mu$ m, the arrangement was complex and irregular, and a diverse microstructure was formed.

#### INTRODUCTION

Zirconium carbide (ZrC) is widely used in the machinery, metallurgy, chemical industry, cemented carbide fields, as well as other fields [1-2] because it has a high melting point (3540 °C), good thermal conductivity and radiation resistance, and excellent comprehensive properties that can improve the strength and corrosion resistance of cemented carbide. ZrC can be combined with C, SiC, TiC, and other carbides to form C/C–ZrC [3], SiC–ZrC [4], TiC–ZrC [5-6], and other system composites. These composites are widely used in the petrochemical industry, iron and steel metallurgy, aerospace, energy, environmental protection, and mechanical and electronic fields, owing to the advantages of their hightemperature resistance, oxidation resistance, and good mechanical properties.

Silicon carbide (SiC) has high hardness and strength at high temperatures and excellent properties, such as a high melting point, high thermal conductivity, a low thermal expansion coefficient, and good corrosion resistance. Therefore, it has a wide range of applications in the machinery, petroleum, chemical, and aviation industries, as well as other fields. However, due to the covalent bonding mechanism of SiC itself, its plastic deformation ability is reduced, its fracture toughness is poor, and its strength is low at room temperature. The practical application of SiC is limited [7-8]. Introducing a secondary-phase material is an effective way to improve the insufficient performance of SiC [9].

ZrC and SiC have a high melting point, good thermal conductivity, and resistance to ablation and erosion of high-speed gas flow, and their oxidation products at high temperatures have good oxygen diffusion ability, thermal stability, and ablation resistance, endowing them with a self-healing potential of ablation defects on the surface of composites in a high-temperature environment [10]. However, the poor oxidation resistance of ZrC makes it unable to serve in a high-temperature environment. According to a previous study [11], the oxidation of ZrC at a high temperature can be effectively prevented by introducing SiC into ZrC. Moreover, according to the principle of solid solution strengthening, the addition of SiC can further enhance the strength of the ZrC matrix. SiC-ZrC composites combine the excellent properties of ZrC and SiC and have great application potential as ultrahigh-temperature structural materials, such as in thermal protection systems, rocket engines, hypersonic vehicles, and other fields. ZrC-SiC composites are considered to be the most attractive heat-resistant structural materials due to their excellent comprehensive properties in chemical stability, high-temperature strength, oxidation resistance, and thermal shock resistance, which can replace

iron, nickel, cobalt-based superalloys, and their intermetallic compounds for use in the aerospace industry and in aerospace structural components. To improve the oxidation and ablation resistance, the density of the ZrC–SiC ceramic matrix composites must be increased, and the content of harmful elements needs to be reduced [12].

The composite of ZrC and SiC can achieve the complementarity of the properties of the two materials, resulting in the better performance of the SiC-ZrC composites, which can be applied in more fields. SiC-ZrC ceramic powders prepared by direct mechanical mixing have inhomogeneity in the composition of the mixed powders, which will affect the microstructure and the related properties of the SiC-ZrC composites to a certain extent. Therefore, homogeneously mixed and non-agglomerated SiC and ZrC powder raw materials need to be synthesised to prepare SiC-ZrC composites with excellent properties. At present, the synthesis methods of SiC-ZrC composite powders mainly include the carbothermal reduction method [13-16], sol-gel method [17-19], and liquid precursor method [4, 20-21]. In the current industrial production, the carbothermal reduction method is used as the main method for synthesising various carbide powders due to its simple synthesis process, simple equipment needed, low preparation cost, and stable product quality [22-23]. Liu et al. [14] prepared ZrC-SiC composite powders through a microwave carbothermal reduction method using zircon and activated carbon as the raw materials and investigated the effects of the heating temperature, embedded powders, and heating methods on the synthesis of the ZrC-SiC composite powders. Liu et al. [15] prepared ZrB<sub>2</sub>--ZrC-SiC nanopowders with a uniform phase distribution from cost-effective ZrOCl<sub>2</sub>·8H<sub>2</sub>O. Zeng et al. [16] successfully synthesised ZrC-SiC composite powders by a combination of the sol-gel technology and carbothermal reduction using zirconium oxychloride octahydrate as the zirconium source, tetraethoxysilane as the silicon source, and phenolic resin as the carbon source.

As an organic carbon source, starch easily forms fine carbon particles during high-temperature carbonisation and decomposition in an argon atmosphere, which is conducive for the generation of an ultrafine carbide powder [24-25]. To further improve the performance of SiC-ZrC composite powders, our research group synthesised SiC-ZrC composite powders at a high temperature in a tube furnace in an argon atmosphere through a carbothermal reduction method using silica sol, zirconium dioxide, and starch as the raw materials. In this study, the theoretical calculation and analysis of the thermodynamics were first carried out. Then, the effect of the reaction temperature on the phase composition, weight loss rate, and microstructure of the synthesised SiC-ZrC composite powder was studied. Moreover, the synthesis mechanism of SiC-ZrC composite powder was discussed.

# EXPERIMENTAL

## Processing

The experimental procedure for synthesising SiC-ZrC composite powders is shown in Figure 1. Zirconium dioxide (ZrO<sub>2</sub>, purity of  $\geq$  99.0 %, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), silica sol (SiO<sub>2</sub>, 28 wt. %, Hunan Changsha Water Glass Factory, Changsha, China), and starch  $((C_6H_{10}O_5)_n, \text{ purity of } \ge 99.0 \%,$ Tianjin Zhiyuan Chemical Reagent Co., Ltd., Tianjin, China) were used as the starting materials for the synthesis of the SiC-ZrC composite powders. The amounts of silica sol, ZrO<sub>2</sub>, and starch were adjusted to yield an SiC/ZrC molar ratio of 7:3 in the expected synthesis product. In addition, the Thermogravimetry and Differential Thermal Analysis (TG-DTA) curve of a single starch raw material shows that starch de-composes under high-temperature conditions and argon atmosphere, resulting in a mass loss of up to 78.2 % [26]. Therefore, in this study, the amount of starch was determined according to the actual mass loss rate during the synthesis reaction. An electronic analytical balance was used to accurately weigh a certain amount of silica sol, zirconium dioxide, and starch raw materials. These raw materials were uniformly placed into the ball mill tank and mixed for 2 h in a planetary ball mill at a speed of 500 r min<sup>-1</sup> using anhydrous ethanol as the dispersing medium and SiC balls as the grinding body (the mass ratio of the balls to the raw materials was set to 2:1). The well-mixed precursor raw materials were taken out and dried at 110 °C for 24 h in an electric blast drying oven. After being ground, they were placed in a high-temperature tubular electric furnace. The synthesis reaction was carried out to synthesise SiC-ZrC composite powders at five different temperatures (1400 °C, 1450 °C, 1500 °C, 1550 °C, and 1600 °C) at a heating rate of 10 °C ·min<sup>-1</sup> in an argon atmosphere. The holding times at the desired temperature were 1.5 h. After the holding time was over, the sample was naturally cooled to room temperature in the furnace.



Figure 1. Preparation process of the SiC-ZrC composite powders.

#### Characterisation

The masses of the powder samples before and after the reaction were weighed using an electronic analytical balance, and the loss-on-ignition rates of the samples were calculated to judge the degree of the synthesis reaction. The phase composition of the synthesised powder samples was analysed using an X-ray diffractometer (XRD, Y-2000, China). The microstructure of the synthesised powder samples was observed using a scanning electron microscope (SEM, EM-30AX, Korea).

#### **RESULTS AND DISCUSSION**

## Thermodynamic analysis

The synthesis temperature of the SiC–ZrC composite powders under different conditions can be determined by thermodynamic analysis. When the Gibbs free energy ( $\Delta$ G) of the substance is negative, the reaction can proceed forward; that is, the chemical reaction equation proceeds to the right.

The starch in the used raw material will decompose to form elemental carbon under the condition of low temperature (above 200 °C) [27]. The main synthesis reactions between zirconium dioxide ( $ZrO_2$ ), silica sol (mSiO<sub>2</sub>·nH<sub>2</sub>O), and starch ( $C_6H_{10}O_5$ )<sub>n</sub> in the system at high temperature are shown in Equations 1 and 2 [28-30]. The value of  $\Delta G$  can be calculated using Equation 3.

$$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g)$$
 (1)

$$ZrO_{2}(s) + 3C(s) = ZrC(s) + 2CO(g)$$
 (2)

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

Given that CO gas will be produced during the synthesis reaction, it is necessary to consider the influence of the gas partial pressure on the synthesis reaction:

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

Substituting  $\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$  into Equation 4, Equation 5 can be obtained:

$$\Delta G = \Delta H^{\theta} - T\Delta S^{\theta} + RT \ln \left( P_{CO} / P^{\theta} \right)$$
 (5)

where,  $\Delta G^{\theta}$  is the standard Gibbs free energy of the substance; R is the gas constant; K<sub>p</sub> is the reaction equilibrium constant; T is the thermodynamic temperature; P<sup> $\theta$ </sup> and P<sub>CO</sub> are the standard atmospheric pressure and partial pressure of CO, respectively, in Pa.

Bringing the thermodynamic data of each substance into Equation 5, the expressions of  $\Delta G$  of Equations 1 and 2 can be obtained:

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

$$\Delta G_2 = 679733 - 361.34T + 2 \times 8.314 \times T \ln (P_{CO}/P^{\theta}) \quad (7)$$

Taking the values of  $P_{CO}$  as  $1.01 \times 10^1$  Pa,  $1.01 \times 10^3$  Pa, and  $1.01 \times 10^5$  Pa, respectively, and taking the value of P<sup> $\theta$ </sup> as  $1.01 \times 10^5$  Pa, and substituting the values into Equations 6 and 7, the changes of the calculated Gibbs free energy ( $\Delta$ G) with the temperature (T) can be obtained (Figures 2 and 3).

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Figure 2. Variation of the Gibbs free energy ( $\Delta G$ ) with the temperature (T) of the SiC synthesised under different CO partial pressures.



Figure 3. Variation of the Gibbs free energy ( $\Delta G$ ) with the temperature (T) of the ZrC synthesised under different CO partial pressures under different CO partial pressures.

Figures 2 and 3 show that, taking standard atmospheric pressure as an example, through the thermodynamic calculations, when the temperatures in Equations 1 and 2 are 1746 K and 1881 K, respectively,  $\Delta G$  is 0. Therefore, SiC and ZrC can be theoretically generated as long as the reaction temperature is higher than these two values. Compared with the conditions of a protective atmosphere (e.g., argon), in a vacuum environment, when  $\Delta G$  of Equations 1 and 2 is 0, the reaction temperature will decrease. When the  $P_{CO}$  is  $1.01 \times 10^1$  Pa,  $1.01 \times 10^3$ Pa, and  $1.01 \times 10^5$  Pa and the reaction temperatures in Equations 1 and 2 are 1746 K and 1435 K, 1218 K and 1881 K, and 1552 K and 1321 K, respectively,  $\Delta G$  is 0. This shows that  $\Delta G$  in Equations 1 and 2 decreases significantly with an increase in the temperature and a decrease in the P<sub>CO</sub>. Therefore, increasing the reaction

temperature or reducing the gas pressure in the system is more conducive to the synthesis reaction of SiC and ZrC [24, 31].

### Analysis of the reaction loss on ignition

In the process of synthesising SiC-ZrC composite powders by the carbothermal reduction method, gaseous substances, such as CO, will be generated, and the escape of the generated gas will lead to a decrease in the total powder mass. Therefore, the ignition loss rate of the powder mass before and after the synthesis reaction can be calculated, and the degree of the synthesis reaction can be estimated. Table 1 shows the reaction loss on ignition of the SiC-ZrC composite powders synthesised with starch as the carbon source at five different reaction temperatures from 1400 °C to 1600 °C. The rate of reaction loss on ignition tends to increase with an increase in the reaction temperature. This is because when organic starch is selected as the carbon source and it reaches a higher reaction temperature, it will not only be decomposed into elemental carbon and gaseous water, but also generate CO,  $CO_2$ ,  $C_xH_v$ , and other gases [25]. When the reaction temperature was 1400 °C, the reaction loss on ignition was only 20.0 %, indicating that only a small part of the synthesis reaction was carried out at 1400 °C. When the reaction temperature was increased to 1450 °C and 1500 °C, the loss on ignition rate of the reaction reached 68.7 % and 72.9 %, which increased by 48.7 % and 52.9 %, respectively. The loss-on-ignition rate of the reaction changed greatly, which indicated that the synthesis reaction proceeded violently at 1500 °C, and more SiC-ZrC composite powders were formed in the system. When the reaction temperature was at 1550 °C, the reaction loss on ignition accordingly increased to 76.7 %. When the reaction temperature continued to increase to 1600 °C, the loss-on-ignition rate did not change much from that at 1550 °C (only increased by 0.3 %), indicating that the synthesis reaction had approached completion at 1550 °C. This shows that under the experimental conditions, the optimum temperature for synthesising the SiC-ZrC powder with starch as a carbon source is at 1550-1600 °C.

Table 1. Loss-on-ignition rate of SiC–ZrC composite powders synthesised by holding for 1.5 h at different reaction temperatures.

No.	Reaction temperature (°C)	Ignition rate (%)
1	1400	20.0
2	1450	68.7
3	1500	72.9
4	1550	76.7
5	1600	77.0

#### Phase composition analysis

Figure 4 shows the X-ray diffraction (XRD) patterns of the powder samples prepared at different reaction temperatures with starch as the carbon source, zirconium dioxide as the zirconium source, and silica sol as the silicon source. Figures 4a to 4b show that there are mainly ZrO<sub>2</sub> diffraction peaks before calcination of the precursor dry mixed powder and the powder after calcination at 1400 °C, indicating that the synthesis reaction did not proceed after calcination at 1400 °C. However, the diffraction peaks of the powder samples calcined at 1400 °C are sharper, and the full width at half maximum is narrower, which indicates that the degree of crystallization of ZrO<sub>2</sub> has been improved. Figure 4c shows obvious characteristic diffraction peaks of ZrSiO<sub>4</sub> at 1450 °C, and it can be inferred that the intermediate product ZrSiO<sub>4</sub> is produced at 1450 °C. Figure 4d shows that the characteristic diffraction peaks of the intermediate product ZrSiO<sub>4</sub> still exist, but at the same time SiC diffraction peaks begin to appear, indicating that a part of SiC has begun to form in the system at 1500 °C, which is basically consistent with the conclusion drawn by Wang et al. through thermodynamic calculation [29]. Figure 4e shows that the diffraction peak of the intermediate product ZrSiO<sub>4</sub> disappears. In addition to the diffraction peak of SiC, the characteristic diffraction peak of ZrC also appears in the system. This shows that under the experimental conditions, ZrC can only be formed when the reaction temperature is above 1550 °C, which is consistent with the research conclusion of Xiang (who found through scanning electron microscopy (SEM), transmission electron microscopy, and other testing methods that some ZrO<sub>2</sub> and C were generated ZrC at 1550 °C) [32]. Compared with Figure 4e, the diffraction peaks of ZrC and SiC in Figure 4f are sharper, indicating that the reaction proceeds more completely at



Figure 4. patterns of powder samples prepared at different reaction temperatures: a) 110 °C + 24 h, b) 1400 °C + 1.5 h, c) 1450 °C + 1.5 h, d) 1500 °C + 1.5 h, e) 1550 °C + 1.5 h, and f) 1600 °C + 1.5 h.

the reaction temperature of 1600 °C, and the resulting powder samples have better crystallinity. Based on the above analysis, under the experimental conditions, using starch as carbon source, zirconium dioxide as zirconium source, and silica sol as silicon source, the suitable conditions for synthesizing SiC–ZrC composite powders by carbothermal reduction reaction are at 1550-1600 °C for 1.5 h. This is consistent with the analytical results of the reaction loss-on-ignition rate.

#### Microstructural analysis

Figure 5 shows the SEM images of the precursor mixed powder samples prepared by drying at 110 °C for 24 h and the powder samples calcined at different reaction temperatures and kept for 1.5 h. Figure 5a shows that the powder samples dried at 100 °C for 24 h exhibited irregular lumps, and the particle size ranged from 4  $\mu$ m to 15  $\mu$ m. The uncalcined powder has a larger



a) 110 °C + 24 h



b) 1400 °C + 1.5 h



c) 1450 °C + 1.5 h

Figure 5. SEM images of the powder samples prepared at different reaction temperatures: a)  $110 \text{ }^{\circ}\text{C} + 24 \text{ h}$ , b)  $1400 \text{ }^{\circ}\text{C} + 1.5 \text{ h}$ , c)  $1450 \text{ }^{\circ}\text{C} + 1.5 \text{ h}$ .



f) 1600 °C + 1.5 h

Figure 5. SEM images of the powder samples prepared at different reaction temperatures: d) 1500  $^{\circ}$ C + 1.5 h, e) 1550  $^{\circ}$ C + 1.5 h, and f) 1600  $^{\circ}$ C + 1.5 h.

particle size and well-formed irregular particles. This indicates that the uncalcined powders are larger in size and form irregular particles. Figure 5b shows that the powder samples are bulky, and the grain size is large, indicating that the reaction has not yet proceeded. Figure 5c shows that the powder samples are mainly composed of irregular flake-like structures, quasi-columnar structures, quasi-spherical particles, and irregular polygonal blocks. The phenomenon of mutual bonding between the particles is less, and most particles have smooth surfaces. Figure 5d shows that the grains change from flaky and column-like to spherical-like with nanospherical particles, the crystal grain size is not uniform, and there is a certain agglomeration phenomenon. The main reason is that the reaction temperature is not high enough, the synthesis reaction is not fully carried out, and the particles are not fully developed. Figure 5e shows that a small amount of whiskers are produced, the former spherical particles are transformed into floccules, and the grain size is obviously smaller (ranging between 100 and 200 nm). Figure 5f shows that the particles are connected by a large number of SiC whiskers, forming a fluffy floc structure. Compared with the powder samples synthesised at 1550 °C, the powder samples synthesised at 1600 °C had more whiskers. Moreover, the length of the whiskers was mostly 10  $\mu$ m, and the orientation was complex and irregular, forming a diverse microstructure composed of a large number of whiskers and spherical-like, flake-like, and column-like particles.

#### Synthesis mechanism analysis

The chemical reactions that may occur during the synthesis reaction of the SiC-ZrC composite powder are shown in Table 2 [29-30, 33-34]. According to the thermodynamic analysis of Wang et al. [29], the theoretical initial reaction temperature of the SiC in the reaction Equation 1 is at 1444.17 °C. In addition, SiO<sub>2</sub> and C may generate intermediate SiO products through reaction Equations 2 and 3 during the heating process, and the theoretical initial reaction temperature is at 1644.59 °C and 2345.51 °C, respectively. The intermediate SiO product may react with C and CO to generate SiC through reaction Equations 4 and 5, respectively, wherein reaction Equation 5 can spontaneously proceed at high temperature with  $\Delta G < 0$  and the theoretical initial reaction temperature is at 924.2 °C. Although increasing the reaction temperature can be beneficial to the synthesis reaction, it will also promote the production and escape of the intermediate SiO product. At present, there are two main synthesis mechanisms for SiC whiskers: gassolid (VS) and gas-liquid-solid (VLS). The synthesis of SiC whiskers in the absence of additives during the carbothermic reduction reaction is generally believed to follow the VS mechanism [33-34].

According to the calculation of Li et al. [30], the standard Gibbs free energies of Equations 7, 8, and 9 are always positive when they are below 2000 K, whereas that of Equation 6 is negative when it is above 1900 K (1627 °C). This indicates that when the temperature is below 2000 K, the generation of ZrC from C and  $ZrO_2$ 

Table 2. Possible reactions during the synthesis of the SiC–ZrC composite powders.

No.	Reaction equation
1	$SiO_{2}(s) + 3C(s) = SiC(s) + 2CO(g)$
2	$\operatorname{SiO}_{2}(s) + C(s) = \operatorname{SiO}(g) + \operatorname{CO}(g)$
3	$SiO_{2}(s) + 2CO(g) = Si(l) + 2CO_{2}(g)$
4	$\operatorname{SiO}(g) + 2C(s) = \operatorname{SiC}(s) + \operatorname{CO}(g)$
5	$SiO(g) + 3CO(g) = SiC(s) + 2CO_2(g)$
6	$ZrO_{2}(s) + 3C(s) = ZrC(s) + 2CO(g)$
7	$\operatorname{ZrO}_{2}(s) + C(s) = \operatorname{ZrO}(g) + \operatorname{CO}(g)$
8	$2ZrO_{2}(s) + C(s) = 2ZrO(g) + CO_{2}(g)$
9	$ZrO_{2}(s) + 2C(s) = ZrC(s) + CO_{2}(g)$

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is carried out according to reaction Equation 6. With an increasing temperature, the Gibbs free energy of the standard reaction of each reaction Equation gradually decreased, indicating that the higher the temperature, the easier the synthesis reaction. In this study, the partial pressure of CO was reduced by controlling the flow of argon gas (2 L·min<sup>-1</sup>) during high-temperature calcination to form the reaction conditions favourable for the synthesis of the powder samples.

# CONCLUSIONS

The effect of the different reaction temperatures on the synthesis of an SiC–ZrC composite powder was studied. Under the conditions of this experiment, starch was used as the carbon source, zirconium dioxide was used as the zirconium source, and silica sol was used as the silicon source. The optimum condition for the reaction to synthesise the SiC–ZrC composite powder was 1550 °C–1600 °C for 1.5 h.

A thermodynamic theoretical calculation and synthesis mechanism analysis were carried out for the synthesis of the SiC–ZrC composite powder. The results showed that high-temperature and low-pressure conditions are conducive to the synthesis reaction, so the synthesis reaction can be adjusted by controlling the flow rate of argon during calcination.

The SiC–ZrC composite powder synthesised by calcining at 1550 °C and holding for 1.5 h is mainly composed of a certain amount of whiskers, spherical particles, floc particles, and other structures, and the grain size is small (ranging between 100 and 200 nm). More whiskers were produced in the powder samples synthesised at 1600 °C. The length of the whiskers was mostly 10  $\mu$ m, and the arrangement was complex and irregular, forming a large number of whiskers and a certain amount of spherical particles, flakes, and diverse microstructures composed of quasi-columnar and columnar particles.

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