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Study on the preparation of silicon carbide from carbon in waste cathodes

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Abstract

Silicon carbide as the core material for third-generation semiconductors plays an important role in many fields; however, its large-scale applications as well as low-cost synthesis remain a challenge. Silicon carbide was prepared via carbothermal reduction using silicon dioxide and purified waste cathodes as the carbon source. The optimum conditions for preparing silicon carbide using waste cathodes are temperature = 1550 °C, molar ratio of carbon to silicon = 3:1 and holding time = 3 h. The microstructure of the prepared silicon carbide was investigated using x-ray diffraction (XRD), infrared spectroscopy and scanning electron microscopy (SEM). The XRD results of the prepared silicon carbide showed that β-SiC was the main phase of the prepared silicon carbide. The SEM results showed that the prepared silicon carbide was fibrous. The growth mechanism of silicon carbide was proposed using the thermodynamic calculations of chemical reactions.

1. Introduction

Waste cathodes are a type of hazardous solid waste discharged from the electrolytic aluminium industry [1]. During electrolysis, cathodes are inevitably subjected to constant corrosion by high-temperature electrolytes, molten aluminium, sodium metal and other substances [2]. Currently, most of the electrolytic aluminium cells are replaced after 5–8 years of use [3]. Waste cathodes are made of carbon, fluoride and other inorganic impurities [4, 5]. Currently, spent cathodes are mainly landfilled or deposited in piles, which wastes a considerable area of land and pollutes the environment. Spent cathodes contain large amounts of graphitic carbon, which can be recovered and utilised.

Silicon carbide (SiC) was first discovered in 1824 by the Swedish scientist Berzelius during the process of making diamonds. As a single-crystal fibre, SiC has excellent properties, such as a wide band gap, high thermal conductivity, high temperature stability, high strength and chemical resistance [6–8]. SiC is chemically stable and resistant to high temperature, corrosion and oxidation as well as having high thermal conductivity, low coefficient of thermal expansion and high hardness. It is widely used in several fields as abrasives, high-temperature heat-conducting materials and steel-making aids [8–11]. Recently, research on the synthesis methods, functional properties (photoelectromagnetic properties) and applications of SiC materials has received widespread attention and has become one of the hot spots in the field of materials science for enabling their wide use. Therefore, several researchers have explored various methods for preparing SiC whiskers, including carbon thermal reduction, spark plasma sintering, polymer precursor pyrolysis, chemical vapour deposition and microwave heating methods [12–16]. Among these, carbon thermal reduction is a promising method owing to its economical, efficient and large-scale preparation [8].

In carbon thermal reduction, raw materials (carbon and silicon sources) have an important influence on the formation of SiC. Currently, SiC is mainly produced industrially using petroleum coke (or coal coke) as the
carbon source and quartz sand (SiO$_2$) via a high-temperature carbothermal reaction \cite{17, 18}; alternatively low-cost raw materials have been employed for preparing SiC whiskers. Li \cite{19} synthesised SiC whiskers using industrial waste micro-silica powder and graphite via carbothermal reduction. Lodhe \cite{20} prepared nano-scale SiC whiskers using rice husk and coconut husk via carbothermal reduction at 1400 °C. Zhang \cite{21} produced 20 μm–long SiC whiskers using rice husk and silicone waste catalysts. Luo \cite{22} found that SiC whiskers can be prepared using coal ash and water glass. In addition, several researchers have shown that the synthesis of SiC whiskers from biomass materials is feasible \cite{23}. Our group found that waste cathodes contain a large amount of carbon and a small amount of SiC and silica. The purification of carbon present in the waste cathodes and its use as a carbon source in SiC preparation will be environmentally as well as economically viable. The prepared SiC can also be used as a heat-resistant material for producing electrolytic aluminium. Limited research has been conducted on the use of waste cathodes as the carbon source for the preparation of SiC. The use of waste cathodes instead of graphite as the carbon source for the preparation of SiC can reduce the cost of preparing SiC.

Therefore, in this study, purified waste cathodes were chosen as the raw material for preparing SiC whiskers via carbon thermal reduction, providing a new synthetic route for a large-scale controlled preparation. The effects of the preparation temperature, the molar ratio of the carbon to silicon atoms and the holding time on the preparation of SiC were investigated using x-ray diffraction (XRD). Subsequently, the structural analysis of SiC was conducted using scanning electron microscopy (SEM) and infrared (IR) spectroscopy, and the possible growth mechanism of SiC was described based on the thermodynamics of chemical reactions.

2. Method

2.1. Materials
The waste cathodes used in this study were obtained from an electrolytic aluminium plant in Guizhou, China. The cathodes were crushed and ground to 150 mesh, and the carbon content of the waste cathodes after washing and leaching was 89.93%, which was medium carbon graphite. Figure 1 shows its XRD pattern. The main component of the waste cathodes treated by the washing–leaching process was graphite. Silica is an analytically pure agent (99% silica content) obtained from Tianjin Zhiyuan Chemical Reagent Co, China.

2.2. Preparation of SiC
The leached waste cathode carbon and silicon dioxide were mixed at a certain ratio using a ball mill. The mixed raw material was placed in a high-alumina crucible. The crucible was covered with a crucible lid to isolate the air and placed in a high-temperature energy-saving electric furnace (KSS-1600 °C) at 1450 °C–1600 °C; the heating rates were 10, 8, 4 and 2 °C min$^{-1}$ for 0 °C–800 °C, 800 °C–1200 °C, 1200 °C–1400 °C and ≥1400 °C, respectively. After reaching the required temperature, the powder was held at that temperature for a certain time and then cooled. The prepared SiC powder was heated to 800 °C in air and roasted for 2 h to remove the unreacted carbon. The preparation procedure of the SiC product at 1450 °C, 1500 °C, 1550 °C and 1600 °C with a carbon to silicon ratio of 3:1 and a holding time of 4 h was identical to the process described above. To analyse the effect of different carbon to silicon molar ratios on the preparation of SiC, the carbon to silicon molar ratios

![Figure 1. XRD diagram of a spent cathode.](image-url)
were set to 1:1, 2:1, 3:1, 4:1 and 5:1 and the same procedure was followed as mentioned above, where the temperature was 1550 °C and the holding time was 4 h. To analyse the effect of different holding times on the preparation of SiC, the temperature was set to 1550 °C, the molar ratio of carbon to silicon was set to 3:1 and holding times were set to 1, 2, 3, 4 and 5 h while following the same procedure as mentioned above. The flow chart of the SiC preparation process is shown in figure 2.

2.3. Characterisation of SiC

The prepared SiC powder was subjected to a physical phase analysis. The test sample was ground to a size of −0.075 mm and tested to determine the physical phase of the SiC powder using the x-ray powder diffraction technique on a Panaco x-ray Analytical Instruments (Netherlands) X Pert powder diffractometer using a Cu target of 2.2 kW, a tube voltage of 35 kV, a tube current of 25 mA, a step speed of 5° min⁻¹, step size of 0.02 and a scan range of 5°–85° for the 2θ angle. The functional groups of SiC were analysed using a VERTEX 70 Fourier transform micro-IR spectrometer from Bruker, Germany. The microstructure of the prepared SiC was investigated using a scanning electron microscope (SU8010 Hitachi, Japan).

3. Results and discussion

3.1. Effect of temperature on the preparation of SiC from waste cathodes

Figure 3(a) shows the XRD plots of the prepared SiC at different temperatures. Figure 3(b) shows the content of each substance in the prepared SiC powder.

Figure 3(a) shows the effect of different temperatures on the preparation of SiC powder. The XRD patterns show the characteristic diffraction peaks of square quartz at approximately 21.7°, 28.2°, 31.2°, 42.4°, 44.5°, 46.8° and 48.3°. The characteristic diffraction peaks of β-SiC are observed at 35.6°, 41.3°, 59.9°, 71.8° and 75.5°, which correspond to the (111), (200), (220), (311) and (222) planes of β-SiC, respectively, where 35.6°, 41.3° and 59.9° are the three strong peaks of β-SiC. In the figure, a weak peak appears at 33.6°, corresponding to a stacking layer fault defect in β-SiC [24, 25]. This stacking defect can be attributed to the (1011) crystal plane of 6H-SiC, indicating that other crystalline SiC structures are also present in the β-SiC obtained from the reaction and are present in the β-SiC as structural defects. Because the stacking defect energy of SiC is very low (34 erg cm⁻¹), which is approximately one-hundredth of its (111) surface energy (2830 erg cm⁻¹), it is quite susceptible to a high density of stacking layer errors [26, 27]. As shown in the figure, when the temperature is 1450 °C, the characteristic diffraction peak of the square quartz at 21.7° is very strong, mainly indicating that other crystalline
SiC structures are also present in the $\beta$-SiC obtained from the reaction and are present in the $\beta$-SiC as structural defects. the transformation of $\beta$-quartz into square quartz in silica, when very little $\beta$-SiC powder is produced. When the reaction temperature is 1500 °C, the characteristic diffraction peaks of square quartz at 21.7° weaken and the characteristic diffraction peaks of $\beta$-SiC at 35.6° increase in intensity compared with the peak obtained at 1450 °C. Further, the diffraction peaks at 28.2°, 31.2°, 42.4°, 44.5°, 46.8° and 48.3° disappear, indicating that the carbothermal reduction reaction starts becoming more intense and the quartz crystalline phase. At 1550 °C, the intensities of the characteristic diffraction peaks of $\beta$-SiC at 35.6°, 43.2° and 59.7° increase compared with those of the peaks obtained at 1500 °C, indicating that the reaction product is $\beta$-SiC. When the temperature is further increased to 1600 °C, the three characteristic diffraction peaks of $\beta$-SiC observed at 35.6°, 43.2° and 59.7° increase slightly in intensity compared with those of the peaks obtained at 1550 °C, indicating that the reaction product is $\beta$-SiC. 1600 °C is slightly enhanced, indicating a slight increase in $\beta$-SiC compared to 1550 °C.

As shown in figure 3(b), the SiC content generated at 1450 °C is rarely 15.7% and its main component is silicon dioxide, accounting for 84.3%. As the temperature increases, the SiC content increases gradually. When the temperature is 1500 °C, the SiC content reaches 79% and the silicon dioxide content decreases to only 21%. At 1550 °C and 1600 °C, the SiC content in the product remains essentially unchanged and the amount of silicon dioxide is already very small. Considering that more energy is required to increase the temperature, 1550 °C is appropriate.

The IR spectra of the prepared SiC at different temperatures are shown in figure 4. The figure shows that at 1450 °C the product mainly shows characteristic peaks at 1100, 810, 620, 560 and 470 cm$^{-1}$. The peak observed at 810 cm$^{-1}$ is the Si–C absorption peak of $\beta$-SiC in the product, and the absorption peak observed at 1100 cm$^{-1}$ is the Si–O–Si anti-symmetric stretching vibration peak. The peaks observed at 620, 560 and 470 cm$^{-1}$ are the Si–O bending vibration peaks [28–30]. At 1500 °C, the peaks at 1100, 620 and 470 cm$^{-1}$ weaken and the characteristic peak at 560 cm$^{-1}$ disappears, indicating a decrease in the amount of silica in the product. The peak observed at 810 cm$^{-1}$ enhances the characteristic peak, indicating an increase in the amount of $\beta$-SiC in the product. At 1550 °C, compared with the peaks observed at 1500 °C, the peaks observed at 1100 and 470 cm$^{-1}$ weaken, the peak observed at 620 cm$^{-1}$ disappears and the peak observed at 810 cm$^{-1}$ increases. At 1600 °C, the characteristic IR peaks are essentially the same as those observed at 1550 °C, which is consistent with the XRD plot, indicating that the increase in the temperature beyond 1550 °C had little effect on the product. The characteristic peak of SiO$_2$ was still present at 1100 cm$^{-1}$ at 1550 °C, indicating that the sample contained a small amount of silica.

Figure 5 shows SEM images of SiC at different reaction temperatures. As shown in the figure, the produced SiC is mainly fibrous. With increasing temperature, increasingly fibrous SiC is produced. A small amount of fibrous SiC is produced at 1450 °C, but this has little effect when the temperature reaches 1550 °C.

### 3.2. Influence of carbon to silicon molar ratio on the preparation of SiC using spent cathodes

The SiC prepared at different molar ratios of carbon to silicon was analysed using XRD, and the results are shown in figure 6(a). Figure 6(b) shows the content of SiC and silicon dioxide in the prepared SiC powder. Figure 6(a) shows that when the C–Si molar ratio of SiC is 1:1, the main characteristic peaks of XRD are observed at 21.9°, 28.2°, 31.2°, 42.4°, 44.5°, 46.8°, 48.3° and others are the characteristic peaks of square quartz, while the characteristic peak of $\beta$-SiC at 35.6° is very weak, indicating that the amount of SiC generated at a C–Si molar ratio of SiC of 1:1 is very small. This is probably due to the small amount of carbon, which makes the
amount of produced SiC very small, and because the crucible contains a certain amount of air that consumes some of the carbon, both of which result in very little SiC being produced. When the molar ratio of carbon to silicon is 2:1, the characteristic peaks of square quartz are weaker than when the molar ratio of carbon to silicon is 1:1, especially at $\sim 21.9^\circ$, while the characteristic peak of $\beta$-SiC is considerably stronger at $\sim 35.6^\circ$, and the characteristic peaks of $\beta$-SiC appear at $59.9^\circ$ and $71.8^\circ$, indicating a substantial increase in the $\beta$-SiC content.

When the molar ratio of carbon to silicon is 3:1, the characteristic peaks of square quartz observed at $21.9^\circ$, $28.2^\circ$, $31.2^\circ$, $42.4^\circ$, $44.5^\circ$, $46.8^\circ$ and $48.3^\circ$ almost disappear. The characteristic peaks of $\beta$-SiC observed at $35.6^\circ$, $59.9^\circ$ and $71.8^\circ$ are enhanced when the molar ratio of carbon to silicon is 2:1, indicating that at a molar ratio of carbon to silicon of 3:1, the silica has reacted and the main component of the product is $\beta$-SiC. When the molar ratios of carbon to silicon are 4:1 and 5:1, the characteristic peaks of $\beta$-SiC are enhanced to some extent, the main products are $\beta$-SiC. The crystallinity of $\beta$-SiC in the product was better than the product obtained at a C–Si molar ratio of 3:1, with a slight increase in yield.

The effect of the molar ratio of silicon and carbon on the preparation of $\beta$-SiC may be ascribed to the fact that the carbothermal reduction reaction occurs during the preparation of SiC, where carbon is preferentially heated in the mixture of silica and charcoal powders and the silica reacts preferentially around the charcoal that has been partially heated to a high temperature. With increasing amount of charcoal, the charcoal is heated to a
higher temperature, which is beneficial to the generation of $\beta$-SiC powder. When the amount of charcoal is already saturated at a certain value, further increase in the amount of charcoal will not affect the generation of $\beta$-SiC powder [31].

As shown in figure 6(b), at a carbon to silicon molar ratio of 1:1, the generated SiC content is rarely 16.2% and its main component is silicon dioxide, accounting for 83.8%. With an increase in the molar ratio of carbon to silicon, the SiC content also gradually increases. When the C–Si molar ratio of SiC is 2:1, the SiC content reaches 68.6% and the silicon dioxide content decreases to only 31.4%. When the molar ratio of carbon to silicon is 3:1, the SiC content reaches 99.8%, indicating that the silica in the reactants has been completely reacted and its content is 0.2%. When the molar ratio of carbon to silicon is increased beyond 3:1, the content of SiC and silicon dioxide remains unchanged. Therefore, the molar ratio of carbon to silicon of 3:1 is more appropriate.

The IR spectra of SiC prepared at different carbon to silicon ratios are shown in figure 7. This figure shows that at a carbon to silicon molar ratio of 1:1, the product mainly shows characteristic peaks at 1100, 810, 620 and 470 cm$^{-1}$. The Si–C absorption peak of $\beta$-SiC in the product is observed at 810 cm$^{-1}$, and the absorption peak observed at 1100 cm$^{-1}$ is the Si–O peak. The peaks observed at 620 and 470 cm$^{-1}$ are attributed to Si–O bending vibration. At a C–Si molar ratio of 2:1, the peaks observed at 1100, 620 and 470 cm$^{-1}$ weaken, indicating a decrease in the amount of silica in the product. The peak observed at 810 cm$^{-1}$ shows an increase in the characteristic peak, indicating an increase in the amount of $\beta$-SiC in the product. Compared with the peaks observed at the C–Si molar ratio of 2:1, at a C–Si molar ratio of 3:1, the peaks observed at 1100 and 470 cm$^{-1}$ are weaker, the peak at 620 cm$^{-1}$ disappears and the peak at 810 cm$^{-1}$ increases. The characteristic IR peaks at the C–Si molar ratios of 4:1 and 5:1 are in general agreement with those obtained at the C–Si molar ratio of 3:1, which is consistent with the XRD pattern. This indicates that increasing the amount of carbon beyond the C–Si molar ratio of 3:1 has little effect on the product.

SEM was conducted for the SiC prepared at different molar ratios of carbon to silicon, and the results are shown in figure 8. This figure shows that with an increase in the C–Si molar ratio of SiC, the SiC becomes more fibrous. After the C–Si molar ratio of SiC reaches 3:1, a further increase in the molar ratio does not considerably affect the fibrous nature of SiC.

### 3.3. Effect of holding time on the preparation of SiC using spent cathodes

The SiC prepared at different molar ratios of carbon to silicon was analysed using XRD, and the results are shown in figure 9(a) and 9(b), presenting the content of SiC and silicon dioxide in the prepared SiC powder.

Figure 9(a) shows that when the holding time is 1 h, the main characteristic XRD peaks are observed at 21.9°, 28.2°, 31.2°, 42.4°, 44.5°, 46.8°, 48.3° and the other characteristic peaks are for square quartz, while the characteristic peak of $\beta$-SiC observed at 35.6° is very weak, indicating that the amount of SiC generated at the holding time of 1 h is low. The reason for this may be that the holding time is so short that silicon dioxide does not have time to react with the spent cathode carbon before it starts to cool down, resulting in the production of a very small amount of SiC. When the holding time is 2 h, the characteristic peaks of square quartz are considerably weaker than the peaks obtained when the holding time was 1 h. In particular, the intensity of the characteristic peak observed at 21.9° is considerably weaker, and the characteristic peaks observed at 42.4°, 44.5°, 46.8° and 48.3° disappear. By contrast, the characteristic peak of $\beta$-SiC observed at 35.6° as well as 59.9°
Figure 8. SEM images of the SiC prepared with different molar ratios of carbon to silicon. (a-1:1, b-2:1, c-3:1, d-4:1 and e-5:1)

Figure 9. (a) XRD patterns and (b) physical phase content of the SiC prepared at different holding times.
and 71.8° are enhanced considerably, indicating a substantial increase in the β-SiC content. When the holding time is 3 h, the characteristic peaks of square quartz observed at 21.9°, 28.2°, 31.2°, 42.4°, 44.5°, 46.8° and 48.3° disappear, while the characteristic peaks of β-SiC observed at 35.6°, 59.9° and 71.8° are enhanced compared with the peaks obtained when the holding time was 2 h. This indicates that the β-SiC content increased considerably when the holding time was 3 h. When the holding time was 3 h, silica had reacted and the main component of the product was β-SiC. When the holding time is 4 and 5 h, the characteristic peaks of β-SiC are enhanced to a certain extent, indicating that the crystallinity of β-SiC in the product is better than the peaks obtained when the holding time was 3 h, and the yield is slightly increased.

As shown in figure 9(b), at a holding time of 1 h, the generated SiC content is rarely 47.1% and its main component is silicon dioxide, accounting for 52.9%. With an increase in the holding time, the SiC content gradually increases. When the holding time is 2 h, the SiC content reaches 84.8% and the silicon dioxide content decreases to 15.2%. When the holding time is 3 h, the SiC content reaches 99.7%, indicating that the silica in the reactant has completely reacted, and its content is 0.3%. When the holding time is increased beyond 3 h, the SiC content and silicon dioxide content remain unchanged. Therefore, the holding time of 3 h is more suitable.

Figure 10 shows the IR spectra of SiC powders prepared using leached waste cathode carbon and silicon dioxide at 1550 °C and a carbon to silicon molar ratio of 3:1 at different holding times. As shown in the figure, at a holding time of 1 h, the product mainly shows characteristic peaks at 1100, 810, 620 and 470 cm⁻¹. The Si–C absorption peak of β-SiC in the product is observed at 810 cm⁻¹. The absorption peak observed at 1100 cm⁻¹ is the anti-symmetric stretching vibration peak of Si–O–Si. The peaks observed at 620 and 470 cm⁻¹ are attributed to the Si–O bending vibration. When the holding time is 2 h, the peaks observed at 1100, 620 and 470 cm⁻¹ weaken, indicating a decrease in the amount of silica in the product. The peak observed at 810 cm⁻¹ shows an increase in the characteristic peak, indicating an increase in the amount of β-SiC in the product. Compared with the peaks obtained at the holding time of 2 h, at 3 h, the peaks observed at 1100 and 470 cm⁻¹ weaken, the peak observed at 620 cm⁻¹ disappears and the peak observed at 810 cm⁻¹ increases. When the holding times are 4 and 5 h, the characteristic IR peaks are almost the same as those obtained at 3 h. This is consistent with the XRD pattern, indicating that the product was not considerably affected by the extension of the holding time after 3 h.

The SEM analysis of the prepared SiC was conducted, and the results are shown in figure 11. The SEM images of the prepared SiC powder at different holding times (figure 11) show that when the holding time is shorter, its SiC fibres are less compared the SiC fibres obtained when the holding time is longer and the SiC fibres become coarser with increasing holding time.

3.4. Growth mechanism analysis of SiC

The following equations are the chemical equations for the chemical reactions that may occur during the preparation of SiC from waste cathodes (1)–(11).

\[ \text{Si} + \text{C} = \text{SiC} \]  
\[ \text{SiO}_2 + \text{C} = \text{SiO}_2(g) + \text{CO}_2(g) \]
Figure 11. SEM images of SiC at different holding times. (a-1, b-2, c-3, d-4 and e-5 h).

\[
\begin{align*}
\text{SiO}_2 + \text{CO}_2(g) &= \text{SiO}_3(g) + \text{CO}_2(g) \\
\text{SiO}_2 + \text{Si} &= 2\text{SiO}_2(g) \\
2\text{Si} + \text{O}_2(g) &= 2\text{SiO}_2(g) \\
\text{CO}_2(g) + \text{C}(g) &= 2\text{CO}(g) \\
\text{SiO}_3(g) + 2\text{C}(g) &= \text{CO}_2(g) + \text{SiC} \\
\text{O}_2(g) + 2\text{C} &= 2\text{CO}_2(g) \\
2\text{SiO}_2(g) + 3\text{C} &= 2\text{SiC} + 2\text{CO}_2(g) \\
3\text{CO}_2(g) + \text{SiO}_2(g) &= 2\text{CO}_2(g) + \text{SiC} \\
\text{CO}_2(g) + 3\text{SiO}_2(g) &= 2\text{SiO}_2 + \text{SiC}
\end{align*}
\]
Under isobaric conditions, equations (12)–(15) are used to describe the relation between the thermodynamic functions entropy ($S$), enthalpy ($H$), Gibbs free energy ($G$) and heat capacity ($C_p$).

$$ C_p = \left( \frac{\partial H}{\partial T} \right)_p $$  \hspace{1cm} (12)

$$ ds = \frac{\delta Q_p}{9m} = \frac{C_p dT}{T} $$  \hspace{1cm} (13)

$$ \Delta G^0_f = \Delta H^0_f - T \Delta S^0_f $$  \hspace{1cm} (14)

$$ \Delta G_m^0(T) = \Delta_r H_m^0(298K) - T \Delta_r H_m^0(298K) = A + BT $$  \hspace{1cm} (15)

The Gibbs free energy values of the reactions (1)–(11) as a function of temperature are shown in figure 12. Thermodynamic data were obtained via HSC9.5 calculations.

The main reactions that occur during the preparation of SiC are divided into eutectic generation, solidification of crystalline nuclei and growth stages \[32, 33\].

The four reactions that may generate SiO and CO are (2)–(8), and figure 12 shows that the Gibbs free energy values of reactions (2)–(4) are greater than 0 at temperatures between 1400 °C and 1600 °C. Theoretically, these reactions cannot proceed spontaneously. The Gibbs free energy values of reactions (3)–(8) are negative at 1400 °C–1600 °C; therefore, these reactions can proceed spontaneously. Reactions (3) and (8) are the reactions of Si and C with oxygen to form silica and carbon dioxide, respectively. However, a small amount of oxygen exists in the reactor, which can occur at the beginning of the reaction when the reactor contains oxygen, and as the oxygen is consumed, the reaction does not proceed properly. Therefore, in the process of preparing SiC, CO and SiO are generated mainly by reactions (6) and (7).

The condensation reactions of the SiC nuclei are presented by reactions (7) and (9). As shown in figure 12, the Gibbs free energy values of reactions (7) and (9) are less than 0; therefore, these reactions can proceed spontaneously. The change in the Gibbs free energy value of reaction (7) is less with increasing temperature than that of reaction (9), indicating that reaction (7) is less affected by temperature. The Gibbs free energy of reaction (9) is first less than that of reaction (7) and then becomes greater than the Gibbs free energy of reaction (7) with an increase in the temperature. Reaction (7) is more likely to occur when SiC is prepared at high temperatures.

After the nucleation reaction is complete, the SiC growth occurs via reactions (10) and (11). Figure 12 shows that the Gibbs free energy of reaction (10) at temperatures between 1400 °C and 1600 °C is greater than 0, indicating that the reaction cannot proceed spontaneously. The Gibbs free energy of reaction (11) is negative, indicating that the reaction can proceed spontaneously. During cooling, the silica phase wraps around the SiC whiskers while crystallisation, forming an amorphous silica layer, which is because the solidification rate of the SiC nuclei is faster than that of the viscous silica phase \[8, 34, 35\]. Therefore, the growth reaction of SiC is given by reaction (11).

(1) SiO(g) and CO(g) generation reactions:

$$ \text{SiO}_2 + \text{C} \rightarrow \text{SiO}_2(g) + \text{CO}(g) $$

$$ \text{CO}_{2(g)} + \text{C}_{(g)} \rightarrow 2\text{CO}(g) $$
SiC nucleation reaction:

\[
\text{SiO}_{(g)} + 2\text{C} = \text{SiC} + \text{CO} \\
2\text{SiO}_{(g)} + 3\text{C} = 2\text{SiC} + \text{CO}_{2(g)}
\]

Growth reaction of SiC:

\[
\text{3SiO}_{(g)} + \text{CO}_{(g)} = 2\text{SiO}_{2} + \text{SiC} \\
\text{3CO}_{(g)} + \text{SiO}_{(g)} = 2\text{CO}_{2(g)} + \text{SiC}
\]

A schematic of the growth mechanism of SiC is shown in figure 13. As the temperature increases, the feedstock gases (SiO and CO) begin to be produced. The SiO gas then enters the eutectic and reacts with the carbon in graphite to form the SiC nuclei. Finally, the SiC molecules produced at the gas–liquid interface of the eutectic are submerged in the eutectic and deposited on the SiC nuclei, thus promoting whisker growth.

4. Conclusion

Single-crystal SiC was prepared via the carbothermal reduction method using a mixture of waste cathodes and silicon dioxide as the material. The content of the prepared SiC powder was related to the temperature, molar ratio of carbon to silicon and the holding time. The purity of SiC was high when the temperature was 1550 °C, the carbon to silicon ratio was 3:1 and the holding time was 4 h. The XRD results showed that SiC had a high density of stacked faults. The SEM results showed that the SiC prepared using a waste cathode as the carbon source was fibrous. IR spectroscopy shows that the prepared SiC contains a small amount of silicon dioxide. Through chemical reaction thermodynamics, the growth mechanism of SiC is proposed, starting with the generation of SiO and CO, followed by the generation of SiC nuclei for SiO and finally the deposition of the generated SiC on the SiC nuclei to promote the growth of SiC.

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Data availability statement
All data that support the findings of this study are included within the article (and any supplementary files).

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