Microwave-assisted Synthesis of a ZrC-SiC Nanocomposite by Carbothermal Reduction and its Effect on Mean Particle Size

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ZrC-SiC nanopowders were prepared by carbothermal reduction of ZrO$_2$ and SiO$_2$ with carbon black in argon gas atmosphere, using microwave energy as an alternative heating source. The samples were characterized by XRD, SEM and BET surface area analysis. The results indicate that highly crystalline ZrC-SiC composites with a mean particle size of about 80 nm can be synthesized at a relatively low temperature (~1420 °C). Microwave-assisted heating to obtain the ZrC-SiC nanopowders significantly reduces the synthesis time to only 40 min when compared with the long reaction times involved in conventional carbothermal reduction, which requires about 8 hours to obtain ZrC and 2 hours to obtain SiC.

Keywords: carbothermal reduction, microwave, ZrC-SiC nanopowder

1. Introduction

Zirconium carbide (ZrC), a refractory transition metal carbide of considerable technological interest, exhibits the characteristic properties of metals and ceramics owing to the simultaneous presence of a mixture of ionic, covalent and metallic bonds in its NaCl-type crystal structure. These exceptional properties, which include ultra-high melting point (3540 °C), good resistance to high-speed gas or particle erosion and good ablation resistance, make ZrC suitable for many applications, such as cutting tools, wear resistant components, field emitters, thermophotovoltaic radiators and diffusion barrier coatings on nuclear particle resistant components, field emitters, thermophotovoltaic absorbers, and microwave absorbers. ZrC-SiC composites are promising UHTCs that should exhibit the combination of high melting temperature and high temperature mechanical properties of ZrC and the passivation quality of SiC.

Some synthesis methods have been developed to obtain ZrC-SiC, namely, carbothermal reduction, in which the reactants are Zr(OR)$_4$, TEOS and AcOH, ZrSiO$_4$ and C$_x$, or ZrO$_2$, SiO$_2$ and C; in situ reaction, using Si powders and phenolic resin with Zr powders or (3ZrO$_2$:CO$_2$:H$_2$O)$_n$ and polymer-derived ceramics, using ZrC and [Si(H(CH$_3$)$_2$CH$_2$)$_n$]. However, the carbothermal reduction of ZrO$_2$/SiO$_2$ is regarded as the most common method due to its simplicity and easy control of the composition.

The formation of ZrC from ZrO$_2$ during the conventional carbothermal reduction is represented by following general reaction:

$$\text{ZrO}_2(s) + 3\text{C}(s) \rightarrow \text{ZrC}(s) + 2\text{CO}(g) \quad (1)$$

This process can take place in three reaction steps: (a) formation of CO by a solid state reaction between ZrO$_2$ and carbon particles with the subsequent formation of super-stoichiometric ZrC, (b) incorporation of carbon into the crystal lattice to form super-stoichiometric ZrC, and (c) substitution of oxygen with carbon in ZrC$_x$O$_{2-x}$ to form ZrC. Nucleation of ZrC$_x$O$_{2-x}$ may take place inside the oxide particles, according to the abovementioned reaction model, or in amorphous carbon, as suggested in a recent study. In a conventional furnace, the carbothermal reduction of ZrO$_2$ and carbon requires relatively high temperatures and long exposure times to form ZrC, e.g., 1460 °C/12 h and 1750 °C/8 h. On the other hand, the formation of SiC from SiO$_2$ during conventional carbothermal reduction is represented by the following general reaction:

$$\text{SiO}_2(s) + 3\text{C}(s) \rightarrow \text{SiC}(s) + 2\text{CO}(g) \quad (2)$$

This reaction consists of a two-step gas-solid reaction:

$$\text{SiO}_2(s) + \text{C}(s) \rightarrow \text{SiO}(g) + \text{CO}(g) \quad (3)$$

$$\text{SiO}(g) + 2\text{C}(g) \rightarrow \text{SiC}(s) + \text{CO}(g) \quad (4)$$

This reaction is believed to be a SiO(g)-CO(g) gas-gas reaction at 1600 °C or higher, and is attributed to the SiO(g)-C(s) gas-solid reaction at 1500 °C or lower, favoring the formation of powder. In a conventional furnace, SiC can be
synthesized above 1500 °C/~2h\textsuperscript{16}, assuming that the overall reaction to form ZrC-SiC by conventional carbothermal reduction corresponds to the sum of Equations (1) and (2)\textsuperscript{6,7}:

\[ \text{ZrO}_2(s) + \text{SiO}_2(s) + 6\text{C}(s) \rightarrow \text{ZrC}(s) + \text{SiC}(s) + 4\text{CO}(g) \]  

The results obtained by conventional heating indicate that long reaction times and high reaction temperatures are required, which translate into a high cost to synthesize these powders. Moreover, the particle size of these powders is at the micron and sub-micron scale\textsuperscript{11,14,16}.

However, the use of microwave energy as an alternative heating source may solve the problems arising from conventional carbothermal reduction\textsuperscript{17-19}. In microwave heating, the interactions between the microwaves and the molecular structure of the materials result in fast heating, a marked decrease in the activation energies of the reaction, and an increase in the diffusion rates of the process\textsuperscript{20}. In most cases, when microwave energy is applied to carbothermal reduction reactions, it represents a simpler and faster route than the conventional one, also considering the greater adsorption in the case of C-containing materials\textsuperscript{7,15,22}. In this work, an investigation was made into the synthesis of ZrC-SiC nanocomposites by microwave-assisted carbothermal reduction and its effect on mean particle size. The use of microwaves as the energy source for the carbothermal reduction process is economically promising, very fast and relatively simple.

2. Experimental Procedure

Zirconia (ALDRICH, 99%, particle size<100 nm), silica gel (High-purity grade, particle size<100 nm) and carbon black (particle size<100 nm), in a Zr:Si:C molar ratio of 1:1:6, were stirred into isopropyl alcohol at 65°C for 30 minutes and then partially dried. The weights of the required reactants were calculated assuming that the overall reaction corresponds to Equation (5). The mass was extruded into pellets. The reaction system designed for the synthesis was based on a reaction system used to prepare Al\textsubscript{4}O\textsubscript{5}/SiC powders\textsuperscript{22}. About 1.5g of pellets were weighed in a mullite/alumina rectangular crucible, which was inserted into a low porosity ceramic tube, coated with refractory fiber to prevent heat loss, at the center of the oven cavity of a multimodal microwave applicator (2.45GHz, Cober, MS6K). The reactions were performed at 3 kW for reaction times in the range of 40-60 min. The temperature was measured using an infrared pyrometer (Raytek, RAYMA2SCSFIL) positioned directly above the pellets, using a circular transparent quartz glass window placed at one end of the ceramic tube. The synthesized powders were deagglomerated in a mortar, yielding very fine dark samples.

The crystalline phases of the powders were determined from X-ray diffraction patterns recorded by a diffractometer operating with Cu Kα radiation (XRD, Siemens, D5010) from 20° to 80° (2θ) and a scan step of 2°/min. The crystallite size (D) of the carbide phases was calculated from the reflection of the (111) plane (the highest intensity peak of ZrC and SiC) of the XRD profile, in accordance with the Scherrer formula\textsuperscript{23}:

\[ D = \frac{k\lambda}{\beta \cdot \cos \theta} \]  

where \( k \) is a constant related to the crystallite shape, \( \lambda \) is the X-ray wavelength, \( \beta \) is the half-maximum breadth, and \( \theta \) is the Bragg angle of the (111) plane. The specific surface area of the synthesized powders was measured by the BET method, based on \( N_2 \) adsorption/desorption curves (Micromeritics, ASAP 2020), and the particle size (equivalent spherical diameter) was also determined by this technique, using the following equation:

\[ D_{\text{BET}} = \frac{6}{\rho \cdot S_{\text{BET}}} \]  

where \( D_{\text{BET}} \) is the equivalent average diameter (µm), \( S_{\text{BET}} \) is the surface area determined by BET (m\textsuperscript{2}/g), and \( \rho \) is the density (g/cm\textsuperscript{3}) of the powders. The powder density was determined using a helium pycnometer (Micromeritics, ACCUPYC 1330). Lastly, the morphology was examined by field emission scanning electron microscopy (FEG-SEM, Philips, XL30).

3. Results and Discussions

X-ray diffraction (XRD) patterns of the products of the reactions in ZrO\textsubscript{2}, SiO\textsubscript{2}, and C mixtures obtained by microwave-assisted carbothermal reduction, applying a constant power of 3 kW for different reaction times, are presented in Figure 1. The XRD peaks of the initial mixture (ZrO\textsubscript{2}+SiO\textsubscript{2}+C), included for comparison, are all due to the monoclinic phase of ZrO\textsubscript{2} (JCPDS 83-944), because there is no reaction between the starting materials (t=0 min). It is worth noting that SiO\textsubscript{2} and C phases do not appear due to their amorphous state. The powder synthesized at 3 kW for 40 min is composed mainly of ZrC (JCPDS 89-3829) and SiC (JCPDS 73-1708), indicating that the carbothermal reductions of ZrO\textsubscript{2} and SiO\textsubscript{2} were substantially completed. At the end of 40 min, the reaction temperature reached ~1420 °C. The temperature was measured using an infrared pyrometer (Raytek, RAYMA2SCSFIL) positioned directly above the pellets, using a circular transparent quartz glass window placed at one end of the ceramic tube. This experimental assembly for precise measurement of the reaction temperature of the carbothermal reduction of ZrC-SiC composites did not require the microwave irradiation to be interrupted, thus enabling data on the in situ reaction temperature to be recorded. This procedure differed from the one employed by Das et al.\textsuperscript{7}, who used a shielded Pt/Rh thermocouple in contact with the sample after interrupting the microwave irradiation. It is believed that the amorphous carbon reacts
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with the oxides and forms SiC and ZrC, according to Equation (5). This formation of carbide phases, which is favored by raising the temperature to 1420 °C, can be attributed to the interaction between the electromagnetic field and the initial mixture (ZrO$_2$+SiO$_2$+C), which produces a microwave-induced electrical current in carbon particles due to their absorption properties. This process generates heat in the carbon particles (originating mainly from Joule losses), which is subsequently transferred to SiO$_2$ and ZrO$_2$ particles, favoring the SiO$_2$→SiC and ZrO$_2$→ZrC conversions described by Equations (1) and (2), respectively. The difference between the highest peak intensities corresponding to ZrC and SiC phases may be due to less SiC in the sample, possibly caused by the volatilization of SiO(g) during the reaction, as suggested in the conventional carbothermal reduction of zircon (ZrSiO$_4$) and activated carbon (carbothermal reduction in a conventional furnace), as follows:

$$\text{SiC(s)} + 2\text{SiO}_2\text{(s)} \rightarrow 3\text{SiO}_2\text{(g)} + \text{CO(g)}$$ (8)
$$3\text{SiC(s)} + 2\text{ZrO}_2\text{(s)} \rightarrow 2\text{ZrC} + 3\text{SiO}_2\text{(g)} + \text{CO(g)}$$ (9)

Moreover, SiC also reduces ZrC$_x$O$_y$:

$$\text{ZrC}_x\text{O}_y\text{(s)} + \text{SiC(s)} \rightarrow \text{ZrC(s)} + \text{SiO}_2\text{(g)} + \text{CO(g)}$$ (10)

Therefore, there is very likely a loss of SiO(g) in the outlet gas during the carbothermal reduction, given the continuous consumption of SiC via side reaction until the formation of ZrC is completed, as presented in Equations (9) and (10). The presence of traces, identified as m-ZrO$_2$ in Figure 1, may be attributed to the loss of material through the volatilization of gaseous species (SiO and CO) in the outlet gas during the reduction reaction, leaving behind unreacted ZrO$_2$. However, the amount of m-ZrO$_2$ is very small. Although the reaction time was increased to 50 min and to 60 min, and the temperature to 1440 °C and 1450 °C, respectively, the behavior pattern was very similar. According to the Scherrer equation$^3$, the mean crystallite size of ZrC was approximately 35 nm, while that of SiC was approximately 26 nm. This indicates that almost pure ZrC-SiC powders of nanometric crystallite size can be produced in a reaction time of less than 1 hour. Compared to the conventional carbothermal reduction, the current method has the advantage of involving a shorter reaction time, which can be attributed to the combination of nanoscale precursors and the microwave heating technique, as reported in the literature for other similar materials$^{17,18}$. The particle size and morphology of ZrC-SiC powders obtained by microwave-assisted carbothermal reduction for different reaction times are presented in Figure 3. Note that the morphology depicted in all the images is similar. Figure 3 reveals the presence of primary particles (80-100 nm) that aggregate to form agglomerates (<250 nm). This agglomeration is caused by the tendency of very fine particles.
The overall reaction rate using microwave heating was very fast and yielded nanometric particles. Increasing the reaction time resulted in negligible increases in the mean particle size due to melting and agglomeration of primary particles. Compared to a similar method, this approach reduced the particle size of the ZrC-SiC powders from the micron to the nanometric scale.

4. Conclusions

In summary, microwave-assisted carbothermal reduction was used to produce well crystallized ZrC-SiC nanocomposites of ZrO₂, SiO₂, and C. An almost pure ZrC-SiC composite was obtained at 3 kW of power in a reaction time of 40 min at 1420 °C. Short reaction times used in the carbothermal reduction favored the production of ZrC-SiC nanopowders with particles in the range of 80-100 nm. Longer reaction times increased the overall particle size of ZrC-SiC due to melting and agglomeration of primary particles. The advantage of this method over conventional carbothermal reduction is its shorter reaction time and lower temperature, in addition to producing nanometric products. Microwave-assisted carbothermal reduction is a promising route for the synthesis of ZrC-SiC nanocomposites.

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6. References

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