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Synthesis of WC powder through microwave heating of WO_3–C mixture

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Abstract: A simple, easy, and low-cost process for the fabrication of tungsten carbide (WC) powder through microwave heating of WO_3–C mixtures was developed. Thermodynamic calculations and experimental investigations were carried out for WO_3–C and W–C systems, and a formation mechanism was proposed. In the results, for the synthesis of WC, the use of over stoichiometric amount of C together with a specially assembled experimental setup (which effectively retains heat in the system) is necessary. The WC powder is successfully obtained by heating WO_3:5C mixture for 900 s in a domestic microwave oven.

Keywords: tungsten carbide; microwave heating; carbothermic reduction; thermodynamic analysis

1. Introduction

Tungsten carbide (WC) is the well-known metal carbide with a wide range of industrial applications. This compound is usually used in the production of cutting and punching tools as well as wire drawing dies. WC has the unique properties, including high hardness, good corrosion resistance, high thermal stability, and excellent abrasion resistance [1–3].

WC is commercially produced via a high-temperature reaction between W and C under a controlled atmosphere. This method suffers from low reaction rate that prolongs the process and makes the product very expensive [4–5]. To overcome this obstacle, new techniques such as combustion synthesis [6], chemical vapor deposition [7], mechanochemical synthesis [8], and microwave heating [9] have been proposed.

In the microwave heating method, the interaction of microwaves with magnetic and electric spins leads to the uniform generation of heat in the whole body of the sample. Thus, the temperature gradient is expected to be minimal, resulting in a more homogeneous final product [10–11]. The application of microwave energy in materials synthesis provides other advantages, such as high production rate and less environmental pollution [12–14].

Thus far, little research has been reported for the production of WC through microwave heating. In the viewpoint of W source, the research can be categorized into the following groups.

(1) WC synthesis using elemental W (method 1). The formation of WC from W–C binary mixtures has been investigated by Vallance *et al.* [15], Gerdes *et al.* [16] and Wu *et al.* [17]. Their results show that the successful synthesis of WC requires atmosphere control in the system and the use of a high-power microwave device (approximately 3 kW) [15–16]. The synthesis time is affected by the power of the microwave device, varying from 40 s to several minutes [15]. In addition, Wu *et al.* [17] showed that a nanosized WC final product could be achieved when the initial W powder was nanosized.

(2) WC synthesis using tungsten oxide (WO_3) (method 2). The obvious advantage of using WO_3 as a reagent is the reduction of processing costs. Sakaki *et al.* [9] investigated the *in situ* synthesis of WC from ternary WO_3–Al–C mixtures in a domestic microwave oven. In this case, Al was added to the initial mixture to reduce WO_3, whereas C was used as the carbide-forming agent. The aluminothermic reduction of WO_3 was demonstrated to exhibit combustive behavior.

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Al_2O_3 particles were fused to the carbide particles as a consequence of very high system temperatures during the synthesis. Hence, obtaining a product that consisted only of WC powder was difficult [9]. With the aim of using carbon for both the reduction and the carbide formation steps, Essaki *et al.* [18–20] experimentally demonstrated that WC could be formed by heating WO_3–C mixtures in a domestic microwave oven. However, their experimental setup and synthesis process were complicated, and the product was a mixture of WC and W_2C phases. The presence of W_2C in the product was not desirable because its properties were inferior to those of WC.

To develop a simple, easy, and inexpensive process for W_2C-free tungsten carbide preparation through microwave heating of WO_3–C mixtures, the present study was designed to elucidate the WC formation mechanism. To this end, the formation of WC phase by WO_3–C and W–C binary systems was investigated. The thermodynamic calculations were also performed to gain a deeper understanding of the synthesis process.

2. Experimental procedure

2.1. Microwave heating setups

A simple route was developed for the WC phase synthesis in a domestic microwave oven. A microwave oven (Samsung GE2370G) with a power output of 850 W was used to perform the experiments. In a series of preliminary experiments, it was observed that the powder mixtures exhibited low microwave susceptibility; i.e., they could not substantially absorb the microwave energy. Therefore, a small block of silicon carbide (SiC) was selected to place underneath the green samples to increase the microwave heating efficiency.

Two setups were used for the microwave heating of green samples, as shown in Fig. 1. Notably, in these setups, the components made of Al_2O_3 and SiO_2 were observed to be transparent to the microwaves, and therefore did not affect the absorption of microwave energy by the samples. These components were merely used to prevent the samples from oxidizing in the presence of air. The advantage of setup B, in comparison to setup A, was its ability to effectively prevent

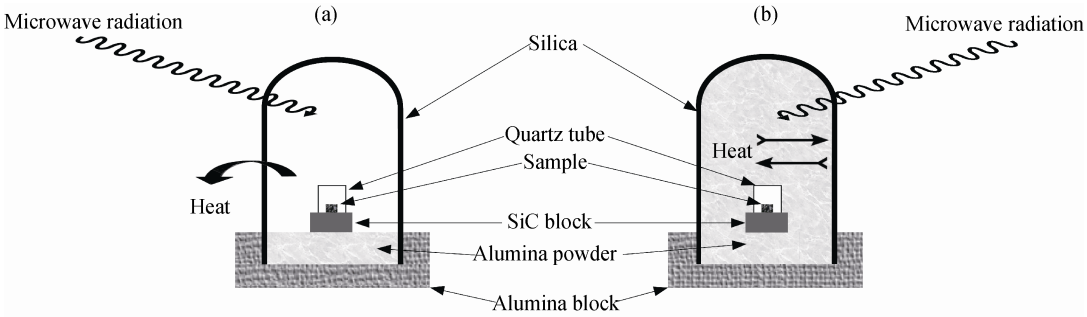

Fig. 1. Schematic of two different experimental setups used in this study: (a) setup A; (b) setup B.

heat loss from the system as a consequence of the low thermal conductivity of Al_2O_3 powder. This configuration maintained the thermal energy inside the system and enabled higher temperatures.

2.2. Synthesis and characterization

Analytical-grade WO_3 (Aldrich 232785), W (Wako 202-03442), and C (Wako 070-01325) were used as the starting materials. Different ratios of the reagents were weighed and subsequently mixed using a planetary mill. The milling time, milling speed, and balls-to-powder mass ratio (BPR) were 900 s, 250 r/min, and 10, respectively. The mixtures were then pressed into green cylindrical samples (10 mm diameter and 5-mm height) using an axial hydraulic press with a loading pressure of 500 kg/cm^2.

The obtained compacts were heat treated for the required durations. Complete details of the chemical composition, setup, and microwave heating time of each experiment are given in Table 1. After the completion of microwave heating, the setup was removed from the oven and allowed to be cool naturally. The produced samples were then finely ground to obtain powders suitable for X-ray diffraction (XRD; JEOL JDX8030 with a Cu K_α radiation source) analysis.

Table 1. Chemical composition, microwave heating time, and the setup used for various samples prepared in this study

Sample	Composition by mole proportion	Microwave heating time / s	Setup
1	WO_3:4C	180	A
2	WO_3:4C	600	A
3	W:0.5C	600	A
4	W:0.5C	600	B
5	W:C	600	A
6	W:C	600	B
7	W:2C	600	A
8	W:2C	600	B
9	WO_3:5C	900	B

In all parts of this study, thermodynamic calculations were performed to gain insight into probable chemical reactions as well as justify the results. These calculations were done by the available thermodynamic data (FactSage Thermochemical Database System) relevant to the temperature range from 300 to 1800 K. The maximum temperature was set at 1800 K because achieving temperatures greater than 1800 K using a domestic microwave oven was considered unlikely.

3. Results and discussion

3.1. Thermodynamic evaluations

Synthesis of WC from WO_3–C mixtures through heating in a domestic microwave oven was investigated in the present work. In our basic concept, carbon was not only for the oxide reduction but also for the carbide formation.

3.1.1. Carbothermic reduction of WO_3

The simplest forms of reduction reactions in the WO_3–C system are as following equations.

$$WO_3 + 3C = W + 3CO\ (g) \quad (1)$$

$$WO_3 + 1.5C = W + 1.5CO_2\ (g) \quad (2)$$

Fig. 2(a) shows the results of thermodynamic calculations for Eqs. (1) and (2). In the temperature range from 300 to 970 K, both reactions have the positive standard Gibbs free energy ($\Delta G^{\ominus}$) values, indicating that none of these reactions are thermodynamically favorable. The $\Delta G^{\ominus}$ values of reduction reaction attain the negative values at temperatures greater than 970 K, indicating a greater likelihood of metallic tungsten formation. Regarding Fig. 2(a), Eq. (1) is more favorable than Eq. (2) in the temperature range from 970 to 1800 K because of its more negative $\Delta G^{\ominus}$ values. Hence, from a thermodynamics standpoint, in a WO_3–C mixture, tungsten will be reduced through Eq. (1); that is, 3 mol of carbon is necessary for the reduction of WO_3. Fig. 2(a) also reveals that Eq. (1) is an endothermic reaction and therefore requires sufficient heat input to proceed.

3.1.2. Formation of WC

Following the carbothermic reduction of WO_3 via Eq. (1), reduced W is expected to react with carbon to form tungsten carbides. The carbide formation reactions are shown as

$$W + C = WC \quad (3)$$

$$W + 0.5C = 0.5W_2C \quad (4)$$

Fig. 2(b) presents the results of thermodynamic calculations for Eqs. (3) and (4), showing that both reactions possess negative $\Delta G^{\ominus}$ values. These $\Delta G^{\ominus}$ values reveal that the formation of both WC and W_2C phases is possible in the absence of a kinetic obstacle. However, because the $\Delta G^{\ominus}$ value for Eq. (3) is more negative than that for Eq. (4), the WC phase is apparently more thermodynamically stable [6]. Fig. 2(b) also shows that over a wide range of temperature, Eqs. (3) and (4) are both exothermic.

3.2. Experimental results

3.2.1. WO_3:4C mixture

Thermodynamic evaluations presented in the previous section reveal that, for a successful synthesis of the WC phase from a WO_3–C mixture, the C/WO_3 mole ratio should be equal to four. That is, for the production of 1 mol of WC, 3 mol of carbon is required for the reduction of WO_3 and one additional mole is needed for carbide formation.

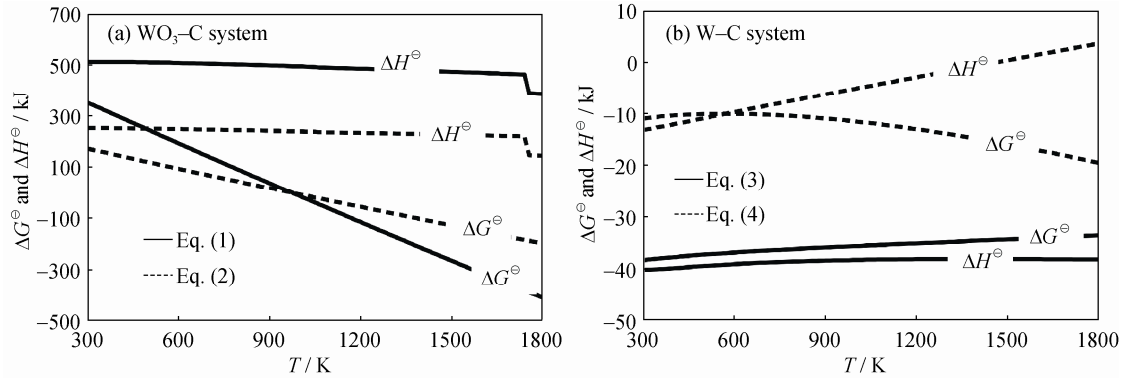

Fig. 2. $\Delta G^{\ominus}$ –T and $\Delta H^{\ominus}$ –T curves of carbothermic reduction (a) and carbide-forming reactions (b) calculated in the range from 300 to 1800 K.

Fig. 3 represents the XRD patterns of WO_3:4C mixtures heated in setup A for 180 and 600 s. As evident in Fig. 3(a), no sign of tungsten carbide formation is observed after 180 s of heating and the product mainly consists of various tungsten oxides. The presence of $WO_{2.9}$, $WO_{2.72}$, WO_2, and W phases in the sample indicates that, in contrast to Eq. (1), the reduction of WO_3 by carbon proceeds stepwise, as shown in Eqs. (5)–(8).

$$WO_3 + 0.1C = WO_{2.9} + 0.1CO\ (g) \quad (5)$$

$$WO_{2.9} + 0.18C = WO_{2.72} + 0.18CO\ (g) \quad (6)$$

$$WO_{2.72} + 0.72C = WO_2 + 0.72CO\ (g) \quad (7)$$

$$WO_2 + 2C = W + 2CO\ (g) \quad (8)$$

Fig. 3(a) indicated that the reduction reactions (Eqs. (5)–(8)) were not completed; therefore, the microwave heating time was prolonged. A longer heating time is believed to be beneficial because it results in the transfer of more energy to the system, which increases the system temperature and promotes the reactions. The aforementioned prediction is in agreement with Table 2, which summarizes the $\Delta G^{\ominus}$ values for Eqs. (5)–(8). As represented in Table 2, although a partial reduction of tungsten oxides (i.e., Eqs. (5) and (6)) is possible at relatively low temperatures, higher temperatures are necessary for complete WO_3 reduction.

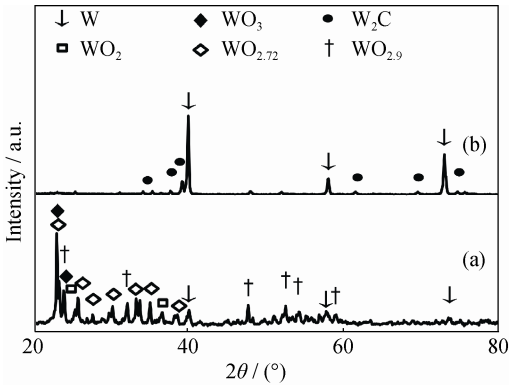

Fig. 3. XRD patterns of WO_3:4C mixtures heated for 180 (a) and 600 s (b) by setup A.

Table 2. Variations of $\Delta G^{\ominus}$ value in stepwise carbothermic reduction reactions of WO_3 from 300 to 1800 K

Temperature / K	300	665	700	935	1020	1800
Eq. (5)	++	+	0	–	– –	– – –
Eq. (6)	+	0	–	– –	– – –	– – – –
Eq. (7)	+++	++	+	0	–	– –
Eq. (8)	++++	+++	++	+	0	– –

Fig. 3(b) shows the XRD pattern of a WO_3:4C mixture after 600 s of heating in setup A (sample 2 in Table 1). No peaks attributable to tungsten oxides are observed in this figure, indicating the completion of WO_3 reduction step and demonstrating the positive effect of a longer heating time. Unexpectedly, however, the sample contains mainly elemental tungsten accompanied by only small amounts of carbide phase. Thus, in this experiment, the carbide formation step did not substantially proceed.

To gain better understanding of the WC formation reactions, some complementary experiments were performed with W–C mixtures containing different amounts of carbon. Furthermore, to attain the higher temperature in reaction system by better thermally insulation, the experimental setup was modified. This new and efficient setup (setup B) was constructed and used alongside setup A for comparison.

3.2.2. Complementary experiments

(1) W:0.5C mixture. Fig. 4 represents the XRD patterns of W:0.5C mixtures after heating in setups A and B for 600 s (samples 3 and 4 in Table 1). Fig. 4(a) shows that the microwave heating of sample in setup A does not result in the formation of a carbide phase, presumably because the system lacks sufficient thermal energy to drive the carbide-forming reactions forward (i.e., Eqs. (3) and (4)).

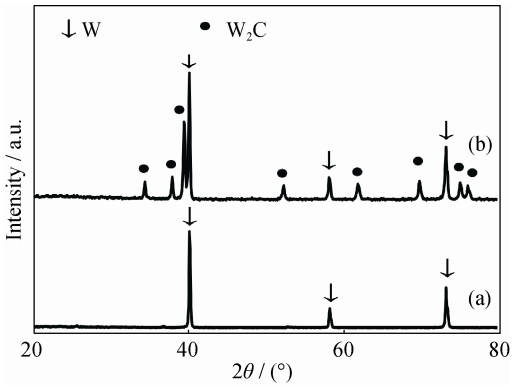

Fig. 4. XRD patterns of the W:0.5C mixtures heated for 600 s using setup A (a) and setup B (b).

To prevent the excessive loss of thermal energy from the system and achieve higher temperatures, the modified experimental setup was used (setup B). Fig. 4(b) shows that, when setup B is employed, the W_2C phase is produced in the sample, in agreement with aforementioned reasoning and predictions.

Because the thermodynamic calculations in section 3.1.2 show that WC is the predominant phase under the conditions in present study, the question arises as to why the obtained sample (as shown in Fig. 4(b)) is composed of W_2C–W instead of WC–W. One possible explanation is that, from a kinetics standpoint, the formation of WC can occur via the following steps, as shown in Fig. 5. Some of these steps (reactions) may proceed in parallel, whereas others may proceed in series. Given such a scheme, the absence of WC in Fig. 4(b) is due to the favorable kinetics of step III in comparison to step IV and the insufficient carbon in the system to participate in step IV, i.e., Eq. (9).

$$0.5W_2C + 0.5C = WC \quad (9)$$

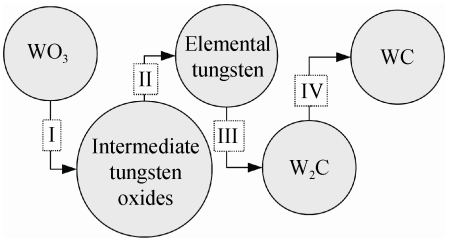

Fig. 5. Sequence of WC phase formation from WO_3–C mixtures: step I — reduction of WO_3 to intermediate tungsten oxides (e.g., $WO_{2.9}$); step II — reduction of intermediate oxides to elemental W; step III — formation of tungsten lower carbide (i.e., W_2C); step IV — formation of WC phase.

In Fig. 4(b), the presence of some elemental tungsten alongside the W_2C phase indicates either insufficient reaction time or insufficient carbon for the completion of step III (i.e., Eq. (4)). Carbon insufficiency in the system can be due to the unpredicted carbon burn reaction caused by air infiltration into the reaction chamber.

(2) W:C mixture. XRD patterns of W:C mixtures after 600 s of heating in setups A and B (samples 5 and 6 in Table 1) are shown in Fig. 6. A comparison of Figs. 6(a) and 4(a) shows that, when the amount of carbon increases from 0.5 to 1 mol, a small peak assigned to W_2C appears. However, because of the low temperature of system, the product mainly consists of unreacted W. In the case of the sample heated in setup B (Fig. 6(b)), the main constituents are WC and W_2C, accompanied by a small amount of unreacted W. These observations confirm the important role of the C amount in W–C mixture as well as the critical effect of using setup B. The presence of W_2C and W phases in Fig. 6(b) is explained by the aforementioned kinetics scheme in conjunction with the likely occurrence of the carbon burn phenomenon through reaction with infiltrated air. These results imply that, to obtain a pure WC powder, the addition of some excess carbon (relative to the stoichiometric amount) may be required.

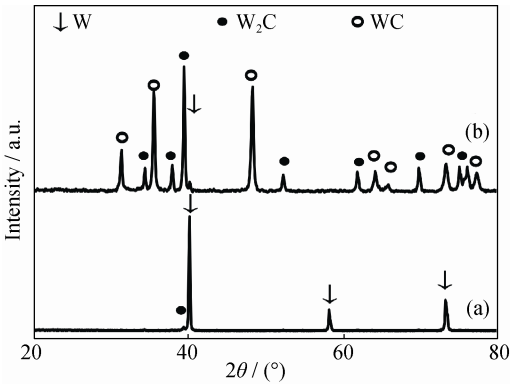

Fig. 6. XRD patterns of the W:C mixtures heated for 600 s using setup A (a) and setup B (b).

(3) W:2C mixture. Fig. 7 shows the XRD patterns of W:2C mixtures after 600 s of microwave heating in setups A and B. A comparison of Fig. 4(a), Fig. 6(a), and Fig. 7(a) (corresponding to W:0.5C, W:C, and W:2C mixtures, respectively) reveals that setup A is incapable of producing tungsten carbide phases because it suffers from serious thermal energy loss. Hence, setup B (which can efficiently retain thermal energy in the system) should be used for the successful synthesis of WC. As evident in Fig. 7(b), the product of W:2C mixture heated in setup B consists of WC phase. The amounts of W_2C and W phases are below the detection limit of the X-ray diffractometer, and no sign of these phases is visible in Fig. 7(b). The over-stoichiometric amount of carbon apparently compensates for the carbon loss of system, enabling completion of Eq. (9).

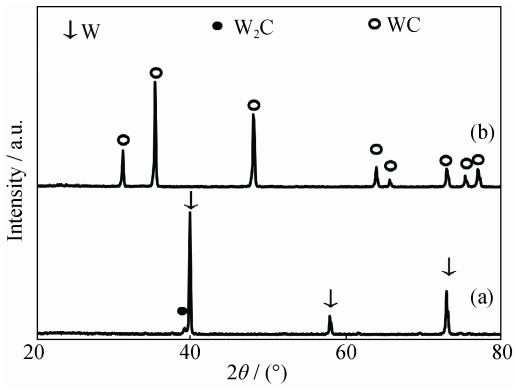

Fig. 7. XRD patterns belonging to the W:2C mixtures heated for 600 s using setup A (a) and setup B (b).

3.2.3. WO_3:5C mixture

The combined results and observations concerning W:0.5C, W:C, and W:2C mixtures presented thus far indicate that, to produce WC powder free from either W or W_2C, the use of the heat-loss-preventing setup together with a sufficient excess of carbon was critical. To test the validity of the aforementioned conclusion concerning the WO_3–C system, a WO_3:5C mixture was heated for 900 s in a domestic microwave using setup B. This mixture contained 3 mol of C for the reduction of WO_3, 1 mol for WC formation, and one extra mole to compensate for the carbon loss. Notably, a longer heating time were used for this specific sample compared to that for sample 2 to ensure the completion of reactions.

The XRD pattern of the heated WO_3:5C mixture is shown in Fig. 8. The product clearly consists of WC, demonstrating the completion of both the reduction and the carbonization steps. Thus, a simple and inexpensive process was developed for fabricating WC powder through heating a WO_3–C mixture in a low-power domestic microwave oven.

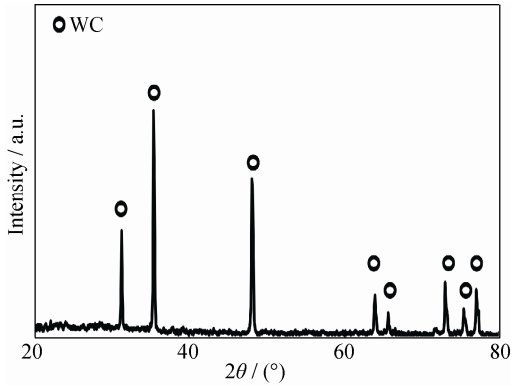

Fig. 8. XRD pattern belonging to the WO_3:5C mixture heated for 900 s using setup B.

4. Conclusions

(1) The carbothermic reduction reaction of WO_3 occurs stepwise, which results in the formation of intermediate tungsten oxides, i.e., $WO_{2.9}$, $WO_{2.72}$, and WO_2.

(2) Initiation of carbide-forming reactions requires higher temperatures than that of carbothermic reduction reactions.

(3) Although thermodynamic evaluations show that WC is the stable carbide phase under the conditions used in this work, the W_2C phase is formed in the samples. The presence of W_2C is attributed to the favorable kinetics of its formation as well as to the carbon insufficiency (i.e., carbon burn) in the system.

(4) By preventing the excessive heat loss from the system (through the use of a more efficient experimental setup) and adding the adequate amounts of excess carbon, the WC powder is synthesized by microwave heating of an initial WO_3:5C mixture for 900 s.

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