

An investigation of the fabrication of tungsten carbide–alumina composite powder from WO_3 , Al and C reactants through microwave-assisted SHS process

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ABSTRACT

Possibility of synthesis of tungsten carbide–alumina composite powder from WO_3 –Al–C mixture via microwave-assisted SHS process in a domestic microwave oven has been investigated. By comparison of the results of thermodynamic calculations with experimental findings, it was found that during microwave heating of WO_3 :2Al:C mixture, synthesis process initiates by vigorous exothermic reaction of WO_3 with Al which results in a great deal of heat. Major portion of tungsten carbide phase in the product is W_2C , whose formation is supposed to be related to the high thermodynamic stability of this compound at high temperatures. W_2C formation could also be related to carbon loss phenomenon in the mixture, as a consequence of some carbon burn. It has been concluded that addition of excess carbon to the initial mixture together with extension of the microwave processing time, increase the amount of WC phase in the product in expense of W_2C . Experimental results showed that only small amounts of W_2C remain in the product with around 80 mol% excess initial carbon and about 10 min of microwave heating time.

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1. Introduction

WC– Al_2O_3 composites demonstrate excellent properties such as low density, good strength at high temperatures, high hardness, good fracture toughness and high chemical inertness. Hence, these composites have found several applications such as cutting, drilling and machining tools as well as coating materials [1–4]. Conventional production methods of WC and/or WC– Al_2O_3 composite powders require long time heating at high temperatures and under the controlled atmospheres [5,6]. Such process conditions make the products very expensive.

Several attempts have been made to develop low-cost production routes for WC– Al_2O_3 composite powders in which simple production method, cheap reagents and short time reactions can be employed [7–12]. One of these new routes is Self-propagating High Temperature Synthesis (SHS) process.

In a SHS route, also known as Combustion Synthesis (CS) process [13,14], the heat released from an exothermic reaction in a part of the system activates the reaction in the adjacent part, so that the reaction propagates through whole system almost spontaneously

[15,16]. According to the criterion proposed by Merzhanov, when the adiabatic temperature¹ (T_{ad}) of a reaction is higher than 1800 K, the mode of reaction is expected to be SHS [17]. The significant features of the SHS route are the process simplicity, high purity of the products, low process cost, high synthesis rate and energy independency of the system. Solid state SHS reactions could begin either from one spot of the mixture (activated by the heat generated by use of an ignition mixture or an electrical element) or in the whole body of the system (by use of, for example an electric furnace) [14,18].

Fabrication of WC– Al_2O_3 composite powders from WO_3 –Al–C reactants through SHS route has been reported by Zhang et al. [9] and Niyomwas [10], where the SHS reaction was initiated by use of an electrical element. It has been shown in their works that the obtained powders consist of unwanted W_2C phase with inferior properties. In order to decrease the amount of W_2C compound in the product, use of activated carbon [9] and mixture diluents such as Al_2O_3 and NaCl [10] has been proposed. It has been claimed that the remained W_2C phase can also be leached out by use of a HNO_3 –HF solution [9].

Recently, use of microwave energy for the initiation of SHS reactions has gained some attention [19–21]. In microwave heating, heat is generated within the samples by the interaction of electromagnetic wave

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¹ The highest temperature which a system could reach under adiabatic conditions.

with target materials. Efficiency of microwave heating is controlled by the magnetic and dielectric properties of target material, microwave frequency, power of microwave source, operating temperature and thermal conductivity of the materials [22,23]. Since in microwave processing heat is generated inside the sample, temperature gradient would be smaller than that of the conventional heating methods, such as electric furnace heating [24]. This in turn could yield more homogeneous products during SHS processing. Other advantages of the microwave heating are: possibility of selective heating of the materials, less environmental pollution and reducing the time of processing as well as the production cost [25,26].

Aim of the present research work has been to investigate the possibility of synthesis of WC–Al₂O₃ composite by use of WO₃–Al–C starting mixtures and through microwave heating process. For the purpose of the clarification of the reaction mechanism, WO₃–Al–C ternary system was divided into the relevant sub-binary systems. Effect of carbon amount in the initial mixture on the final product was also investigated. Thermodynamic calculations were also performed to get an insight about the possible chemical reactions. For this purpose, values of ΔG°_{298} , ΔH°_{298} and T_{ad} have been computed by use of necessary thermodynamic data extracted from relevant references [27].

2. Procedure

Analytical grade WO₃, Al and C powders were used as the initial reactants. Required amounts of raw materials were carefully weighted and mixed by the use of a low energy laboratory ball-mill under the following conditions: milling speed = 250 rpm, ball to powder mass ratio = 10, milling time = 5 min, balls and milling put materials = hardened steel. A predetermined mass of initial mixture was pressed by the use of a single-axis hydraulic press under 500 kg/cm² pressure to obtain cylindrical green samples with about 10 mm diameter and about 4 mm height.

Microwave heating was performed in a domestic microwave oven (SAMSUNG: GE2370G) with 850 W microwave output power. Preliminary experiments proved that the microwave absorption capability of the samples is unacceptably low. Hence, a block of silicon carbide (SiC) was placed beneath the samples to act as a susceptor [22,28] and promote the synthesis process, by adequate heat absorption. Schematic illustration of the experimental setup is shown in Fig. 1. Other components of the reaction chamber were made of Al₂O₃ and SiO₂, due to low microwave absorption capacity of these materials [22,24]. The components of experimental setup were arranged in such a way that an isolate atmosphere can be provided for the samples during heating course. Samples were heated for adequate time. Occurrence of SHS mode reaction during microwave heating was recognized through observation of physical phenomena such as flushing and inflaming of the samples. In the present research work, it has been observed that SHS reactions occur after about 1 min

of microwave heating. For mixtures with gradual type reactions, 2 min of microwave heating was performed. After the heating course, microwave oven was switched off and the setup was allowed to be cooled slowly. Obtained products were then crushed and ground adequately and their phase compositions were determined by the use of an X-ray diffraction instrument (XRD: JEOL-JDX8030) with a Cu–K α radiation. Total and free (un-reacted) carbon amounts of synthesized powders were measured according to ISO-3907 and ISO-3908 international standards, respectively. Carbon loss and free (un-reacted) carbon extents have been determined by comparing the mentioned measured amounts with initial carbon content of the mixture. Microstructures of some processed powders were investigated by a scanning electron microscope (SEM: TESCAN-VEGA II).

3. Results and discussion

Table 1 shows the types of occurred reactions in various investigated mixtures.

3.1. WO₃–Al–C ternary mixture

The simplest form of chemical reaction in WO₃:2Al:C mixture, which is the summation of aluminothermic reduction reaction of WO₃ plus carburization reaction of reduced tungsten, could be written as reaction (1).



ΔG°_{298} value of reaction (1) is -856 kJ which implies the great probability of the reaction. Thermodynamic calculations also show that reaction (1) is highly exothermic ($\Delta H^\circ_{298} = -872$ kJ) with $T_{ad} = 3910$ K. Since T_{ad} of this reaction is higher than 1800 K, the type of this reaction is expected to be SHS, according to the Merzhanov criterion.

Fig. 2 represents the XRD patterns of WO₃:2Al:C mixture before and after microwave heating. As figure shows, no peak of the starting reagents remained in the XRD pattern of the heated sample. Abrupt change of XRD pattern together with observation of ignition phenomenon (see Table 1) show that the type of occurred reaction is SHS; the fact which is in accordance with the thermodynamic predictions. Occurrence of the SHS reaction during microwave heating of WO₃:2Al:C mixture could also be concluded from the formation of large and dense agglomerates in the product (see Fig. 3-A). Since T_{ad} of WO₃:2Al:C system is higher than the melting point of Al₂O₃ (2327 K), formation of these agglomerates, as a consequence of bonding of tungsten carbide particles by molten alumina, is anticipated.

The presence of W₂C peaks in the XRD pattern of heated sample shows that the occurred reaction differs somewhat from the expected one, i.e., reaction (1). In order to determine the actual occurred reaction in the ternary WO₃:2Al:C mixture and clarify the cause of W₂C formation, the effect of microwave heating on three sub-binary mixtures was studied, whose results are presented and discussed in the following section.

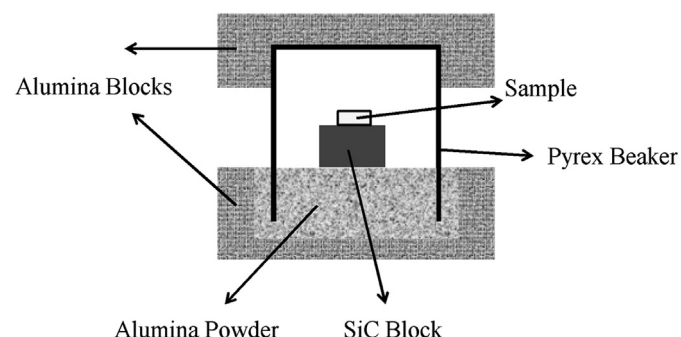


Fig. 1. Schematic illustration of the experimental setup.

Table 1
Type of reaction occurred in various mixtures.

Sample number	Composition	Type of reaction
S1	WO ₃ + 2Al + C	SHS
S2	WO ₃ + 3C	Gradual
S3	4Al + 3C	Gradual
S4	WO ₃ + 2Al	SHS
S5	WO ₃ + 2Al + 1.4C	SHS
S6	WO ₃ + 2Al + 1.8C	SHS
S7	WO ₃ + 2Al + 2C	Gradual

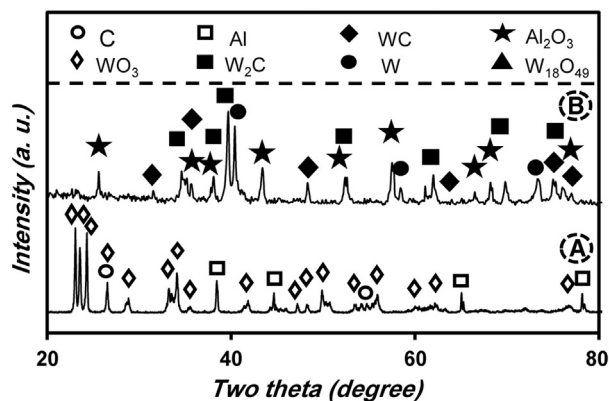


Fig. 2. XRD patterns of $\text{WO}_3\text{:}2\text{Al:C}$ system (sample S1) before (A) and after (B) microwave heating.

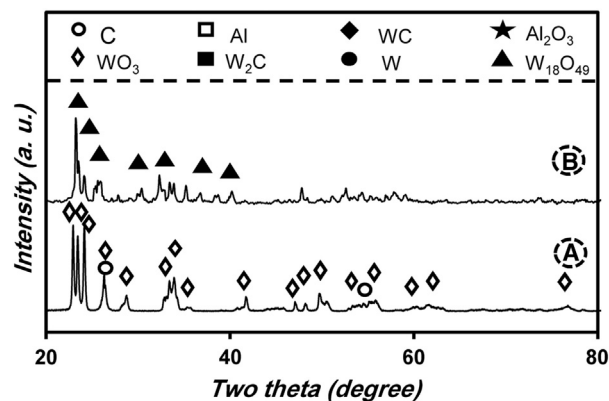


Fig. 4. XRD patterns of $\text{WO}_3\text{:}3\text{C}$ system (sample S2) before (A) and after (B) microwave heating.

3.2. Binary sub-systems

- $\text{WO}_3\text{--C}$ sub-system:
 $\text{WO}_3\text{--C}$ system was the first binary sub-system studied in this research work. Expected chemical reactions in this binary sub-system are:



Both above reactions have positive ΔG°_{298} values (352 kJ and 172 kJ, respectively) and both are endothermic ($\Delta H^\circ_{298, \text{reaction}(2)} = 511$ kJ and $\Delta H^\circ_{298, \text{reaction}(3)} = 252$ kJ). Although both reactions are impossible from the thermodynamic standpoint, one may argue that additional energy provided by microwave heating may compensate the energy shortage and promotes the reactions to go ahead. XRD patterns of $\text{WO}_3\text{:}3\text{C}$ mixture heated for 2 min (Fig. 4) show no peak of W which reveals that heating by a low energy domestic microwave oven, like that employed in the present study, cannot provide sufficient heat necessary for the carbothermic reduction of tungsten trioxide. Nevertheless, partial reduction seems to be happened leading to the formation of some tungsten lower oxides such as $\text{W}_{18}\text{O}_{49}$.

- Al--C sub-system:
 The probable reaction in the Al--C binary mixture could be written as reaction (4).



According to the results of thermodynamic calculations ($\Delta G^\circ_{298} = -203$ kJ, $\Delta H^\circ_{298} = -215$ kJ and $T_{\text{ad}} = 1570$ K) formation of Al_4C_3 compound through reaction (4) is anticipated. T_{ad} of reaction (4) is less than 1800 K; hence, the type of this reaction is expected to be gradual, if performed individually. In spite of the above prediction, XRD pattern of $4\text{Al:}3\text{C}$ mixture heated by microwave irradiation for 2 min (Fig. 5) shows that seemingly no chemical reaction has been happened. Non-occurrence of reaction (4) could be related to either the existence of some kinetic obstacles and/or insufficiency of microwave heating time.

- $\text{WO}_3\text{--Al}$ sub-system:
 The last investigated binary sub-system was $\text{WO}_3\text{--Al}$ mixture. Reaction (5) shows the expected reaction in this system.



Reaction (5) has a very big negative ΔG°_{298} value (-818 kJ) which shows a great tendency of reaction (5) to occur. This reaction is highly

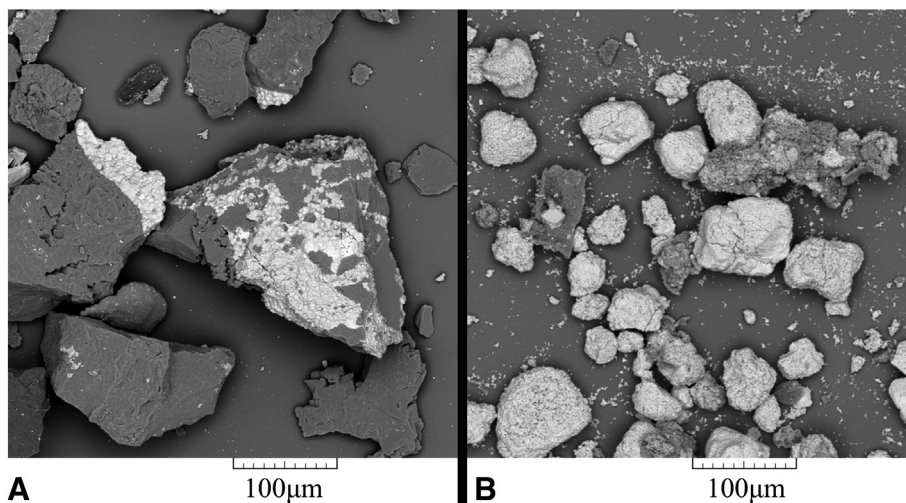


Fig. 3. BSE-SEM images (at $500\times$ magnification) of $\text{WO}_3\text{:}2\text{Al:C}$ (A) and $\text{WO}_3\text{:}2\text{Al:}2\text{C}$ (B) mixtures after microwave heating. Bright regions are representatives of heavy elements-containing phases, such as $\text{W/W}_2\text{C/WC/WO}_3$, while gray domains represent the light elements-containing phases, such as $\text{Al/Al}_2\text{O}_3\text{/C}$.

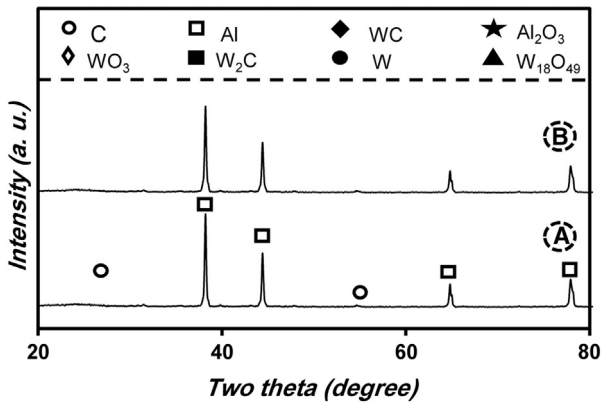


Fig. 5. XRD patterns of 4Al:3C system (sample S3) before (A) and after (B) microwave heating.

exothermic ($\Delta H^\circ_{298} = -832$ kJ) with a T_{ad} value greater than 1800 K (around 3880 K). Hence, the type of this reaction is anticipated to be SHS, according to the Merzhanov rule. This prediction is in a good agreement with the experimental observations (Table 1). XRD patterns of $WO_3:2Al$ samples before and after microwave heating are shown in Fig. 6. As Fig. 6 shows, no trace of initial reagents could be found in the XRD pattern of heated mixture. Formation of W and Al_2O_3 compounds is the clear sign of the occurrence of reaction (5).

3.3. Reaction mechanism and the effect of carbon amount

By comparing the results obtained from WO_3-C , $Al-C$ and WO_3-Al binary mixtures, it could be concluded that during microwave heating of $WO_3:2Al:C$ mixture, the overall reaction is initiated by the reaction of WO_3 with Al leading to the formation of $W-Al_2O_3$ composite powder together with a large amount of heat. According to the thermodynamic calculations for reaction (6), ($\Delta G^\circ_{298} = -38$ kJ, $\Delta H^\circ_{298} = -40$ kJ and $T_{ad} = 1160$ K) as well as experimental data presented by Vallance [29], it is anticipated that the reduced W would react by C to produce WC phase.



However, most of WC phase has been replaced by W_2C as the XRD pattern of the processed sample shows (Fig. 2). Since properties of W_2C phase are inferior to WC, formation of W_2C phase is undesirable and should be prevented. Presence of unwanted W_2C phase could be related to the following reasons:

- Thermodynamic calculations show that W_2C phase is more stable than WC phase at high temperatures [7,9,30,31]. Hence, formation

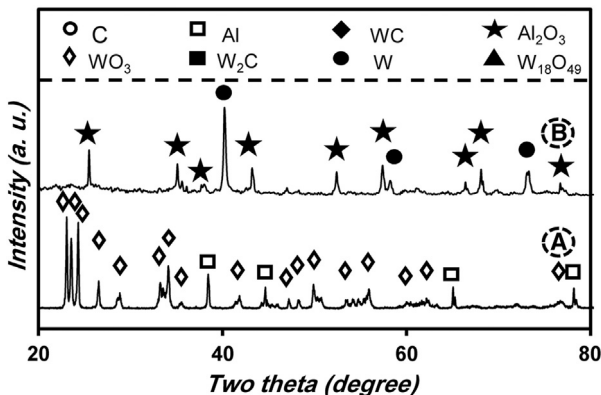


Fig. 6. XRD patterns of $WO_3:2Al$ system (sample S4) before (A) and after (B) microwave heating.

of W_2C phase can be reasonably attributed to high temperatures resulted from the heat released by aluminothermic reduction reaction of tungsten trioxide.

- It has been reported earlier that during production of WC powder from a W:C mixture, carbon deficiency would bring about W_2C formation [31,32], the phenomenon which could be possibly another cause of the presence of W_2C phase in this research work. In other words, it would be rational to assume that some portion of initial carbon has been burned out at high mixture temperature by entrapped air during the microwave heating process, which in turns leads to the carbon deficiency and production of W_2C compound, consequently. Large carbon loss in $WO_3:2Al:C$ system (presented in Table 2) shows that this postulation is true and supports the occurrence of reaction (7).



$$(\Delta G^\circ_{298} = -10 \text{ kJ}, \Delta H^\circ_{298} = -13 \text{ kJ and } T_{ad} = 600 \text{ K})$$

Based on the above justifications, it seems that formation of W_2C phase in the final product could be prevented if one of the following ideas is applied:

- Decreasing the maximum temperature of the system (for instance, by adding some appropriate coolants) to the extent that WC phase becomes thermodynamically predominant.
- Using higher amounts of carbon in the initial mixture in order to compensate the carbon loss.

In the present research work, applicability of the latter idea for the production of $WC-Al_2O_3$ composite free from unwanted W_2C compound has been examined by investigation of $WO_3:2Al:(1+x)C$ systems, where x denotes excess carbon on a molar basis.

Fig. 7 shows the XRD patterns of $WO_3:2Al:(1+x)C$ samples with different amounts of carbon ($0 \leq x \leq 1$) after the microwave heating process. As Table 1 shows, for $0 \leq x \leq 0.8$ values, type of occurred reactions is SHS. Table 2 demonstrates that by increasing the carbon amount in $WO_3:2Al:(1+x)C$ mixtures from 0 to 0.8 mol, the amount of carbon loss in the product has been decreased while free carbon amount has been increased. As a consequence, WC phase should be increased in expense of W and W_2C due to the occurrence of reactions (6) and (8). This postulation is supported by XRD patterns shown in Fig. 7.



$$(\Delta G^\circ_{298} = -27 \text{ kJ}, \Delta H^\circ_{298} = -27 \text{ kJ and } T_{ad} = 900 \text{ K})$$

Another phenomenon which decreases W_2C can be explained by absorption of some heat released from aluminothermic reduction reaction of WO_3 by excess C. This phenomenon would decrease the system

Table 2

Carbon loss values and free carbon amounts of various heated $WO_3:2Al:(1+x)C$ mixtures.

Sample number	Composition	C loss (wt.%)	Free/Un-reacted C (wt.%)
S1	$WO_3 + 2Al + C$	~50	~0
S5	$WO_3 + 2Al + 1.4C$	~45	~5
S6	$WO_3 + 2Al + 1.8C$	~40	~10

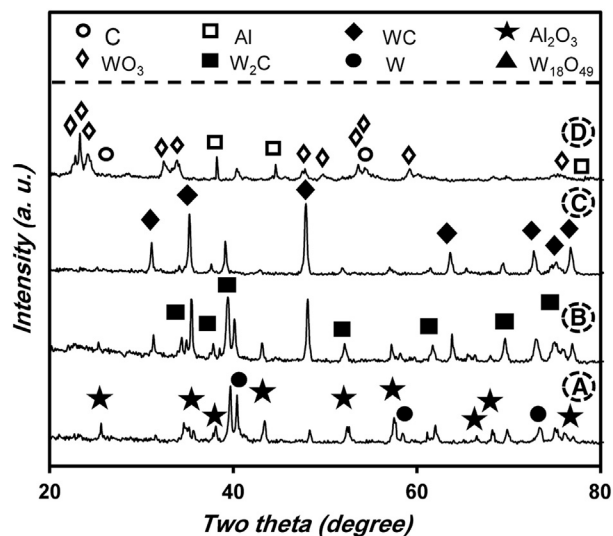


Fig. 7. XRD patterns of $\text{WO}_3\text{:}2\text{Al}\text{:}(1+x)\text{C}$ systems. Samples S1 (A), S5 (B) and S6 (C) heated until the occurrence of SHS reaction. Sample S7 (d) heated for 2 min.

maximum temperature which in turn decreases the thermodynamic stability of W_2C phase.

Fig. 7 shows that for $\text{WO}_3\text{:}2\text{Al}\text{:}1.8\text{C}$ mixture, peaks of W_2C phase are still visible. Hence, more carbon amount should be added into the initial mixture. As Table 1 shows, by increasing C amount from 1.8 mol to 2 mol, type of the reaction changes from a SHS state to a gradual mode. This could be related to the fact that SHS reaction in the $\text{WO}_3\text{--Al--C}$ mixtures initiates by the reaction of WO_3 with Al and the presence of high amounts of carbon in the mixture, could separate WO_3 and Al particles and postpone the reaction progress.

With regard to the justification presented in Section 3.1 ($\text{WO}_3\text{--Al--C}$ ternary mixture), formation of agglomerates will not take place in $\text{WO}_3\text{:}2\text{Al}\text{:}2\text{C}$ system due to the occurrence of gradual reaction. This conclusion has been supported by the SEM observations (Fig. 3-B).

Fig. 7 shows that non-occurrence of SHS reaction in the $\text{WO}_3\text{:}2\text{Al}\text{:}2\text{C}$ mixture brings about an incomplete reduction reaction which can be deducted by the presence of some unreacted portions of WO_3 and Al reagents in the relevant XRD pattern.

Since fabrication of tungsten carbide (WC) phase is a time consuming process [31,32], another method for the elimination of W_2C phase from the product obtained through microwave heating of $\text{WO}_3\text{:}2\text{Al}\text{:}1.8\text{C}$ mixture could be the continuation of heating beyond the occurrence time of SHS reaction, recognized by spontaneous ignition of the sample. XRD pattern of $\text{WO}_3\text{:}2\text{Al}\text{:}1.8\text{C}$ mixture heated for 10 min is compared with that of the same mixture heated just to the ignition point, in Fig. 8. This figure shows that WC– Al_2O_3 composite powder with small amount of W_2C phase can be successfully synthesized by addition of sufficient excess carbon and giving enough time under microwave heating. As seen in Fig. 8, by heating continuation W_2C peaks have been decreased considerably, which is an indication of gradual conversion of W_2C to WC by free carbon remained after SHS reaction (reaction (8)). The presence of traces of W_2C phase in the XRD pattern of $\text{WO}_3\text{:}2\text{Al}\text{:}1.8\text{C}$ mixture heated for 10 min reveals that the heating time has not been sufficient for completion of reaction (8). It seems that for the production of a W_2C free WC– Al_2O_3 composite powder, longer times of microwave heating should be applied. However, our experiments revealed that the setup employed in this research work cannot resist against oxygen penetration into the chamber for more than 10 min and longer microwave heating would only bring about partial oxidation of W, W_2C and WC products. Hence, full elimination of W_2C phase requires employing a new experimental setup which could provide oxygen free environment for longer times.

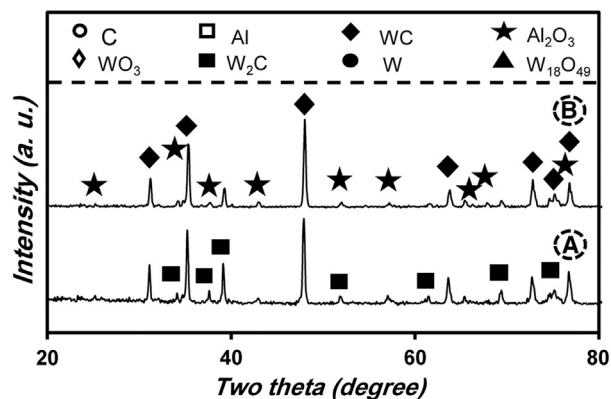


Fig. 8. XRD patterns of $\text{WO}_3\text{:}2\text{Al}\text{:}1.8\text{C}$ system (sample S6) heated until the occurrence of SHS reaction (A) and 10 min (B).

4. Conclusion

Thermodynamic calculations as well as experimental investigations have been performed to evaluate the possibility of production of tungsten carbide–alumina composite powder from $\text{WO}_3\text{--Al--C}$ mixture via microwave-assisted SHS process in a domestic microwave device and to clarify the reaction mechanism. It was found that:

- In $\text{WO}_3\text{--Al--C}$ ternary system, the overall reaction initiates by highly exothermic reduction of WO_3 by Al.
- The product resulted from microwave heating of $\text{WO}_3\text{:}2\text{Al}\text{:}C$ mixture consists of large agglomerates which are supposed to be formed during SHS mode reaction in the system. Presence of undesirable W_2C phase in the product is presumably related to high thermodynamic stability of this phase at high temperatures resulted from aluminothermic reduction of WO_3 together with carbon deficiency due to the probable carbon burn reaction.
- In $\text{WO}_3\text{:}2\text{Al}\text{:}(1+x)\text{C}$ systems, the type of occurred reactions depends on the amount of excess initial carbon (i.e. x) and for mixtures with $x \geq 1$, the reaction type changes from SHS to gradual. It seems that excess carbon particles act as a barrier that lowers the chance of contacts of WO_3 and Al particles which hampers their reaction leading to an incomplete synthesis process.
- For $\text{WO}_3\text{:}2\text{Al}\text{:}(1+x)\text{C}$ mixtures with $0 \leq x \leq 0.8$, the amount of carbon has a significant effect on the carbon loss and free carbon amounts as well as the type of tungsten carbide phase (i.e. WC or W_2C) in the system. By increasing the carbon content in the mixture, WC content in the product increases in expense of W_2C phase.
- Another parameter which promotes the conversion reaction of W_2C phase to WC is found as time of microwave heating process. By increase of heating time and in the presence of excess carbon, more portion of W_2C converts to WC phase.

In this research work, the highest amount of WC phase is obtained from $\text{WO}_3\text{:}2\text{Al}\text{:}1.8\text{C}$ mixture heated for 10 min.

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