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Evaluation of process behavior and crystallite specifications of mechano-chemically synthesized WC–Al_2O_3 nano-composites

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ABSTRACT

A new route for the synthesis of WC–Al_2O_3 composite free from unwanted W_2C phase through mechano-chemical treatment of WO_3–xAl–$y(4 - 1.5x)$C mixture has been investigated. It has been concluded that by substitution of 10 mol% of 2 mol Al ($x = 1.8$) with equivalent stoichiometric amount of C together with 20 mol% excess carbon addition ($y = 1.2$), i.e., using a WO_3:1.8Al:1.56C initial mixture, W_2C free WC–Al_2O_3 composite can be successfully obtained by about 6 h milling. Crystallite size and lattice strain of the WC–Al_2O_3 composite synthesized in the present study as well as those obtained by the previous successful routes have been reported. The results revealed that a powder whose synthesis route involves lower adiabatic temperature as well as longer milling time would have a smaller crystallite size and higher lattice strain. Furthermore, TEM observations showed that all synthesized powders contain the agglomerates which consist of nano-size particles.

1. Introduction

Superior properties of tungsten carbide (WC) including high hardness and fracture toughness as well as good thermal stability, enables the engineers to use this compound and/or its composites in a wide range of applications such as cutting tools, die materials and wear resistant parts [1–3]. At present, two main methods are industrially used for the production of tungsten carbide. The first method, being referred to as carburization process, is a high temperature reaction of elemental tungsten and carbon under a controlled atmosphere. The second method is the high temperature reaction of tungsten oxide and carbon under a controlled atmosphere, which is called the direct method [1,4]. The above processes are costly, since they are performed at high temperatures and long times. Furthermore, in such processes the product becomes macro-sized. In order to decrease the production expenditure and yield submicron or nano-size tungsten carbide, several new methods have been proposed [5–8]. One of these new methods is the mechano-chemical synthesis route.

Mechano-chemical synthesis involves the milling of reactants powders by help of the high energy mills. Intensive milling of the reactants increases the internal defects of crystallites which in turn increases the rate of chemical reactions; so that the process occurs at much lower temperatures. Mechano-chemical synthesis has attracted the attention of many researchers due to its low cost and simplicity as well as its ability to produce nano-size products [9–11].

The process of mechano-chemical synthesis of tungsten carbide and/or its composite powders which have been reported by various researchers can be categorized in the following classes:

(I) Milling of initial mixture consisting of W and C reactants. In this route formation of WC takes place gradually [11–14].
(II) Milling of tungsten ore or tungsten trioxide with carbon which results in a significant decrease of temperature of the subsequent thermal process [15–17].
(III) Milling of tungsten oxide with carbon together with a reducing agent, such as Mg [11,18,19], Al [11,20–22] or even Zn [23]. This route involves exothermic reduction reactions which in turn increase the rate of overall reaction.

Reaction mechanism leading to the formation of WC–Al_2O_3 composite powder during mechano-chemical treatment of WO_3–Al–C mixtures has been presented in our previous works [24–26]; where, it has been concluded that the synthesis process initiates with the aluminothermic reduction of WO_3 and tungsten carbide is produced through the reaction between the reduced tungsten and carbon. Also, it has been recognized that in the WO_3:2Al:C system,

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the heat released from aluminothermic reduction of WO_3 rises the temperature of the system to such levels that thermodynamic stability of unwanted W_2C phase increases. At the same time, simultaneous reduction of WO_3 by carbon, activated by severe heating resulted from the heat of aluminothermic reduction reaction, causes the carbon deficiency in the system with a consequence of the formation of W_2C phase.

To prevent the formation of undesirable W_2C phase, three following routes have been suggested in our previous papers based on thermodynamic evaluations together with experimental evidences:

Route 1: distinction between highly exothermic aluminothermic reduction reaction of WO_3 and carbide formation reaction, where, WC–Al_2O_3 composite powder free from unwanted W_2C phase has been successfully obtained after 8 h of milling [25].
Route 2: addition of reducing agent (Al) in some equal portions to the WO_3:C initial mixture, so that the vigorous exothermic reduction of WO_3 by Al proceeds in different stages with less heat release in each step, which in turn decreases the mixture maximum temperature and could eliminate W_2C formation. Experimental results revealed that WC–Al_2O_3 composite powder free from unwanted W_2C phase has been successfully obtained after 7 h of milling [25].
Route 3: Addition of excess carbon to the initial WO_3:2Al:C mixture to compensate the carbon deficiency. Experimental results showed that obtaining a WC–Al_2O_3 composite powder free from unwanted W_2C phase is possible by 6 h milling of WO_3:2Al:1.8C mixture [26].

Another possible route, reported in our previous paper [24] for the elimination of W_2C phase during the mechano-chemical treatment of WO_3:2Al:C mixture is the substitution of some portion of Al with C (reaction (1)) to lower the mixture maximum temperature.

$$WO_3 + xAl + (4 - 1.5x)C = WC + x/2Al_2O_3 + (3 - 1.5x)CO \quad (1)$$

Our previous investigations [24] revealed that with $x \leq 1.6$, released heat from aluminothermic reduction reaction is insufficient to activate the endothermic reduction reaction of WO_3 by C. But, it was observed that absence of carbothermic reduction reaction is accompanied with the consequence of incompletely reduced tungsten oxide (WO_2) phase. Hence, the amount of Al in WO_3:xAl:$(4 - 1.5x)$C mixture should be not less than 1.6 mol. Experimental results also showed that with $1.6 < x \leq 2$, all produced powders consist of W_2C phase.

On the basis of these findings, a new research program aimed at developing another new route for the fabrication of a W_2C free WC–Al_2O_3 composite has been planned based on mechano-chemical treatment of WO_3–1.8Al–y(1.3)C mixtures. In this system, a part of Al has been replaced by carbon and some extra amount of carbon (y folds) relative to its stoichiometric amount has been added to the system for the compensation of carbon deficiency. Experimental results of this part of our study (Route 4) will be presented and discussed in some details later. Another part of this study has been devoted to the evaluation of mechano-chemical synthesis conditions on the crystallite size and lattice strain of four nano-size WC–Al_2O_3 composite powders produced via above mentioned routes.

Table 1
Specifications of the instruments employed in the present research work.

Equipment/model/supplier/country	Application
Permeation Tube/GASTEC/Japan	Control of the CO/CO_2 evolution
CHN Corder analyzer/MT-6/Yanaco/Japan	Total carbon measurement
XRD/RINT-2200 PC (Cu-Kα radiation)/Rigaku/Japan	Phase identification
Thermo Labels/NICHIYU GIKEN KOGYO/Japan	T_{out} measurement
TEM/LEO-922 (200 kV)/Zeiss/Germany	Observation of the particles size and distribution

2. Procedure

Detailed information regarding the experimental procedure of previously studied routes has been reported elsewhere [25,26].

In the present research work, various WO_3–1.8Al–y(1.3)C mixtures (y = 1, 1.2 and 1.4) were milled for different times and the effect of carbon amount on the reaction mechanism as well as the product composition was investigated. This procedure will be referred to hereinafter as Route 4.

Starting materials were: WO_3 (ALDRICH 232785), C (Wako 070-01325) and Al (Wako 014-01785). Table 1 represents the specifications of the instruments employed in this research work. For each experiment, necessary amounts of the starting powders were mixed by hand and transferred to the milling pots. The details of milling operation are given in Table 2. Samples were milled for predetermined time durations with 15 min milling followed by 15 min holding. No holding time was considered for the samples milled for less than 15 min.

Probable evolution of CO/CO_2 gases during milling course was checked during the holding time. Analysis of total carbon in the products was performed and carbon loss percentage (wt%) was calculated by comparing the measured amount of total C with the amount of C in the initial mixture. Milling products were examined through X-ray diffraction analysis. Attached to the pot, Thermo Labels were used to observe the change of pot outside temperature (T_{out}). Mechanically-induced Self-propagating Reaction (MSR) mode reactions were distinguished from gradual ones by the methods employed by Takacs [27], Mingliang [28] and Mulas [29] where sharp changes in XRD patterns of milled sample together with rapid increase of T_{out} have been considered as signs of MSR reactions. Ignition time (t_{ig}) of the MSR reaction (i.e., incubation period before vigorous chemical reaction starts) was estimated by the observation and comparison of recorded values of T_{out} at the end of successive milling periods. Since observation of thermo labels during milling periods is not possible, an exact value for t_{ig} cannot be mentioned. It is only possible to state that t_{ig} lies between the beginning and termination time of a specific milling period during which rapid increase of T_{out} was observed.

Williamson–Hall method [30] was used for the calculation of crystallite size and lattice strain. For this purpose, XRD patterns were obtained by step scan mode (range of measurement: 20°–80°,

Table 2
Details of mechano-chemical treatment conditions employed in the present research work.

Pot volume	Atmosphere	Milling machine	PCA[a]	Number of balls	Pots and balls materials	BPR[b]	Milling speed	Milling temperature
45 cm^3	Air	Pulverisette-7 Fritsch	None	7 (15 mm diameter)	Zirconia	25	700 rpm	Ambient

[a] Process control agent.
[b] Ball to powder mass ratio.

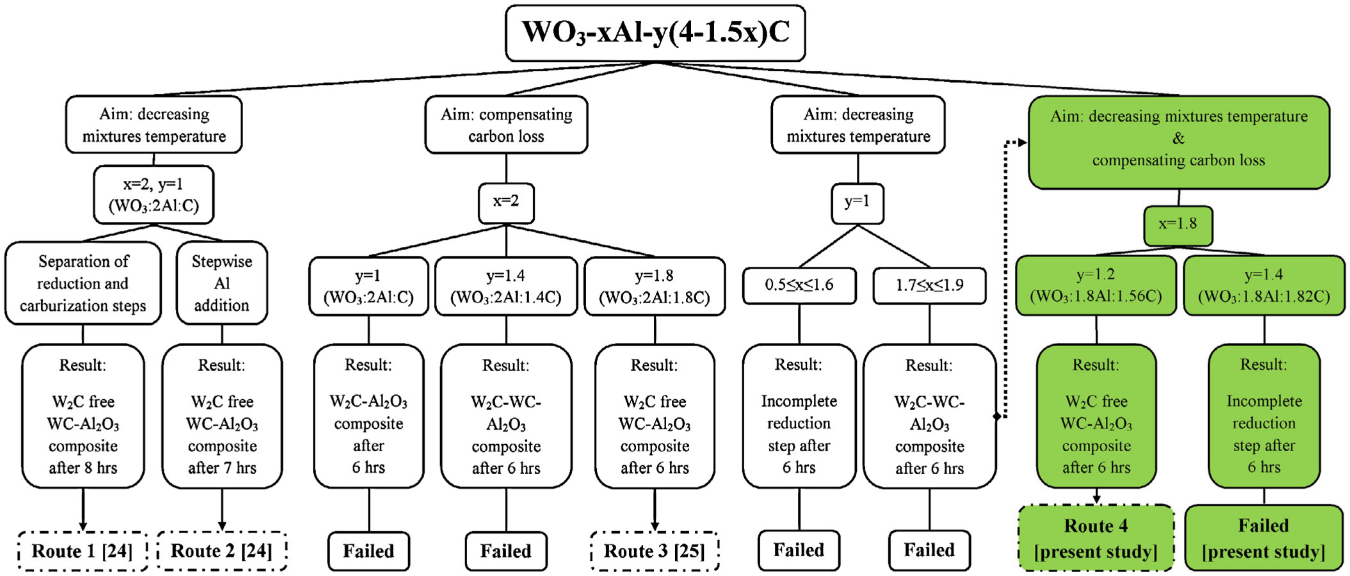

Fig. 1. Schematic presentation of different synthesis routes of WC–Al_2O_3 composites through mechano-chemical treatment of several WO_3–xAl–$y(4-1.5x)$C mixtures.

holding time at each step: 5 s, increment: 0.02°). The peak fitting was done by the "powder cell" freeware software [31]. A sample of analytical alumina was annealed (heated up to 1300 °C, held for 120 min and then cooled at a rate of 2 °C/min) and used to eliminate the instrumental broadening effect [32]. Obtained Caglioti's [33] parameters of annealed alumina are as follows: $U = 0.0011$, $V = 0.0000$, $W = 0.0146$.

Size and distribution of particles were observed by means of a transmission electron microscope (TEM). For this purpose, the powder was dispersed in ethanol (Wako 050-00446) and mounted on a copper grid.

3. Results and discussion

3.1. Synthesis process evaluation

A summary of some different routes which have been examined for the production of W_2C free WC–Al_2O_3 composite powder through mechano-chemical treatment of various WO_3–xAl–$y(4-1.5x)$C mixtures is presented in Fig. 1.

Detailed explanation has been reported in our previous publications [25,26]. With respect to the Route 4 (present study) since this route is being introduced for the first time, it will be presented and discussed in more details. Table 3 shows the type of temperature rise, gas generation state, range of t_{ig} and amount of carbon loss (wt%) of all examined samples of the present research work.

- No additional carbon ($y = 1$): XRD patterns of WO_3:1.8Al:1.3C mixtures after different milling times are presented in Fig. 2. As Fig. 2 shows, milling up to 5 min has not brought about any change in the sample phase composition. Decrease of peaks intensities and broadening of the peaks are related to the crystallite size refinement [34]. Milling continuation has caused a complete change in XRD pattern (sample, Fig. 2-c) which is a sign of the occurrence of chemical reactions. Rapid changes of XRD patterns together with sharp rise of T_{out} (see Table 3) reveal that the type of happened reaction is MSR. The expected

Table 3
Observations and experimental results of the present research work.

Mixture	Temperature rise	Evolved gas	t_{ig} range (min)	C loss (mass%)
WO_3–1.8Al–1.3C	Rapid	CO	5–10	~30
WO_3–1.8Al–1.56C	Rapid	CO	12–15	~30
WO_3–1.8Al–1.82C	Rapid	–	15–30	~0

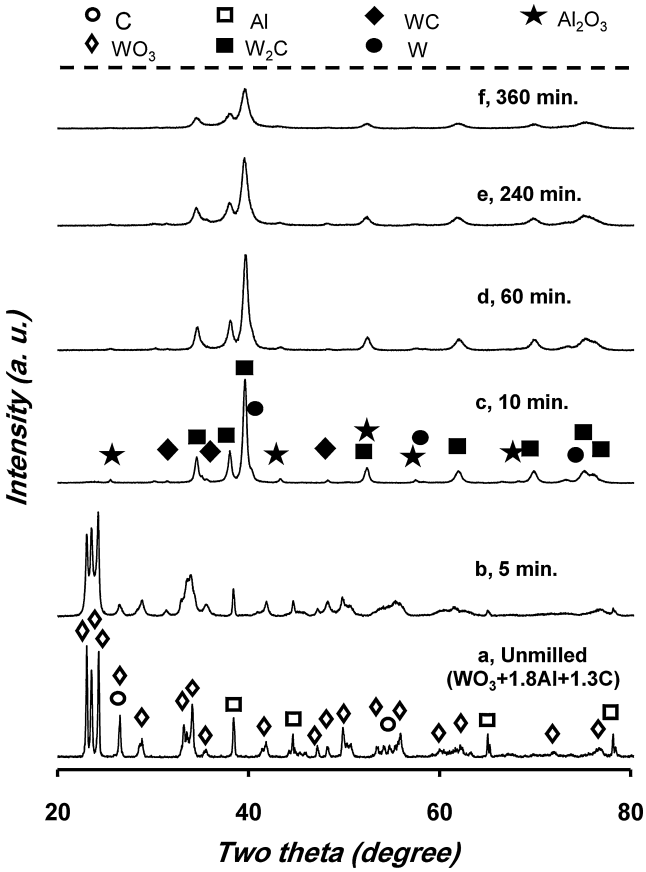

Fig. 2. XRD patterns of WO_3:1.8Al:1.3C ($y = 1$) mixture after different times of milling. Indicated milling time is a cumulative value.

reactions could be written as follows:

$$WO_3 + 1.8Al = 0.1WO_3 + 0.9Al_2O_3 + 0.9W + Q \quad (2)$$

$$0.1WO_3 + 0.3C = 0.1W + 0.3CO\,(g) \quad (3)$$

$$W + C = WC \quad (4)$$

Evolution of CO gas during milling (see Table 3) is an evidence of the occurrence of reaction (3). The presence of W_2C phase in the product (see Fig. 2-c) could be related to the carbon insufficiency in the mixture (reaction (5)) [12,35].

$$W + 0.5C = 0.5W_2C \quad (5)$$

It seems that at high temperatures obtained as a result of released heat of reaction (2), more portion of initial WO_3 is reduced by C instead of Al. Fig. 2 shows that only effect of further milling (beyond 10 min) is crystallite size refinement with no significant change in the final phases composition. With regard to the above discussion, W_2C phase is supposed to be eliminated if more amount of Al is replaced by C, which yields to less heat release. Experimental examination of this idea produced no satisfactory results [24] which may be attributed to the fact that synthesis process in WO_3:x-Al:$(4 - 1.5x)$C system initiates by the reaction of WO_3 and Al particles. Substitution of high amounts of Al by C decreases the chance of WO_3 and Al particles to collide. Then, it would be rational to imagine that the whole reaction becomes diversely affected by higher amounts of C.

Another possible solution to the W_2C formation is supposed to be the addition of excess amounts of C to the initial mixture.

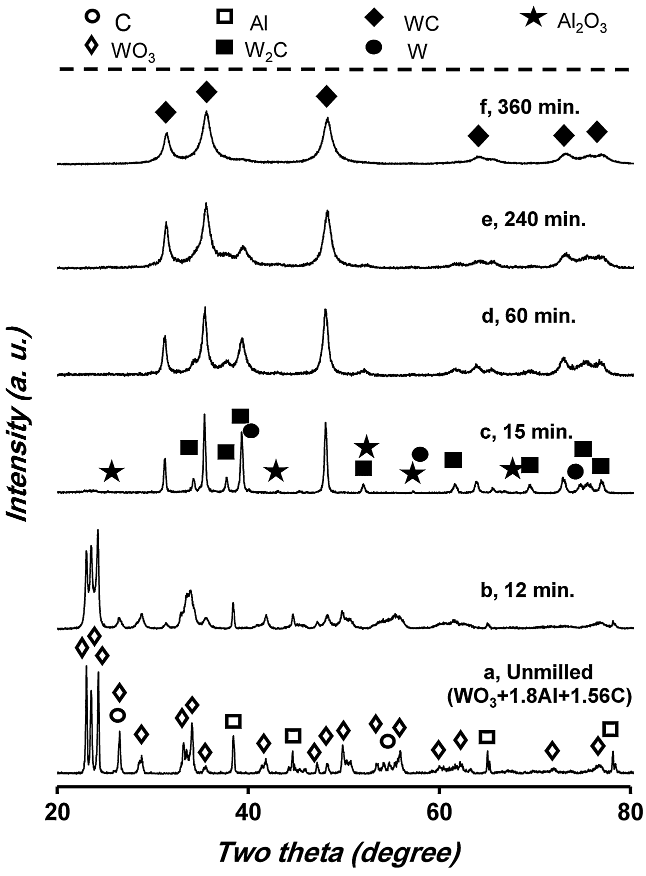

Fig. 3. XRD patterns of WO_3:1.8Al:1.56C ($y = 1.2$) mixture after different times of milling. Indicated milling time is a cumulative value.

- 20% additional carbon ($y = 1.2$): Fig. 3 shows the XRD patterns related to the WO_3:1.8Al:1.56C mixture, where whole carbon amount is 1.2 times of the stoichiometric ratio. Similar to WO_3:1.8Al:1.3C mixture, preliminary effect of milling is crystallite size refinement. After this stage, rapid change of XRD patterns (see Fig. 3-c) and sharp increase of T_{out} reveal that MSR mode reaction has happened in this case. Detection of CO evolution gas during milling (see Table 3) is a sign of the occurrence of carbothermic reduction of WO_3. Lower values of t_{ig} in WO_3:1.8Al:1.3C system compared to that of WO_3:1.8Al:1.56C (see Table 3) is probably related to the isolating function of carbon by its locating between WO_3 and Al particles and hampering the reaction of WO_3 with Al [36].

Fig. 3-c shows that an increase in the initial amount of C in the mixture has brought about a significant increase in WC formation. This could be related to two following reasons:

1. Higher C amounts would decrease the system maximum temperature due to its ability of the absorption of some of the heat released by aluminothermic reduction reaction [37] as well as its role of controlling the rate of aluminothermic reduction and consequently the rate of heat release [38]. Decreasing the mixture temperature, in turn, lowers the thermodynamic stability of W_2C and increases the stability of WC [7].
2. Reaction system will not be encountered with carbon insufficiency with higher carbon amounts in the initial mixture.

As Fig. 3 shows, increasing the milling time brings about an increase in the amount of WC phase in expense of W_2C phase, so that a W_2C free product is obtained after 6 h of milling. Gradual conversion of W_2C phase to WC can be expressed by reaction (6).

$$W_2C + C = 2WC \quad (6)$$

A comparison between excess amount of C which has been added to the initial mixtures for avoiding W_2C phase formation in WO_3:2Al:C [26] and WO_3:1.8Al:1.3C systems reveals that in the later system, required excess carbon decreases considerably from 0.8 to 0.2 of the stoichiometric ratio. This phenomenon is understandable with regard to the fact that adiabatic temperature (T_{ad}) of WO_3:1.8Al:1.3C system (3470 K [24]) is lower than that of WO_3:2Al:C (3910 K [24]). Hence, in the WO_3:1.8Al:1.3C mixture less portion of WO_3 is reduced by C and less carbon loss occurs in the system, consequently.

- 40% additional carbon ($y = 1.4$): the XRD patterns of WO_3:1.8Al:1.82C mixtures, whose carbon amount is 1.4 times of the stoichiometric ratio, are shown in Fig. 4. Similar to the previous cases (WO_3:1.8Al:1.3C and WO_3:1.8Al:1.56C mixtures) preliminary effect of milling is crystallite size refinement. After this initial stage, the MSR mode reaction (sharp change of XRD patterns and rapid increase of T_{out}) has occurred. Nevertheless, formation of CO/CO_2 gas due to the carbothermic reaction has not been observed (refer to Table 3). This phenomenon is supposed to be related to the fact that more C amounts causes severe decrease of the system maximum temperature which in turn lowers considerably the rate of carbothermic reduction of WO_3. Furthermore, absence of carbothermic reduction reaction together with Al deficiency ($x = 1.8$) leads to the incomplete reduction of tungsten oxide.

3.2. Estimation of crystallite size and lattice strain

It has been proved that the crystallite size as well as the lattice strain of any particular powder would affect its behavior during the

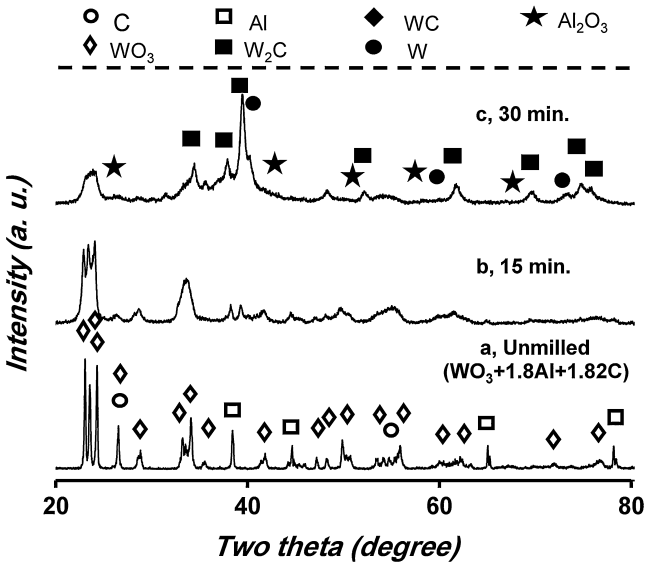

Fig. 4. XRD patterns of WO_3:1.8Al:1.82C ($y = 1.4$) mixture after different times of milling. Indicated milling time is a cumulative value.

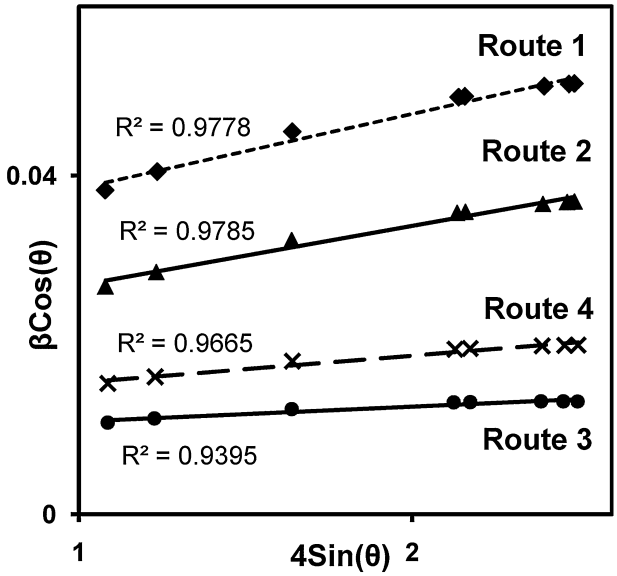

Fig. 6. Williamson–Hall plot for WC–Al_2O_3 composite powders relevant to Routes 1, 2, 3 and 4.

subsequent treatment and could bring about some unexpected consequences [39–42]. Hence, it is very useful to have an estimation of the crystallite size and lattice strain of the produced powders. Fig. 5 represents the XRD patterns of WC–Al_2O_3 samples produced through the Routes 1, 2, 3 and 4. As Fig. 5 shows, the intensity of alumina peaks in the XRD patterns is very low which means the crystallite size and lattice strain for this compound may not be determined with confidence. Since Al_2O_3 and WC are both brittle compounds, it may be assumed that values of crystallite size and lattice strain of Al_2O_3 are around those of WC phase. The Williamson–Hall plots of the samples obtained through four different routes are presented in Fig. 6. The line with higher values of intercept and slope belongs to a powder with smaller crystallite size and higher lattice strain [32]. Table 4 shows the values of crystallite size and lattice strain of different samples. This table shows that synthesis conditions have a great effect on these characteristics. The reason is explained as follows:

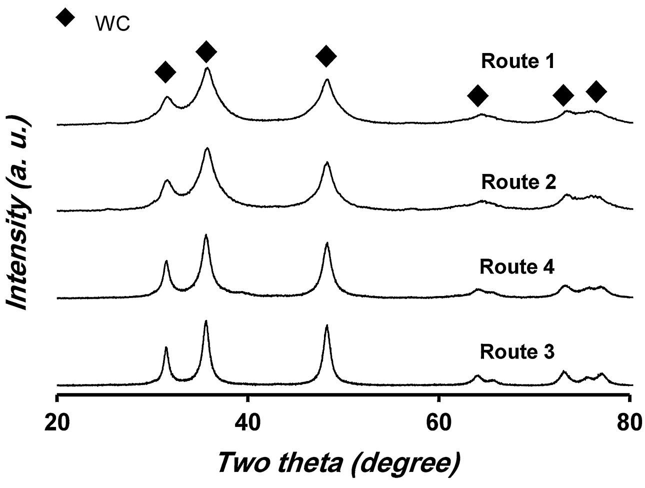

Fig. 5. XRD patterns of WC–Al_2O_3 composite powders produced under optimum conditions of Routes 1, 2, 3 and 4.

- It has been shown that in various materials synthesis methods, higher synthesis temperature results in a larger particle/crystallite size as well as lower lattice strain [43,44]. With regard to the amount of heat as a consequence of initial Al content of the mixture as well as the rate of heat generation as a function of the mode of Al addition, the order of system maximum temperature during the synthesis process is supposed to be: Route 3 > Route 4 > Route 2 > Route 1 which is in accordance to the findings listed in Table 4.
- It has been shown that milling time is a key parameter in mechano-chemical synthesis processes and increasing the milling time would yield a smaller particle/crystallite size as well as higher lattice strain [10]. This judgment provides further support for the findings presented in Table 4 for different routes of WC–Al_2O_3 synthesis.

Fig. 7 shows the BF-TEM images of four produced WC–Al_2O_3 composite powders, obtained via Routes 1, 2, 3 and 4, with two different magnifications. It could be seen that the synthesis conditions have an obvious effect on the size of agglomerates which have been increased by increase of system maximum temperature. This phenomenon could be explained by the fact that at higher temperatures, more initial particles would probably weld together and form larger agglomerates. Fig. 7 also shows that all agglomerates consist of nano-size particles. These observations are in good agreement with the results of Williamson–Hall calculations.

Table 4
Crystallite size and lattice strain of WC–Al_2O_3 composite powders produced via Routes 1, 2, 3 and 4.

Route	Crystallite size (nm)	Lattice strain (%)
3	16	0.2
4	12	0.3
2	7	0.7
1	5	0.9

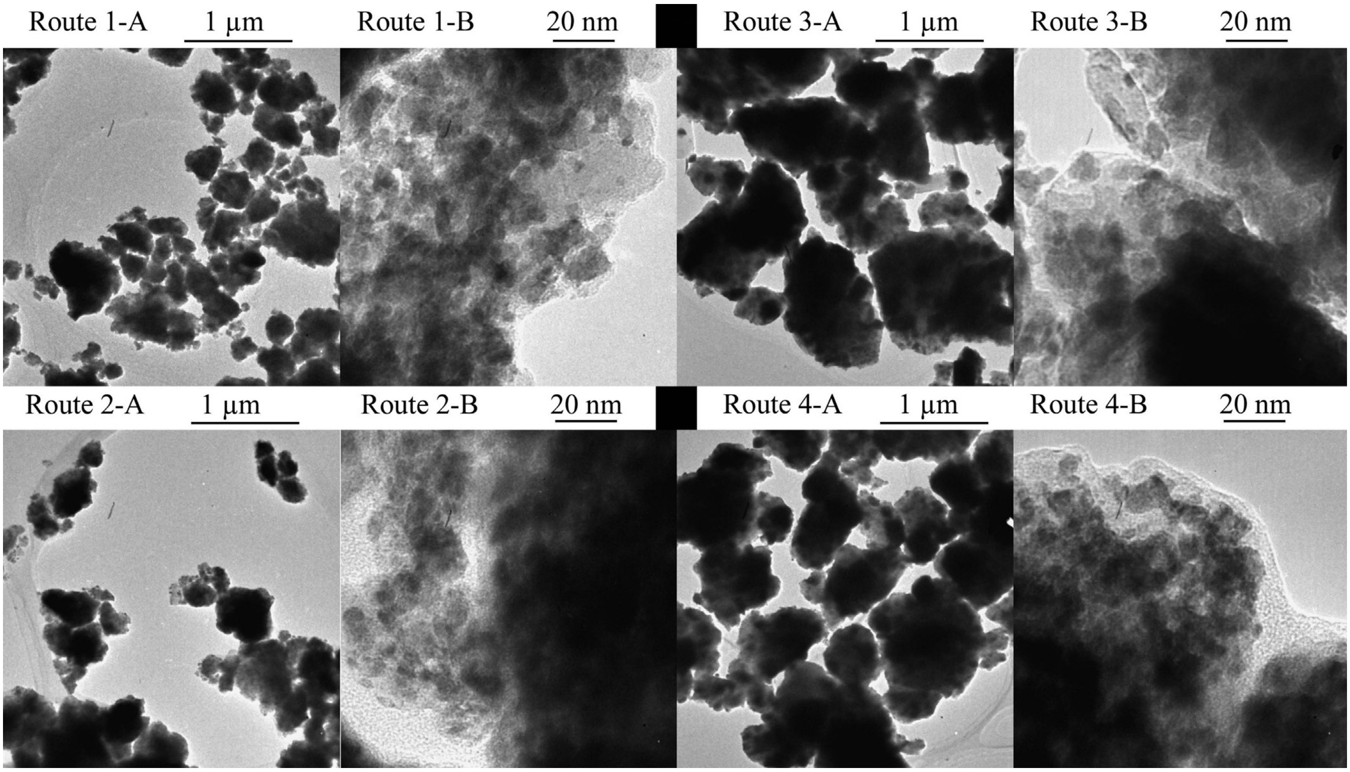

Fig. 7. BF-TEM images of WC–Al_2O_3 composite powders produced by Routes 1, 2, 3 and 4.

4. Conclusion

Attempts have been made in a series of research works to determine the initial composition and conduct the milling process in such a way that the intensity of heat generation and consequently the adiabatic temperature becomes under control so that the formation of unpleasant W_2C phase becomes prohibited.

Various WO_3–1.8Al–y(1.3)C initial mixtures have been milled for different milling times. Results of this part of study can be summarized as follows:

(1) The type of reaction in all studied mixtures (y = 1, 1.2 and 1.4) is MSR.
(2) For the mixtures consisting of 1.3 and 1.56 mol of C (y = 1 and 1.2) evolution of CO gas has been observed which is an evidence of partial carbothermic reduction.
(3) A W_2C free product can be obtained after 6 h milling of WO_3:1.8Al:1.56C (y = 1.2) mixture.
(4) For WO_3:1.8Al:1.82C (y = 1.4) mixture, no CO evolution has been observed which means that no carbothermic reduction reaction has happened.

Comparison of the crystallite size and lattice strain of the WC–Al_2O_3 composites synthesized in the present study as well as those obtained in the previous successful routes revealed that a powder whose synthesis route involves lower adiabatic temperature as well as longer milling time would have a smaller crystallite size and the higher lattice strain.

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