



Control of carbon loss during synthesis of WC powder through ball milling of WO_3 -C-2Al mixture

M. Sakaki^{a,b}, M.Sh. Bafghi^{a,*}, J. Vahdati Khaki^c, Q. Zhang^b, F. Saito^b

^a Department of Metallurgy and Materials Engineering, Iran University of Science and Technology (IUST), Narmak, Tehran 16846-13114, Iran

^b Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

^c Department of Materials and Metallurgical Engineering, Ferdowsi University of Mashhad, Mashhad 91775-1111, Iran

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ABSTRACT

WC- Al_2O_3 composite powder potentially could be synthesized through milling of WO_3 -C-2Al mixture. High temperature resulted from reduction of WO_3 by Al, activates the reduction reaction of WO_3 by C and brings about carbon deficiency in the system which consequently causes the formation of undesirable W_2C phase. Hence, addition of excess amounts of C becomes necessary. The aim of the present study has been to find out some appropriate routes for the fabrication of WC- Al_2O_3 composite powder from WO_3 -2Al-C mixtures in such a way that the formation of W_2C is prevented. Results of high energy milling showed that the mode of reaction in WO_3 -2Al-C mixture is MSR (mechanically induced self-propagating reaction). In this system, evolution of CO gas and high value of C loss were evidences for the need of excess C. For samples produced via suggested routes, no CO evolution was observed and the amounts of total carbon were constant. These observations showed that the proposed routes have been capable of producing WC phase without the presence of W_2C . Mechanism of the reactions in each route has been discussed.

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1. Introduction

Tungsten carbide (WC) and/or its composites have found a wide range of applications in the production of cutting and drilling tools as well as dies and wear resistant parts. This is related to the specific properties of this compound [1–3].

High temperature and prolonged time are needed for the production of WC through the current commercial method (direct reaction of elemental W and C under controlled atmosphere). This causes the product to become expensive [1,4–5]. Therefore, new processes should be employed in order to decrease the production cost.

Mechanical alloying (MA) process, used initially for the production of oxide dispersion strengthened (ODS) alloys, could be employed for the fabrication of some other materials that are difficult to produce through routine processes. MA process is simple, cheap and can be performed at ambient temperature [6].

Synthesis of nano-size WC- Al_2O_3 composite powder through milling of WO_3 -C-2Al mixture has been examined by El-

Eskandarany [7] and Pallone et al. [8]. This method could yield nano-size WC which has much better properties in comparison with the conventionally produced micro-size products [9–10]. The process starts by a highly exothermic reaction of WO_3 with Al, and WC is produced by the reaction of reduced W with C [7]. Mode of reaction is MSR [7,8] and the final carbide phase would be WC, W_2C or a mixture of these compounds [8]. Since the properties of W_2C are inferior to WC, presence of the former compound in the final product is undesirable [1,3].

Formation of W_2C could be explained by the fact that high temperatures, arising as a result of aluminothermic reaction, could activate some side reactions [8], including carbothermic reduction of WO_3 [11], and bring about carbon deficiency in the system. Carbon deficiency in turn results in W_2C formation [8,11]. Hence, additional carbon is needed to prevent W_2C formation [8].

In this research work, two different milling routes have been proposed for the fabrication of WC- Al_2O_3 composite powder. These routes have been designed in such a way that excess amount of carbon becomes unnecessary. The concept behind these two proposed routes has been the management of the heat of aluminothermic reaction. Thermodynamic calculations were made to get an insight about the probable reactions. Experimental tests were performed for the clarification of the reaction mechanism.

* Corresponding author. Tel.: +98 21 73912829; fax: +98 21 77240480.
E-mail address: msbafghi@iust.ac.ir (M.Sh. Bafghi).

2. Experimental

2.1. Explanation

Reaction (1) represents the simple form of the overall reaction which may happen during the milling of WO_3 -2Al-C mixture.



It is believed that this reaction is the sum of the reduction of WO_3 with 2Al, which is a very highly exothermic reaction, followed by the reaction of W with C, leading to WC formation [7].

In the present work, the heat of aluminothermic reaction was managed by performing the milling process through the following two innovative routes.

2.1.1. Route A (Separation of aluminothermic reduction and carbide formation reactions)

In this case, milling process is started with a mixture of WO_3 -2Al powder and continues up to the completion of the aluminothermic reaction (reaction (2)).



At this stage, the milling process is interrupted for 1 h for cooling the product. After cooling, 1 mol of C is added to the milled mixture and milling process is continued with the aim of carbide formation (reaction (3)).



2.1.2. Route B (Spreading the reaction heat over time by conducting the reaction stepwise)

In this case, the reductant (2 mol of Al) is divided into a number of equal parts and added to the WO_3 -C mixture at different steps of milling. Milling process is started with a mixture of WO_3 -0.5Al-C powder and after each 30 min of milling, another 0.5 mol of Al is added to the system and milling is continued. Formation of WC- Al_2O_3 composite powder is the evidence of the end point of the process. The expected reactions will be presented later.

2.2. Procedure

Specifications of the starting materials are given in Table 1. For each run of experiments, calculated amounts of reactants powders were mixed by hand and transferred to the milling pots. Milling experiments were performed in cylindrical zirconia pots (45 cm³ inner volume) by use of a planetary ball mill (Pulverisette-7, Fritsch, Germany). 7 zirconia balls (15 mm diameter) were used for milling and no Process Control Agent (PCA) was added. Milling operation was performed under air atmosphere at room temperature. Ball to powder mass ratio and milling speed were fixed at 25:1 and 700 rpm, respectively.

Samples were milled for up to 8 h with 15 min milling followed by 15 min holding. For the samples milled for less than 15 min, no holding time was considered. Evolution of CO and CO₂ gases, generated by probable reactions during the milling course, was checked during holding time by use of a Permeation Tube Method (GASTEC, Japan). Analysis of total carbon in the products was performed by use of Yanaco CHN Corder type MT-6 analyzer. 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 by an X-ray diffraction instrument (XRD, Rigaku, RINT-2200/PC System) with Cu-K α radiation. Temperature of the outside wall of each milling pot (T_{out}) was determined by use of Thermo Labels (NICHYU GIKEN KOGYO Co., Japan) attached to the pot. Sharp changes in XRD patterns of milled sample together with rapid increase of T_{out} were considered as signs of MSR mode reactions. Ignition time (t_{ig}) of MSR reaction 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 determined. 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} has been observed.

Table 1
Specifications of the starting materials.

Material	Supplier	Art no.
WO_3	ALDRICH (Germany)	232785
C	Wako (Japan)	070-01325
Al	Wako (Japan)	014-01785

3. Results and discussion

3.1. Thermodynamic aspects

Although thermodynamic calculations of non-equilibrium processes such as MA [6] have not been completely understood, using conventional thermodynamic calculations could give a general view about the possible reactions. In order to predict the possibility of the reactions, determine the type of reactions (exo/endermic) and calculate the temperature changes resulting from the reactions, values of ΔG° , ΔH° and T_{ad} for the concerning reactions were calculated. Adiabatic temperature (T_{ad}) is the maximum temperature which could be attained as a result of the reactions heat [12]. Required thermodynamics data were obtained from relevant references [13].

3.1.1. WO_3 -2Al-C system

The results of thermodynamic calculations for this system are shown in Table 2. Although there is a difference between ΔG° and ΔG , ΔG° could presumably be used to explain the behavior of the system. With regard to Table 2, the overall reaction (reaction (1)) has a big negative value of ΔG° . Therefore, it is anticipated that the reaction could easily occur.

Since reaction (1) is a highly exothermic ($\Delta H^\circ = -832$ kJ), the temperature of the bulk powder in the pot could be considerably increased by the reaction heat [14]. High value of calculated adiabatic temperature ($T_{\text{ad}} \sim 4000$ K) confirms this expectation.

Merzhanov has stated that if the value of T_{ad} for a reaction is higher than 1800 K, the reaction wave propagates by itself [15]. Therefore, type of reaction in the WO_3 -2Al-C mixture is MSR.

3.1.2. Route A

ΔG° value for the aluminothermic reduction of WO_3 has a large negative value (Table 2, reaction (2)) and theoretically could occur easily during the milling course. Very high adiabatic temperature (T_{ad}) indicates that the type of this reaction is MSR.

For reaction (3) (WC formation reaction) the possibility of the reaction to occur is low in comparison with reactions (1) and (2). This fact can be concluded by comparing the values of ΔG° for these reactions. Since reaction (3) is not highly exothermic, T_{ad} is lower than 1800 K and therefore the type of this reaction is gradual [14].

3.1.3. Route B

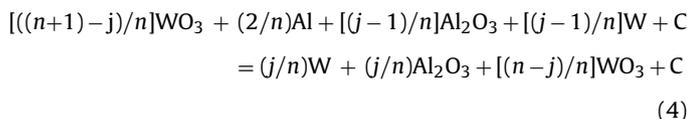
In Route B, the amount of aluminum necessary for the complete aluminothermic reduction is added step by step and in equal parts. If n is the total number of steps, then in each step $1/n$ mol of WO_3 reacts with $2/n$ mol of Al to give $1/n$ mol of W and $1/n$ mol of Al_2O_3 . After the termination of the reaction in a step with a sequential number of j , $(n-j)/n$ mol of WO_3 is left unreacted which will react with added aluminum in the next step. Experimental results (presented later) show that if aluminum is added stepwise (Route B), carbide formation reaction will not be activated and starts to happen only after the elapse of several hours of milling, while aluminothermic reduction reaction takes place very fast. Therefore, the free (unreacted) carbon content of the mixture remains unchanged during the aluminothermic reduction reaction period. Hence, gen-

Table 2

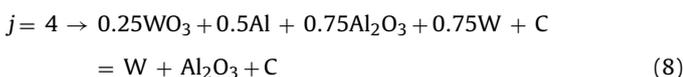
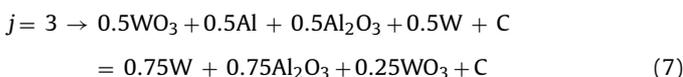
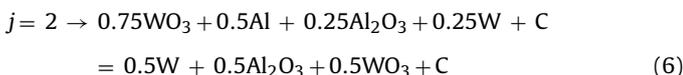
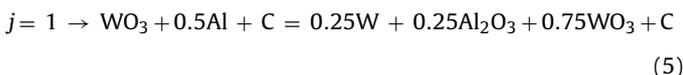
Results of thermodynamic calculations for probable reactions in WO_3 -2Al-C mixture as well as Route A.

System	Reaction number	ΔG° (kJ)	ΔH° (kJ)	T_{ad} (K)
WO_3 -2Al-C mixture	(1)	-856	-872	3910
Route A	(2)	-818	-832	3880
	(3)	-38	-40	580

eral form of the stepwise aluminothermic reduction reaction can be written as follows:



For example, if the process is performed in four steps ($n=4$), for $j=1, 2, 3$ and 4 we have:



Further milling leads to the formation of WC + Al₂O₃ composite powder according to the following reaction:



Since an equal portion of the aluminothermic reaction is performed in each individual step, standard free energy as well as reaction heat which is released in each step is the same. Nevertheless, as the amounts of reactants (WO₃ and Al) decrease and amounts of the products (W and Al₂O₃) increase step by step, T_{ad} of the systems is not the same in each step, due to the differences of the heat capacities.

With regard to thermodynamic calculations for different n and j values (Table 3) following points can be concluded:

- For any n and j value, ΔG° of the reaction has a big negative value, indicating the thermodynamic feasibility of the reaction.
- With $n \leq 3$, reduction reactions are highly exothermic which result in MSR mode reaction.
- The mode of reaction would be gradual for $n \geq 4$.

With the assumption that the reaction heat is low enough to prevent carbon deficiency if the reaction mode is gradual, it was decided to add the necessary Al amount in four steps.

Table 3

Results of thermodynamic calculations for stepwise aluminothermic reduction of WO₃ (n : total number of steps; j : sequential number of each step).

n	J	ΔG° (kJ)	ΔH° (kJ)	T_{ad} (K)
1	1	-818	-832	3680
2	1	-409	-416	2380
	2	-409	-416	2330
3	1	-272	-277	1940
	2	-272	-277	1930
	3	-272	-277	1920
4	1	-204	-208	1750
	2	-204	-208	1740
	3	-204	-208	1650
	4	-204	-208	1560

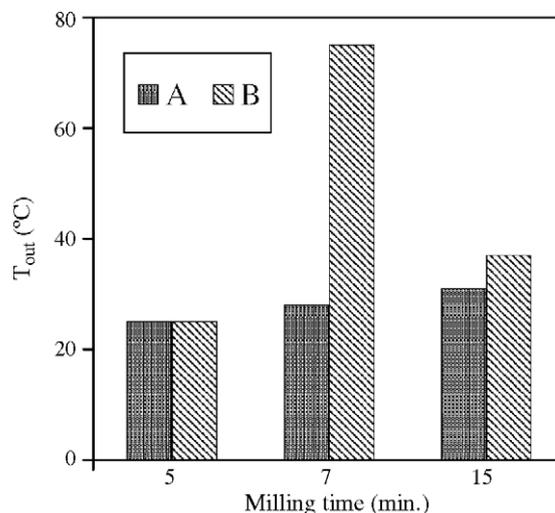


Fig. 1. Variation of temperature of the pot outside wall (T_{out}) during mechanochemical experiment. (A) Gradual (sample belongs to Route B) and (B) rapid (WO₃-2Al-C mixture) mode.

3.2. Experimental findings

Fig. 1 shows some examples of T_{out} variations. Gradual (A) and quick (B) temperature rises are representatives of gradual and MSR reactions, respectively.

For all studied samples, type of temperature rise, gas generation state, range of t_{ig} and carbon loss percentage (wt%) are specified and summarized in Table 4.

3.2.1. WO₃-2Al-C system

Fig. 2 shows the XRD patterns of WO₃-2Al-C mixtures milled for various periods of time. At the first minutes of milling course (Fig. 2a and b), no reaction occurs in the mixture and the only differences are decrease of peaks heights (intensities) as well as broadening of the peaks which could be related to the crystallite refinement and amorphisation phenomena.

Comprehensive change in XRD pattern of a sample milled for 7 min could be observed in Fig. 2c. Here, no signs of starting materials could be seen and new peaks indicating W-Al₂O₃-W₂C are evident. Rapid changes of XRD patterns together with fast increase of T_{out} (see Table 4) show that type of the reaction is MSR. Formation of W₂C phase instead of WC could be related to the following reasons:

- At high temperatures arising from MSR mode reaction, W₂C is thermodynamically more stable than WC [16].
- At high temperature resulted from MSR mode reaction, carbon deficiency occurs which leads to the formation of W₂C instead of WC [8,11]. Evolution of CO gas and high value of C loss (see Table 4) provide further proofs for this conclusion.

Addition of excess amounts of C is needed to compensate the carbon loss and avoid W₂C formation. Experimental results showed that the extent of carbon loss is affected by experimental conditions such as size of the pot, ball to powder ratio, pot and balls materials, etc. Therefore, a general value of excess carbon cannot be determined.

Fig. 2d and e shows that milling beyond 7 min has no appreciable effect on the product composition. Further milling just brings about a decrease in crystallite size and amorphisation phenomenon.

Table 4Type of temperature rise, gas generation state, range of t_{ig} and carbon loss percentage for all studied samples.

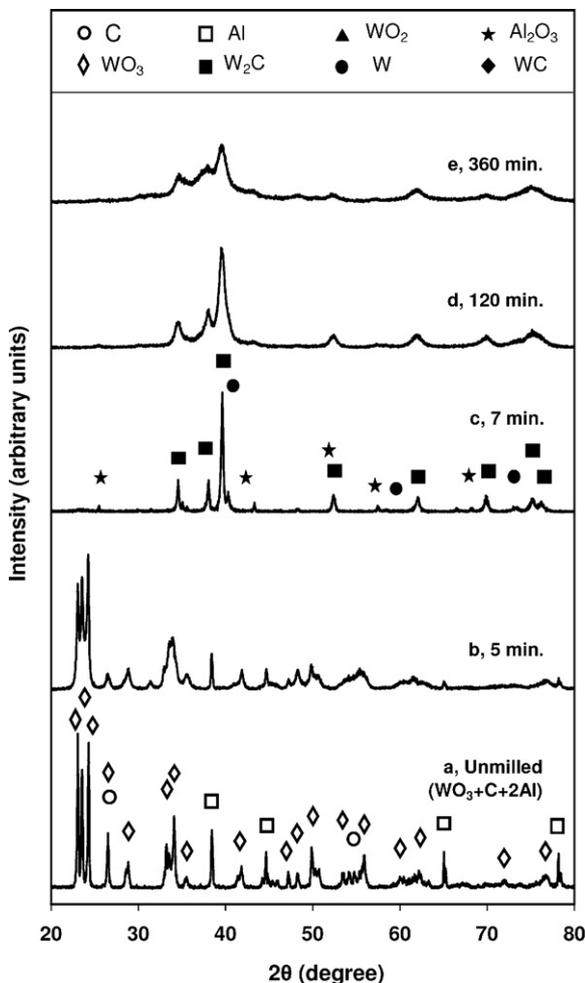
Sample name	Type of temperature rise	Generated gas (CO/CO ₂)	Range of t_{ig} (min)	Carbon loss (wt%)
WO ₃ -2Al-C mixture	Quick	CO	5–7	~50
<i>Route A</i>				
Reaction (2) ^a	Quick	–	2–5	–
Reaction (3) ^b	Gradual	–	–	~0
<i>Route B</i> (all steps)	Gradual	–	–	~0

^a Aluminothermic reduction of WO₃.^b Carbide formation reaction.**3.2.2. Route A**

Fig. 3(cases a, b and c) shows the XRD patterns of milled WO₃-2Al mixture after different milling times. This figure shows that after an initial period of crystal refinement and amorphisation (Fig. 3a and b), reaction between the reactants takes place. Presence of new peaks indicating W and Al₂O₃ (Fig. 3c) is an evidence for the occurrence of aluminothermic reduction of WO₃ (reaction (2)).

Rapid changes in XRD patterns together with fast increase of T_{out} (Table 4) show that the type of reaction (2) is MSR. In Fig. 3, no sign of starting materials could be seen after 5 min of milling.

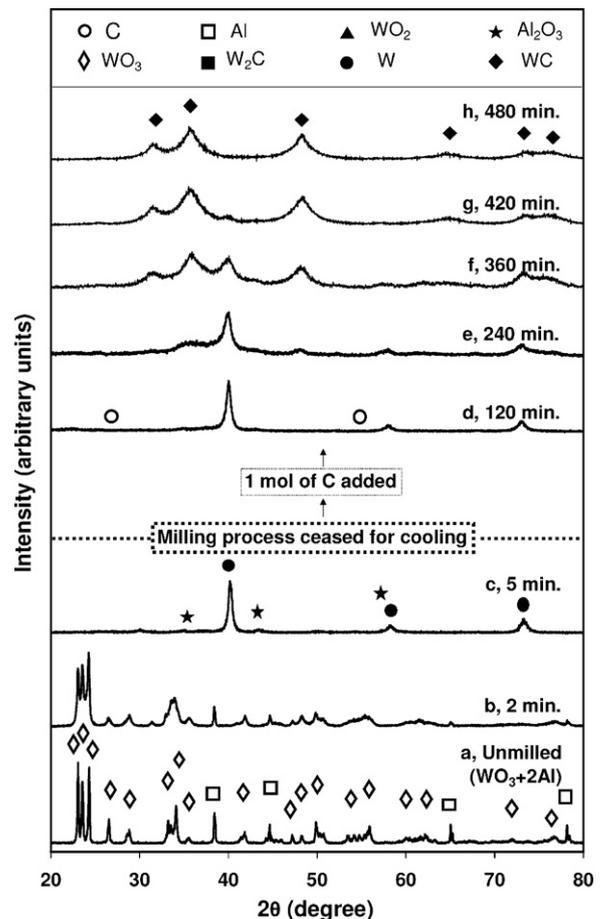
Comparing t_{ig} of WO₃-2Al-C and WO₃-2Al mixtures (Table 4) reveals that the reaction in the latter system is more intensive. This could be explained by the fact that the contact of WO₃ particles with Al ones is essential for the reaction to proceed. Since in WO₃-2Al-C system, carbon acts barrier, rate of aluminothermic reaction decreases with the presence of C.

**Fig. 2.** XRD patterns of WO₃-2Al-C mixtures after different times of milling. Indicated milling time is a cumulative value.

XRD patterns of a previously milled sample with 1 mol carbon addition, milled again for various periods of times are shown in Fig. 3(cases d–h). It is seen that after an initial period of crystallite refinement and amorphisation, carbide formation (reaction (3)) starts and new peaks indicating WC appear. Gradual changes of the resulted XRD patterns together with gradual increase of T_{out} (see Table 4) indicate that the type of this reaction is gradual.

Disappearance of tungsten peaks after 480 min of milling shows that for the completion of carbide formation reaction at ambient temperature a long time of milling is needed.

Since *Route A* has been started with WO₃-2Al mixture (without C) and aluminothermic reaction heat has been lost during the cooling period, no carbon deficiency is expected. No gas evolution and zero value of total carbon loss (see Table 4) are the proofs that this route is capable of producing WC with the elimination of W₂C phase without the need of excess C addition.

**Fig. 3.** XRD patterns of samples belong to *Route A* after different times of milling. Indicated milling time is a cumulative value.

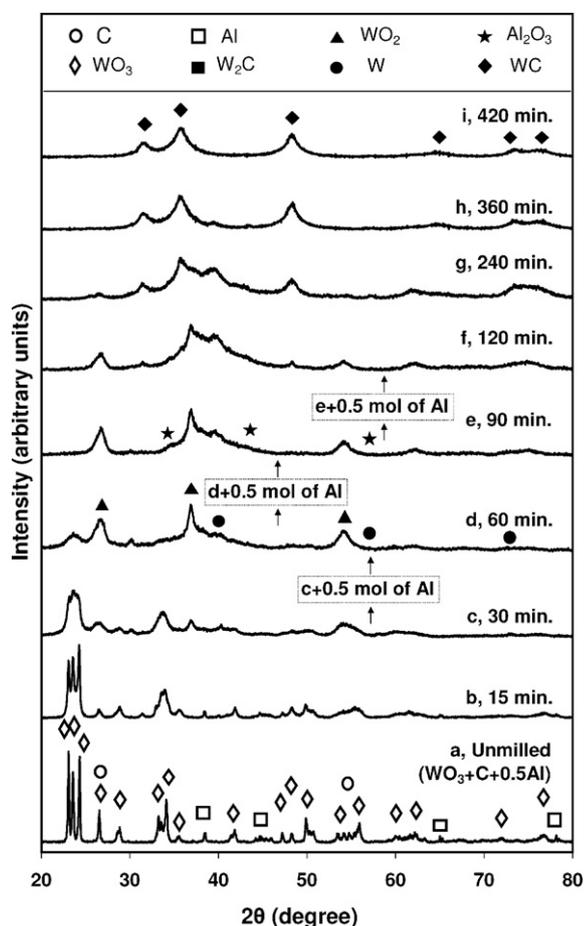


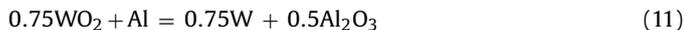
Fig. 4. XRD patterns of samples belong to *Route B* after different time of milling. Indicated milling time is a cumulative value.

3.2.3. *Route B*

XRD patterns of samples belong to *Route B* are shown in Fig. 4. Milling of $\text{WO}_3\text{-C-0.5Al}$ mixture (Fig. 4a–c) brings about crystal refinement and amorphisation, initially. Then, gradual changes occur in the XRD patterns and peaks of W and Al_2O_3 appear. Presence of WO_2 phase in the milled samples could be explained by the following reaction:



With regard to the results of XRD analysis (Fig. 4c–e) by increasing Al content together with further milling, WO_3 disappears gradually and is replaced by W and WO_2 . Fig. 4e, f and g indicates that addition of further amounts of Al together with continuation of milling bring about gradual reduction of WO_2 to W (reaction (11)) as well as WC formation (reaction (9)).



Above mentioned observations show that with gradual addition of Al to the system, WO_2 phase appears as an intermediate phase during the reduction of WO_3 to W.

Tungsten carbide phase becomes evident after about 120 min of milling and carbide formation is completed after milling for around 420 min. Comparison of the XRD patterns show that by use of *Route B*, WC peaks have appeared earlier than *Route A*. This could be related to higher values of T_{ad} and heat effects of the reduction reactions which promote the carbide formation reaction.

Gradual changes of XRD patterns and T_{Out} show that in *Route B* the type of all reactions occurred during milling, is gradual.

Absence of gas evolution indicates that there is no carbon loss and hence no carbon deficiency in the system. This fact is verified by zero value of carbon loss (see Table 4). No carbon deficiency is a consequence of the fact that by applying *Route B*, highly exothermic reaction of tungsten tri-oxide with aluminum ($\Delta H^\circ = -832 \text{ kJ}$) has been divided into four steps with relatively moderate heat release ($\Delta H^\circ = -208 \text{ kJ}$) in each step. Thus, the intensity of temperature rise during milling course has been decreased and carbon deficiency due to the endothermic reaction of tungsten tri-oxide with carbon [11] has been prevented.

Similar to *Route A*, long time of milling is needed for WC formation through *Route B*.

4. Conclusion

Although tungsten carbide can be synthesized by applying mechanochemical processing of the $\text{WO}_3\text{-C-2Al}$ mixture, the product contains undesirable W_2C compound along with WC. Formation of W_2C is a result of high temperatures arising from highly exothermic reduction reaction of WO_3 with Al. In this research work, attempts have been made to manage the heat effect of the aluminothermic reaction, so that the formation of W_2C phase is prevented. A summary of findings of this work is presented as follows:

- (1) In $\text{WO}_3\text{-2Al-C}$ system high temperatures, arising from MSR mode reactions, activate some side reactions and consequently bring about some carbon deficiency. This fact is confirmed by the evolution of CO gas and high amount of carbon loss. Carbon deficiency causes W_2C formation.
- (2) If aluminothermic reduction and carbide formation reactions are performed separately (*Route A*) a product free from W_2C phase can be obtained. This route consists of a MSR mode reduction reaction of WO_3 by Al followed by gradual carbide formation reaction. Since during MSR mode reaction, there is no C in the mixture, the heat is wasted and carbon loss would not occur.
- (3) Gradual addition of necessary aluminum in a number of portions (*Route B*) could also prevent excessive temperature rise and prevent the carbothermic reaction and the formation of W_2C compound. In this route, the type of all reactions is gradual and carbon loss could not occur, due to the decrease of the intensity of reactions heat release.
- (4) A good agreement exists between thermodynamic calculations and experimental results.

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