



Effect of the aluminum content on the behavior of mechanochemical reactions in the WO_3 –C–Al system

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

In order to produce tungsten carbide from its oxide through mechanochemical process, a mixture of tungsten oxide, carbon and aluminum powders was subjected to high energy milling. Excess carbon addition was made in expense of aluminum, so that carbon acts not only as a carbide former agent but also as a reductant. Aluminum and carbon contents of the mixture were altered according to the following reaction: $WO_3 + (4 - 1.5x)C + xAl = WC + (x/2)Al_2O_3 + (3 - 1.5x)CO(g)$. The value of x varied from 0.5 to 1.9 and the effect of Al content on the mechanism of tungsten carbide formation was investigated. Thermodynamic calculations revealed that the amount of Al in the mixture plays a key role. Experimental results showed that at lower Al content in the WO_3 –Al–C mixture ($x=0.5$ – 1.2), reactions proceed through a gradual mode. By increasing Al content ($x=1.3$ – 1.6), type of reactions changed to mechanically induced self-propagating reaction (MSR) with no carbothermic reduction reaction of WO_3 . Further increase of Al content ($x=1.7$ – 1.9) resulted in MSR mode reactions consisting of both aluminothermic and carbothermic reactions. Optimum value of x which yields maximum amount of WC was found to be around 1.7. Discussion has been made to elucidate the phase formation types in accordance with the above three reaction modes.

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1. Introduction

Tungsten carbide (WC) has unique properties such as high melting point, high hardness, high fracture toughness, very high compressive strength, high corrosion resistance and good thermal stability. Such excellent characteristics make this compound a reliable material for a wide range of applications such as fabrication of cutting and drilling tools as well as dies and wear resistant parts. Moreover, it has been reported that tungsten carbide can be used as a catalyst [1–3].

Conventional method of WC production is high temperature solid-state reaction between W and C under controlled atmosphere. Necessity of prior reduction of WO_3 to W together with high energy consumption for WC synthesis, because of long time heating at high temperatures [1,4,5], make the product expensive. Additionally, it has been proved that properties of WC would improve if the size of its particles and/or grains falls into nano-range [6,7]. Current methods of reducing the size of WC particles and/or grains are the control of synthesis and manufacturing conditions and/or

using grain growth inhibitors. These methods have some inherent limitations [3].

New methods such as spray conversion process (SCP), co-precipitation and mechanical alloying (MA) have been introduced for WC production [3,8,9]. MA process, used initially for the production of oxide dispersion strengthened (ODS) alloys, could be employed for the fabrication of some other materials that their production by routine metallurgical processes is quite difficult. MA process is simple, cheap and can be performed at ambient temperature [10].

Synthesis of WC powder through milling of WO_3 –C–2Al mixture has been examined by El-Eskandarany [11] and Pallone et al. [12]. They have shown that the reaction proceeds through a MSR mode process [11,12] and final carbide product would be WC or a mixture of WC and W_2C , depending on the molar ratio of W to C [12]. This process is believed to be capable of yielding nano-size tungsten carbide particles admixed with alumina. Aluminum is used here as a reductant for reducing WO_3 . Afterwards, reduced W reacts with carbon to form tungsten carbide [11,12].

Aluminothermic reduction of WO_3 is a highly exothermic reaction. Therefore, it is logical to assume that the evolved heat could activate the reduction of WO_3 by carbon, which is inherently a highly endothermic reaction. It means that when the WO_3 –C–2Al

* Corresponding author. Tel.: +98 21 73912829; fax: +98 21 77240480.

E-mail address: msbafghi@iust.ac.ir (M.Sh. Bafghi).

Table 1
Specifications of the starting materials.

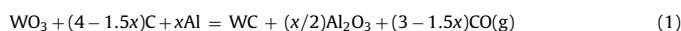
Chemical formula	Purity	Supplier	Art no.
WO ₃	99+%	Aldrich (Germany)	232785
C	99+%	Wako pure chemicals (Japan)	070-01325
Al	99.5+%	Wako pure chemicals (Japan)	014-01785

mixture is subjected to milling, WO₃ may be reduced by both Al and C, simultaneously. Therefore, addition of 2 mol of Al may not be necessary.

The main purpose of the current research work was to provide information about the effect of Al amount in WO₃–C–Al mixture on the carbide formation phenomena and mechanism of reactions during ball milling operation at ambient temperature. Here, carbon is supposed to be used not only as a carbide former agent but also as a reductant. The amount of aluminum in the WO₃–C–Al mixture was insufficient for the reduction of whole WO₃ and only a portion of tungsten oxide was reduced by Al. Thermodynamic calculations were performed to get an insight about the probable reactions.

2. Experimental procedure

Table 1 represents the specifications of starting materials, used in this work. Combination of carbothermic and aluminothermic reduction of WO₃ to W followed by solid-state reaction of W and C to form WC could be shown as reaction (1).



In the above reaction, x represents aluminum amount (mole) in the WO₃–Al–C mixture. Amounts of Al and C in the mixture were changed gradually so that the value of x varied from 0.5 to 1.9 (with 0.1 mol increment). Raw materials were mixed by hand and transformed to the milling pots. Milling experiments were performed in cylindrical zirconia pots (45 cm³ inner vol.) by use of a planetary ball mill (Pulverisette-7, Fritsch, Germany). Seven zirconia balls (15 mm diameter) were used for milling and no process control agent (PCA) was added to the mixture. Milling operation was performed under air atmosphere and 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 2 h with 15 min milling followed by 15 min holding. For the samples milled less than 15 min, no holding time were considered. Evolution of CO and CO₂ gases, generated by probable carbothermic reaction during the milling course, were checked during holding time by use of a Permeation Tube Method (GASTEC, Japan).

Milling products were examined by an X-ray diffraction instrument (XRD, Rigaku, RINT-2200/PC System) with a Cu K α radiation. Temperature of the outside wall of each milling pot (T_{out}) was measured by using Thermo Labels (NICHIIYU 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 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.

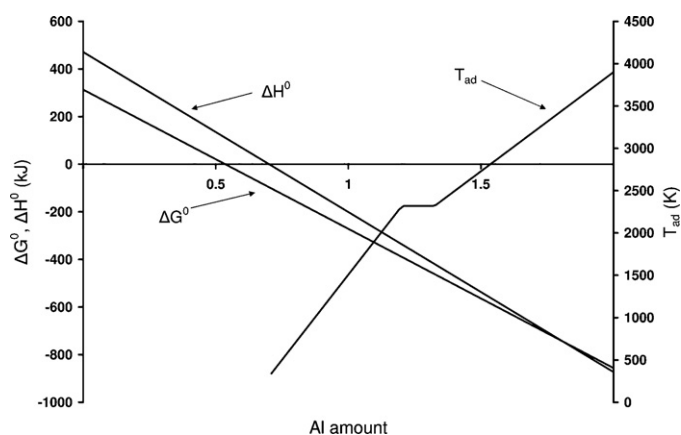


Fig. 1. ΔG° - x , ΔH° - x and T_{ad} - x curves for reaction (1). x represents aluminum amount (mol).

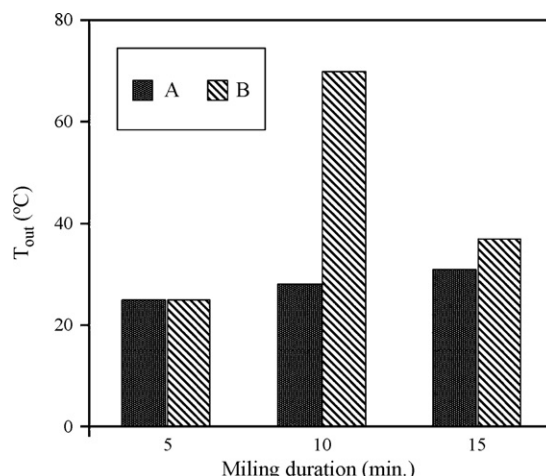


Fig. 2. Variation of temperature of the pot outside wall (T_{out}) during mechanochemical experiment. (A) Gradual (Al = 1 mol) and (B) rapid (Al = 1.8 mol) mode.

3. Results and discussion

3.1. Thermodynamic aspects

Although thermodynamic calculations of non-equilibrium processes such as MA [10] are not completely understood, using conventional thermodynamic calculations could give a general view about the reactions.

Fig. 1 shows ΔG° - x , ΔH° - x and T_{ad} - x curves for reaction (1). Adiabatic temperature (T_{ad}) is the maximum temperature which could be attained as a result of reaction heat [13]. The curves in Fig. 1 have been plotted for $0 \leq x \leq 2$. In thermodynamic calculations, it has been assumed that the milling pots were sealed and isolated. Furthermore, direct reaction of W and C to form WC was assumed to be the only possible carbide formation reaction. Calculations showed that considering other probable reactions, leading to the formation of different carbide phases (e.g. W₂C), does not affect the computation results so much. Required thermodynamic data were obtained from relevant references [14].

ΔG° versus x : Although there is a difference between ΔG° and ΔG , it is believed that ΔG° values could be used to explain the behavior of a system. According to ΔG° - x plot in Fig. 1, for a mixture containing 1 mol of WO₃ and 4 mol of C (without Al), ΔG° has a big positive value (+313 kJ). Therefore, it is anticipated that the reaction could not occur from the thermodynamic view point. According to Fig. 1, as Al content of the mixture increases, ΔG° value declines. ΔG° becomes zero at $x = 0.54$ and finds negative values thereafter, which is thermodynamically favorable. Standard free energy (ΔG°) for a mixture containing 1 mol of WO₃, 2 mol of Al and 1 mol of C has a big negative value (−856 kJ), which shows high possibility and appetite for the reaction.

ΔH° versus x : Although it has been proved that temperature could be increased by ball to ball and ball to wall contacts during milling, it is presumed that these phenomena by themselves,

Table 2

Type of temperature rise, gas generation state and range of t_{ig} for samples with different amounts of Al.

Group	Al amount (x)	Type of temperature rise	Generated gas (CO/CO ₂)	Range of t_{ig} (min)
A	0.5–1.2	Gradual	–	–
B	1.3	Quick	–	30–45
	1.4–1.6	Quick	–	15–30
C	1.7	Quick	CO	15–30
	1.8–1.9	Quick	CO	<15

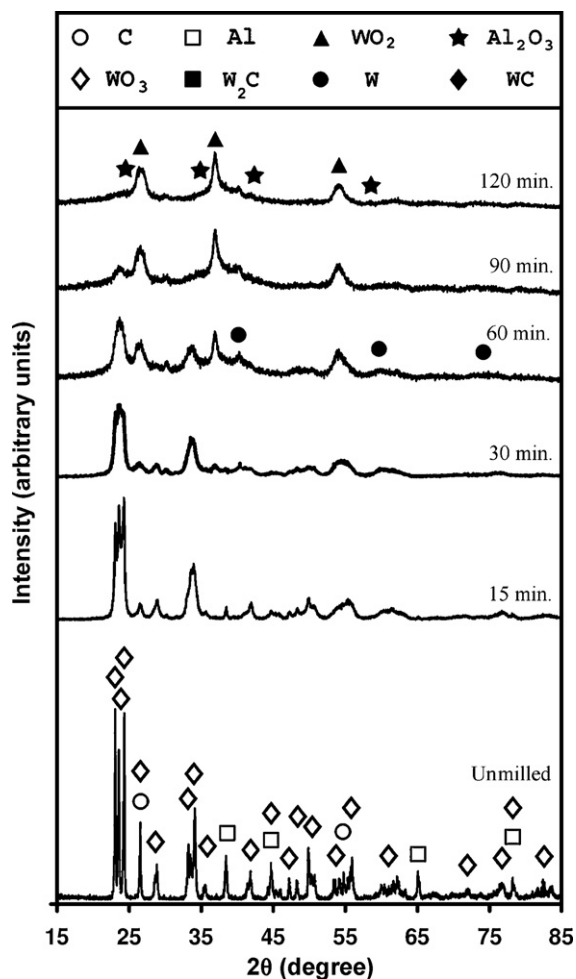


Fig. 3. XRD patterns of typical samples containing 1 mol of Al ($1\text{Al} + 2.5\text{C} + 1\text{WO}_3$) after several milling times.

do not affect the temperature of the bulk mass so much. Therefore, MA process proceeds at ambient temperature. Nevertheless, if a highly endo/exothermic reaction happens in the mixture, bulk temperature of the whole mixture would change [15]. Fig. 1 shows that for a sample without Al ($x=0$), reaction (1) is endothermic ($\Delta H^\circ = +471$ kJ). By increasing the amount of Al, the reaction tends to change gradually from an endothermic to an exothermic one ($x > 0.71$). For a sample containing 2 mol of Al ($x=2$) the reaction is highly exothermic ($\Delta H^\circ = -872$ kJ) thus, the heat of the reaction could change the temperature of the bulk mixture.

T_{ad} versus x : As Fig. 1 shows, for sample in which Al amount is less than 0.71 mol, the reaction is endothermic ($\Delta H^\circ > 0$). Fig. 1 shows that T_{ad} is 340 K at $x=0.71$ and gradually increases up to 3900 K at $x=2$. Increasing T_{ad} by increase of x is related to the increase of the heat generated by the reaction. Flat portion in curve $T_{\text{ad}}-x$ of Fig. 1 is related to the melting of Al_2O_3 . Regarding curve $T_{\text{ad}}-x$, for the mixture in which Al content is higher than 1.06 mol, T_{ad} exceeds 1800 K. Thus, according to Merzhanov's rule [16], mode of the reaction would be MSR thereafter [15,16].

3.2. Experimental findings

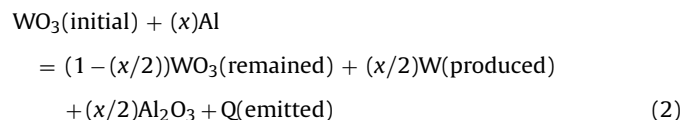
Fig. 2 shows some examples of T_{out} variations. Gradual (A) and quick (B) temperature rise are representatives of gradual and MSR reactions, respectively. Type of temperature rise, gas generation state and range of t_{ig} for all samples of this study are specified and summarized in Table 2.

XRD patterns of samples containing different amounts of Al ($x=1, 1.5$ and 1.8) milled for various periods of time are shown in Figs. 3–5. Moreover, final phases detected after 2 h of milling of samples containing different amounts of Al are compared in Fig. 6.

For better discussion and understanding, the samples are categorized into three groups, as follows.

(A) $0.5 \leq x \leq 1.2$

Fig. 3 shows XRD patterns of some samples of this group. At the first stage of the milling, no changes in the phases are observed. Visible differences are decrease of peaks intensities as well as broadening of the peaks which could be related to the decrease of the crystallites sizes and amorphisation phenomena. After 30 min of milling, heights of Al and WO_3 peaks decrease and new peaks indicating W, appear. This shows that aluminothermic reduction of WO_3 , according to following reaction, has been started.



By further milling, peaks of WO_3 and Al disappear and peaks of Al_2O_3 , W and WO_2 appear, gradually. Gradual changes in XRD

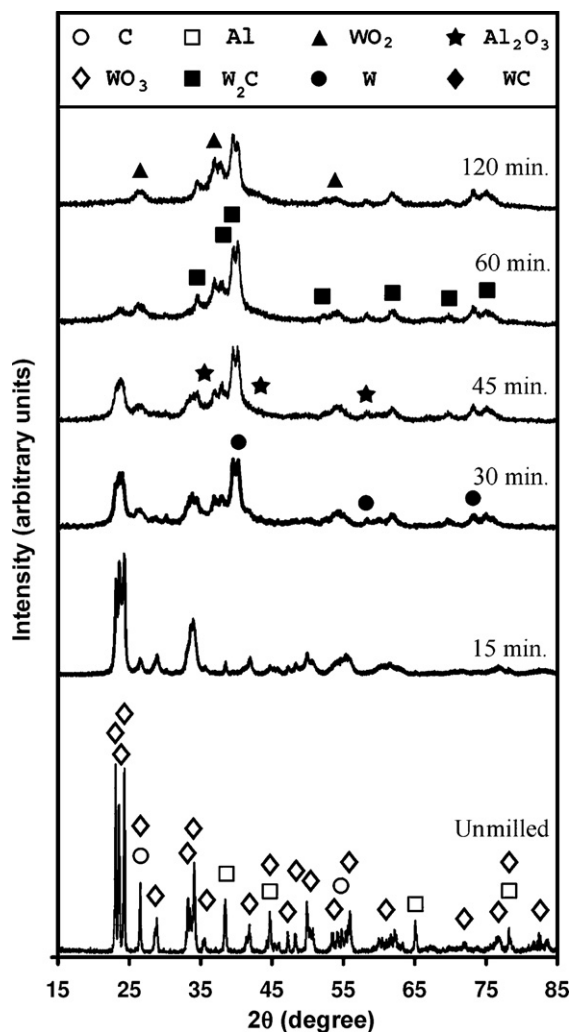


Fig. 4. XRD patterns of typical samples containing 1.5 mol of Al ($1.5\text{Al} + 1.75\text{C} + 1\text{WO}_3$) after several milling times.

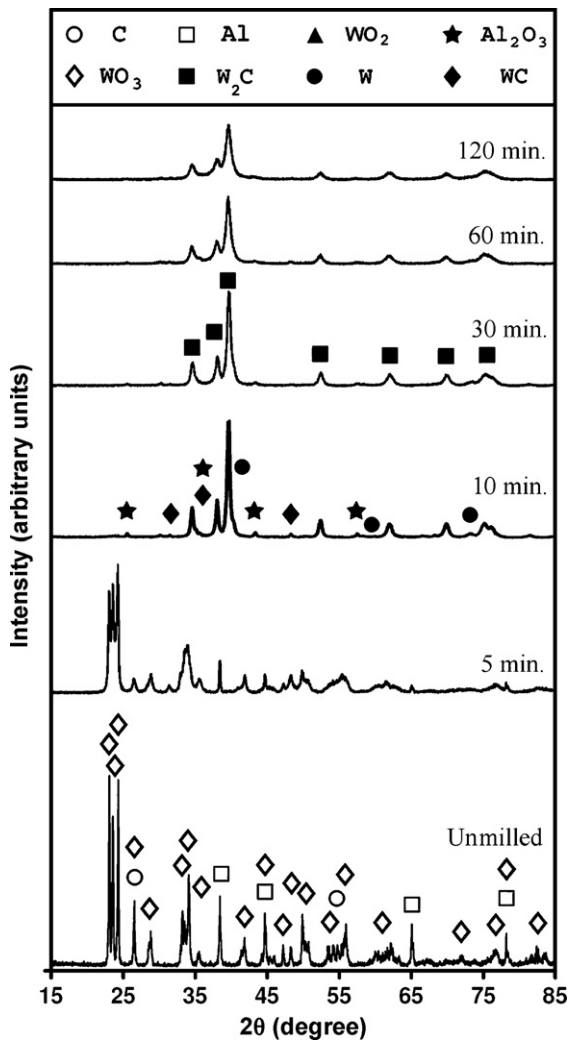
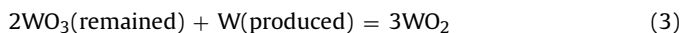


Fig. 5. XRD patterns of typical samples containing 1.8 mol of Al (1.8Al + 1.3C + 1WO₃) after several milling times.

patterns of milled samples and the values of T_{out} (Fig. 3 and Table 2) indicate that the type of reactions is gradual.

Absence of CO/CO₂ gas formation (see Table 2) is an indication that carbothermic reduction of WO₃ cannot proceed. This could be explained by this fact that since in this group of samples Al content is low, generated heat by reaction (2) is not high enough to provide necessary energy for the highly endothermic reduction reaction of WO₃ with C. Because of this, a part of the initial WO₃ in the mixture remains unreacted (see reaction (2) and Fig. 3). Presence of WO₂ phase in the milled samples could be explained by the reaction of remained WO₃ and reduced W, according to reaction (3).



With regard to reactions (2) and (3) final milled powder would be a mixture of WO₃, WO₂, W and Al₂O₃, depending on the x values (see Figs. 3 and 6). As XRD patterns show, formation of tungsten carbide phase is not observed in this group of samples. This may be due to the long milling time needed for the formation of this compound through the reaction between W and C at ambient temperature [17].

(B) $1.3 \leq x \leq 1.6$

XRD patterns of some samples of this group are presented in Fig. 4. Same as group A, milling up to 15 min decreased the peak intensities and broadened the peaks which are related to the crys-

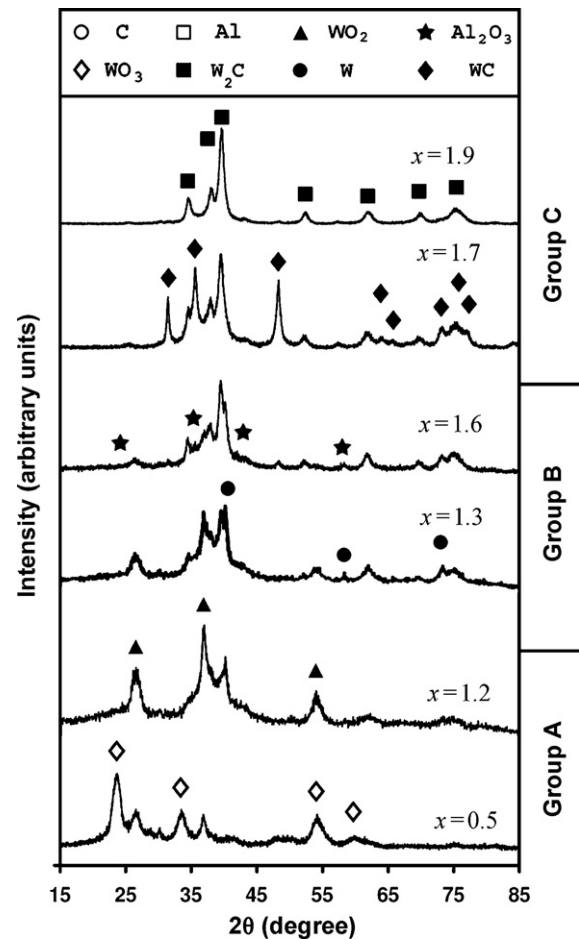
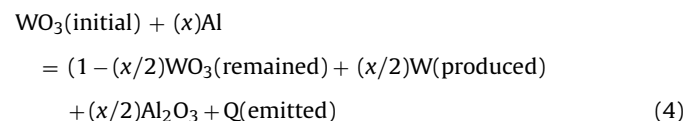
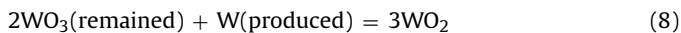


Fig. 6. XRD patterns of typical samples containing different amounts of Al after 2 h of milling.

tal refinement and amorphisation phenomena. Sudden changes in XRD pattern of milled powder after 30 min indicate that the reaction mode is MSR. Rapid rise of T_{out} and presence of W₂C phase (which is stable at high temperatures [18]) could be taken as evidences of high temperatures caused by the heat of reactions. In this group, increased temperature has encouraged the carbide formation reactions (see Figs. 4 and 6).

In group B, it was expected that the high temperature resulting from MSR mode reaction would activate the carbothermic reaction. Nevertheless, formation of CO/CO₂ gas due to carbothermic reaction was not observed (refer to Table 2). This phenomenon could be related to the fact that carbothermic reduction of WO₃ is kinetically very slow and needs high temperatures (~1200 °C) as well as long (several hours) processing time [1,4,5]. Hence in this case, although the temperature is high, time has been too short and generated heat has been mainly lost through the containers (pots) walls. Therefore, similar to group A, some parts of the initial WO₃ in the mixture remain unreacted. A portion of the remained WO₃ could react gradually with W to produce WO₂. Formation of WO₂ is evident in XRD pattern of a sample milled for 120 min (see Fig. 4). Depending on the initial composition, final milled powder could be a mixture of W₂C, WC, W, Al₂O₃ and WO₂ (Figs. 4 and 6). Presumed reactions could be written as follows:





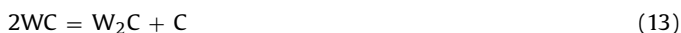
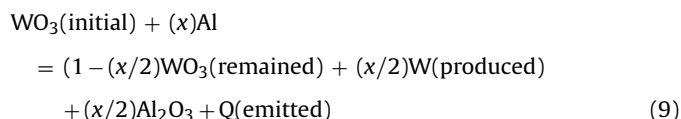
In this group of samples, MSR type reaction has been accelerated by increasing Al content of the mixture (see Table 2). This is because of the fact that by increasing Al content, number of Al particles per unit volume of the mixture increases. This leads to the increase of the chance of Al particles to contact with WO_3 particles and therefore, the aluminothermic reaction would start sooner and proceed easier.

(C) $1.7 \leq x \leq 1.9$

XRD patterns of some samples of this group are shown in Fig. 5. This figure shows that after an initial decrease of the crystallites sizes, sudden changes in XRD patterns of the milled powder happen and peaks of W_2C , WC, Al_2O_3 and W phases appear. Similar to group B, sudden changes of XRD patterns and rapid rise of T_{out} (see Table 2) indicate that the type of reaction is MSR.

According to the XRD pattern of a sample milled for 10 min, no remains of WO_3 are observed (see Fig. 5). Furthermore, evolution of CO gas (see Table 2) is an indication of the occurrence of the carbothermic reduction reaction. It seems that increasing Al content, which increases T_{ad} (Fig. 1), has encouraged the carbothermic reaction.

It is evident from Fig. 5 that further milling beyond 10 min has no appreciable effects on the final phases. Visible differences are broadening of the peaks and decrease of the peaks heights, which are related to the decrease of the crystallites sizes and/or amorphisation. Depending on the initial composition, the final milled powder could be a mixture of W, W_2C , WC and Al_2O_3 (Figs. 5 and 6). Presumed reactions could be written as follows:



In this group of samples the maximum amount of WC was yielded in the mixture containing 1.7 mol of Al, while W_2C was still present. Presence of W_2C in the product (see Figs. 5 and 6) could be explained by the following reasons:

- At high temperatures resulted from MSR mode reactions, W_2C is thermodynamically more stable than WC [18].
- Occurrence of carbothermic reaction, which is activated by the heat of aluminothermic reaction, consumes carbon and causes carbon deficiency in the system.

Increasing W_2C phase in the product, as a result of increasing Al content (see Fig. 6), could be explained as follows:

- By increase of Al, T_{ad} increases (see Fig. 1). Therefore, W_2C becomes thermodynamically a more stable phase compared to WC.
- Increased T_{ad} , as a result of more Al consumption, encourages the carbothermic reaction and therefore brings about more carbon deficiency.

Same as group B, increasing Al content accelerates the MSR mode reactions.

Summary of the discussion, regarding reaction mechanism, is shown schematically in Fig. 7.

4. Conclusion

Both thermodynamic calculations and experimental tests were conducted to investigate the effect of Al amount, within a range of 0.5–1.9 mol, on the reactions resulting from ball milling of WO_3 -C-Al mixture at ambient temperature. Experiments were designed and conducted in such a way that carbon acts not only as a carbide former agent but also as a reductant. Following are the summary of the findings in this work:

- 1) As to the reduction reaction of WO_3 by Al and C followed by solid-state reaction of C and reduced W to form WC, thermodynamic calculations show that by increasing Al amount in the mixture, ΔC° of the overall reaction decreases, higher heat (ΔH°) is generated and higher adiabatic temperature (T_{ad}) is attained. This suggests that increasing Al amount is thermodynamically favorable.
- 2) Depending on the amounts of Al in the WO_3 -Al-C mixtures, reactions can be categorized into three following types resulting different final phases:
 - With Al content in the range of 0.5–1.2 mol, gradual reaction.
 - With Al content in the range of 1.3–1.6 mol, MSR mode reaction without carbothermic reduction (no CO/ CO_2 gas evolution),
 - With Al content in the range of 1.7–1.9 mol, MSR mode reaction together with carbothermic reduction (evolution of CO gas).

Optimum amount of Al, which yields maximum amount of WC, was found to be around 1.7 mol per 1 mol of WO_3 .

References

- [1] P. Schwarzkopf, R. Kieffer, Cemented Carbides, Macmillan, New York, 1960.
- [2] F.V. Lenel, Powder Metallurgy: Principles and Applications, MPIF, Princeton, NJ, 1980.
- [3] E. Lassner, W.D. Schubert, Tungsten (Properties, Chemistry, Technology of the Element, Alloys and Chemical Compound), Kluwer Academic/Plenum Publishers, New York, 1999.
- [4] D.S. Venables, M.E. Brown, Thermochim. Acta 282/283 (1996) 251–264.
- [5] D.S. Venables, M.E. Brown, Thermochim. Acta 282/283 (1996) 265–276.
- [6] W. Liu, X. Song, J. Zhang, F. Yin, G. Zhang, J. Alloys Compd. 458 (1–2) (2008) 366–371.
- [7] X.L. Shi, G.Q. Shao, X.L. Duan, R.Zh. Yuan, H.H. Lin, Mater. Sci. Eng. A 392 (2005) 335–339.

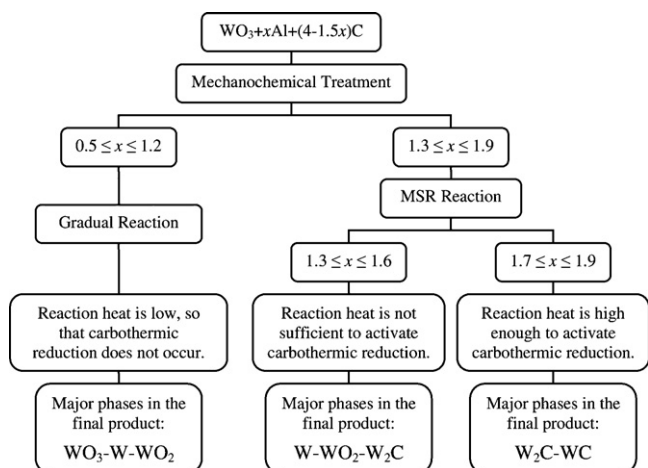


Fig. 7. Three categories of the reactions mechanisms, depending on the x values.

- [8] G.S. Upadhyaya, *Cemented Tungsten Carbides: Production, Properties, and Testing*, NOYES Publications, WestWood, NJ, 1998.
- [9] N.J. Welham, *Mater. Sci. Eng. A* 248 (1–2) (1998) 230–237.
- [10] C. Suryanarayana, *Prog. Mater. Sci.* 46 (2001) 1–184.
- [11] Sh.M. El-Eskandarany, *J. Alloys Compd.* 391 (2005) 228–235.
- [12] E.M.J.A. Pallone, D.R. Martin, R. Tomasi, W.J. Botta Filho, *Mater. Sci. Eng. A* 464 (2007) 47–51.
- [13] Z.A. Munir, *Ceram. Bull.* 67 (2) (1988) 342–349.
- [14] Reaction-Web, Fact-Web Programs, <http://www.crct.polymtl.ca/factweb.php>.
- [15] L. Takacs, *Prog. Mater. Sci.* 47 (2002) 355–414.
- [16] C.R. Bowen, B. Derby, *Br. Ceram. Trans.* 96 (1) (1997) 25–31.
- [17] M.A. Xueming, J.I. Gang, *J. Alloys Compd.* 245 (1996) L30–L32.
- [18] J. Zhang, J.H. Lee, C.W. Won, S.S. Cho, B.S. Chun, *J. Mater. Sci.* 34 (1999) 5211–5214.