

Conversion of W_2C to WC phase during mechano-chemical synthesis of nano-size WC– Al_2O_3 powder using WO_3 –2Al–(1 + x)C mixtures

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ABSTRACT

Due to the weak properties of W_2C phase, its formation during the process of WC synthesis should be prevented. The aim of the present study has been the mechano-chemical synthesis of a WC– Al_2O_3 composite powder free from undesirable W_2C phase through the addition of excess carbon to the WO_3 –2Al–C initial mixture. Based on the thermodynamic calculations and results of the supplementary experiments in W–yC and W_2C –C systems, the possibility of the conversion of W_2C to WC phase through the addition of excess carbon has been investigated. It has been shown that production of a WC– Al_2O_3 composite powder by 360 min mechano-chemical treatment of an initial mixture of WO_3 –2Al–1.8C is possible. TEM observations and Williamson–Hall calculation revealed that the obtained WC– Al_2O_3 powder contains macro-size agglomerates in which each agglomerate consists of nano-size phases.

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1. Introduction

Due to the strong W–C chemical bond, tungsten carbide (WC) and/or its composites can be used in a wide range of applications where the properties such as high hardness, high fracture toughness and good thermal stability are needed [1,2]. These specifications of WC would be improved when the size of its particles or grains falls into the nano range [3].

Ordinary method of WC production is the controlled solid-state reaction between W and C. This process requires a very long time of heating at high temperatures [1]. Such conditions bring about two disadvantages:

- The produced WC becomes expensive.
- The size of particles or grains becomes large (macro-sized).

In order to decrease the fabrication cost and particle or grain size of WC, researchers have proposed the use of different types of new materials such as tungsten salts [4] and tungsten oxide [1] as well as new production routes such as microwave synthesis [5] and Mechanical Alloying (MA) [6]. Compared to other synthesis processes, mechanical alloying is a simple and cheap one. During MA process, energy transfers from moving balls to the powder and conducts various phenomena (e.g. materials refinement, extension of the solid solubility

limits, inducement of the chemical reactions and etc.) at room temperature [7,8].

Nano-size WC and/or its composite powders have been synthesized via three different mechano-chemical routes, by use of different raw materials. These routes are I) long time milling of commercial (macro-size) WC powder [9], II) milling of elemental W with C [9,10] and III) milling of tungsten trioxide [11–15] and even tungsten ores [16,17] (e.g. scheelite) with C in the presence of a reducing agent (mostly Al and Mg).

Among the synthesis routes mentioned above, the latter one is seemingly the most promising case; because it has the lower production cost. This is related to the lower price of tungsten trioxide or tungsten ores in comparison with elemental W. The product (e.g. WC– Al_2O_3 and WC–MgO composite powders) could be consolidated for use in several industrial applications such as wear and heat resistant parts as well as cutting and machining tools [12,18–22]. Nevertheless, Al_2O_3 or MgO can be separated through leaching by adequate leachants under appropriate conditions [11].

Mechano-chemical reactions in the WO_3 –C–R (R: reducing agent) mixtures have been examined by El-Eskandaray and Zakeri as well as authors of the present work. It has been shown that the reactions start with the highly exothermic reduction reaction of WO_3 . El-Eskandaray [11,12] has reported that the reduced tungsten would react subsequently with carbon to produce WC. Zakeri [13] reported the formation of W_2C phase as a consequence of powder in-homogeneity. Formation of W_2C phase has also been observed in our previous research work [14,15]. In our opinion, the presence of W_2C in the product is related to the high thermodynamic stability of W_2C phase at high temperatures resulted from the heat of

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aluminothermic reduction reaction as well as the occurrence of carbon deficiency phenomenon in the system due to occurrence of simultaneous reduction reaction of WO_3 by carbon, which becomes activated at high temperatures. Since the properties of W_2C phase are inferior to WC [1], presence of this phase in the product is undesirable.

On the basis of our above justification, synthesis of WC compound, free from W_2C , is logically expected via one of the following routes:

- Decreasing the mixture maximum temperature which could increase the thermodynamic stability of WC phase and also could cease the carbothermic reduction reaction of WO_3 . This route has been presented in our previous published work [15] where decreasing the mixture maximum temperature was achieved by 1) separation of aluminothermic reduction and carbide formation reactions and 2) spreading the reaction heat over the time by conducting the reduction reaction stepwise.
- Using extra amounts of carbon in the initial mixture. The role of excess C would be the compensation of the carbon loss as well as decreasing the mixture maximum temperature due to the absorption of heat released from aluminothermic reduction reaction.

In the present research work, the applicability of route B for mechano-chemical synthesis of nano-size WC– Al_2O_3 powder from WO_3 –2Al–(1+x)C mixtures has been examined. For this purpose, various WO_3 –2Al–(1+x)C mixtures have been milled. Supplementary tests on the W–yC and W_2C –C mixtures were also performed in order to clarify the occurred reactions in the WO_3 –2Al–(1+x)C mixtures. Finally, the size and distribution of the product have been examined by a TEM instrument and Williamson–Hall [23] method.

2. Experimental procedure

Specifications of the starting materials used in this work, are given in Table 1. For each run of experiments, required amounts of the reactant powders were mixed by hand and transferred 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 840 min with 15 min milling followed by 15 min holding. For the samples milled for less than 15 min, no holding times were considered.

Probable evolution of CO and CO₂ gases during milling course was checked during holding time by use of Permeation Tube (GASTEC, Japan) method. 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 X-ray diffraction instrument (XRD, Rigaku, RINT-2200/PC System) with Cu–K α radiation. Attached to the pot Thermo Labels (NICHYU GIKEN KOGYO Co, Japan) were used to observe the changes of pots outside temperature (T_{out}). MSR (Mechanically-induced Self-propagating Reaction) mode reactions [24]

Table 1
Starting material specifications.

Material	Supplier	Art no.
Tungsten trioxide	ALDRICH (Germany)	232785
Carbon	Wako (Japan)	070-01325
Aluminum	Wako (Japan)	014-01785
Tungsten	Wako (Japan)	202-03442
Alumina	Wako (Japan)	012-01965

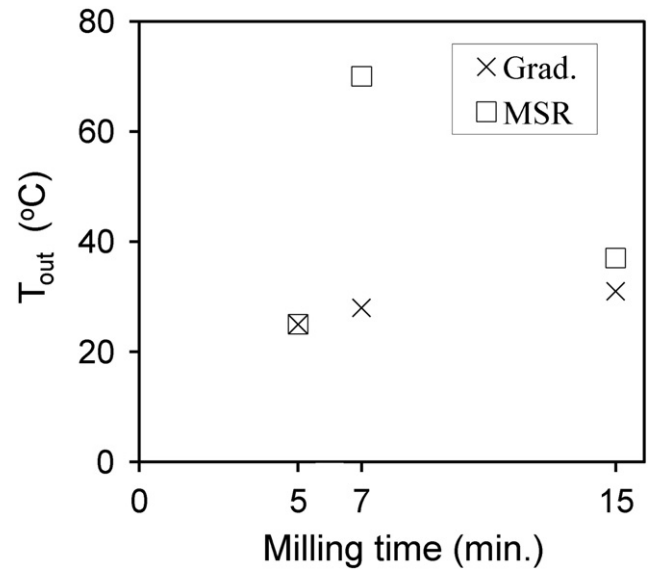


Fig. 1. Variation of the temperature of pots outside wall (T_{out}) during mechano-chemical experiment. x: Gradual (W–C mixture) and □: Rapid (WO_3 –2Al–C mixture) mode.

were distinguished from gradual ones by the methods employed by Takacs [25], Mingliang [26] and Mulas [27] 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 [24]) 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.

Size and distribution of particles were observed by means of a Zeiss 200 kV transmission electron microscope (LEO-922). For this purpose, the powder was dispersed in ethanol (Wako 050-00446) and mounted on a copper grid.

Williamson–Hall method was used for the calculation of crystallite size and lattice strain [23]. For this purpose, XRD patterns were obtained by step scan mode (range of measurement: 20°–80°, holding time at each step: 5 s, increment: 0.02°). The peak fitting was done by the “powder cell” freeware software [28]. 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 [29] effect. The obtained Caglioti’s [30] parameters of annealed alumina are as follows: $U = 0.0011$, $V = 0.0000$, $W = 0.0146$.

3. Results and discussion

Fig. 1 shows some examples of T_{out} variation during the Gradual (A) and MSR (B) mode reactions. For all samples, type of temperature

Table 2
Observations and experimental results of all studied samples.

Mixture	Temperature rise	Evolved gas	t_{ig} range (min)	C loss (mass %)
WO_3 –2Al–C	Rapid	CO	5–7	~50
WO_3 –2Al–1.4C	Rapid	CO	7–10	~40
WO_3 –2Al–1.8C	Rapid	CO	10–12	~30
W–0.25C	Gradual	–	–	0
W–0.5C	Gradual	–	–	0
W–0.75C	Gradual	–	–	0
W–C	Gradual	–	–	0
W_2C –C	Gradual	–	–	0

rise, gas generation state, range of t_{ig} and amount of carbon loss (wt.%) are specified and summarized in Table 2.

XRD patterns of WO_3 -2Al-C, WO_3 -2Al-1.4C and WO_3 -2Al-1.8C mixtures after different milling times are presented in Figs. 2, 3 and 4, respectively. As the figures show, the first effects of milling are decreasing the peak heights (intensities) as well as broadening the peaks (compare Figs. 2-a, 3-a and 4-a with Figs. 2-b, 3-b and 4-b, respectively). These phenomena are attributed to the crystallite refinement and amorphization [31].

After this stage, the chemical reactions occurred in the mixtures and new peaks have appeared (see Figs. 2-c, 3-c and 4-c). Rapid changes of XRD patterns together with fast increase of T_{out} (Table 2) reveal that the mode of reactions occurring in the WO_3 -2Al-(1+x)C (x=0, 0.4 and 0.8) mixtures is MSR. Table 2 shows that the MSR mode of reaction is postponed by increasing the amounts of carbon in the mixtures. This phenomenon could be related to the isolating function of carbon particles, i.e., locating of C species between WO_3 and Al particles and hampering the WO_3 -Al reaction. Similar phenomenon has been observed during mechano-chemical synthesis of Al_2O_3 -NbC powder where addition of Al_2O_3 powder to system retards the reaction [32]. Evolution of CO gas (see Table 2) shows that in all three mixtures, the released heat of the aluminothermic reaction has activated the carbothermic reduction reaction (reaction 1).



Figs. 2-c, 3-c and 4-c show that the type of main carbide phases in the products is related to the initial amount of carbon in the mixture and by increasing the carbon amounts, WC amounts increase. The reasons could be mentioned as follows:

1- Higher C amounts in the mixture, would decrease the chance of Al and WO_3 particles to collide each other. This, in turn, would

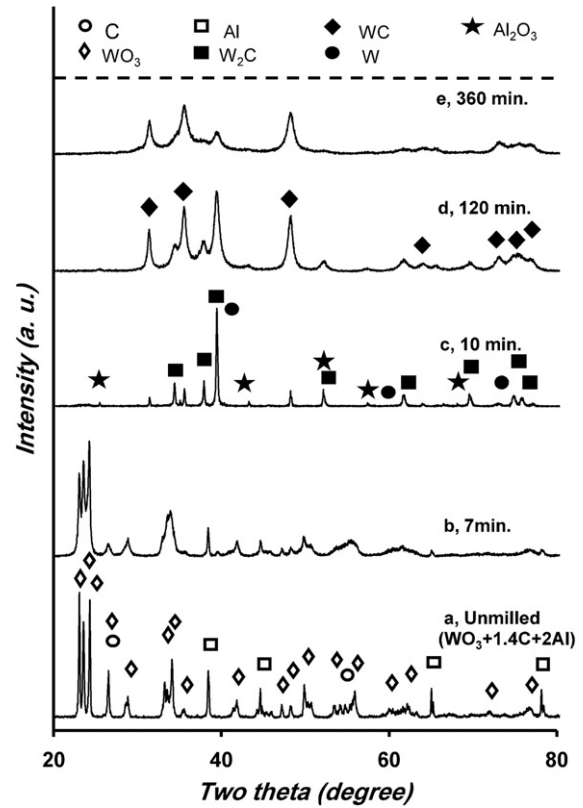


Fig. 3. XRD patterns of WO_3 -2Al-1.4C mixtures after different times of milling. Indicated milling time is a cumulative value.

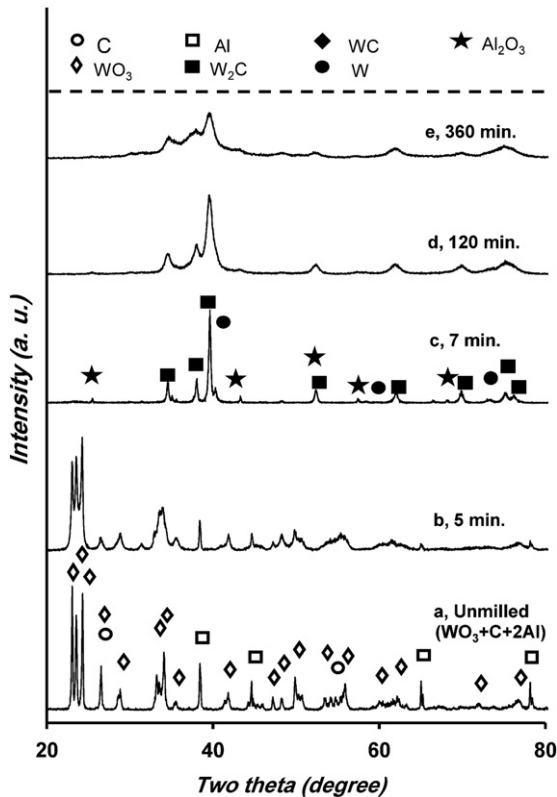


Fig. 2. XRD patterns of WO_3 -2Al-C mixtures after different times of milling. Indicated milling time is a cumulative value.

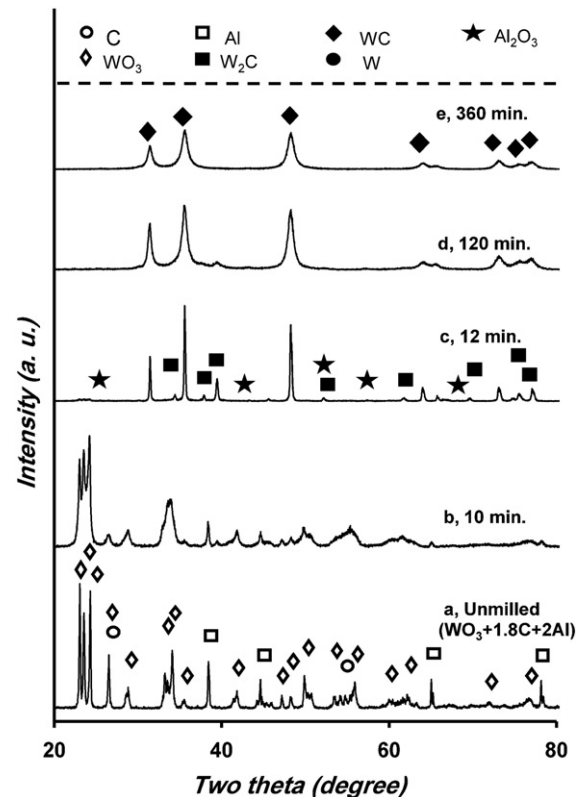


Fig. 4. XRD patterns of WO_3 -2Al-1.8C mixtures after different times of milling. Indicated milling time is a cumulative value.

decrease the rate of aluminothermic reduction reaction and consequently the amount of heat released. Hence, presence of more carbon in the system alleviates heat accumulation [33] and lowers the system maximum temperature. Decrease of the temperature would increase the thermodynamic stability of WC [34] (see Fig. 5).

- 2- Higher C amounts in the mixture, would absorb the heat of aluminothermic reduction reaction (e.g. decrease the system maximum temperature) and increase the thermodynamic stability of WC (see Fig. 5).
- 3- Formation of W_2C , WC or W_2C/WC mixtures could also be caused by carbon loss [14,15] phenomenon (see Table 2) in the mixture. The results of supplementary tests (Table 2 and Fig. 6) on the W-yC ($y = 0.25, 0.5, 0.75$ and 1) mixtures show that milling of various W-yC mixtures brings about the gradual formation of W_2C , W_2C/WC and WC phases, depending on the carbon amount in the mixture (reactions 2 and 3).



This means that for the formation of 1 mol of WC, one carbon mole is necessary [9,10] and carbon insufficiency would inevitably lead to the formation of W_2C compound [35,36]. As seen in Table 2, the remaining carbon (after the termination of experiment) has been decreased from 1 to 0.5, from 1.4 to 0.84 and from 1.8 to 1.26 in $WO_3-2Al-C$, $WO_3-2Al-1.4C$ and $WO_3-2Al-1.8C$ mixtures, respectively. Hence, formation of different types of carbides in the mentioned mixtures is understandable.

Regarding to Figs. 2, 3 and 4, continuation of milling of the $WO_3-2Al-(1+x)C$ mixtures brings about some changes in XRD patterns. In the case of $WO_3-2Al-C$ mixture, the only effects of milling are the decrease of the peak heights (intensities) as well as peak broadening which indicate crystallite refinement and amorphization phenomena [31]. For $WO_3-2Al-1.4C$ mixture, milling brings about increase of the WC phase at the expense of the W_2C phase. The results of supplementary tests on the W_2C-C mixture (Fig. 7) may help to explain this phenomenon. As it could be seen in Fig. 7, milling of W_2C-C mixture yields the formation of WC phase (reaction 4).



Hence, increase in the amount of WC phase with continuation of milling of $WO_3-2Al-1.4C$ mixture is related to the reaction of

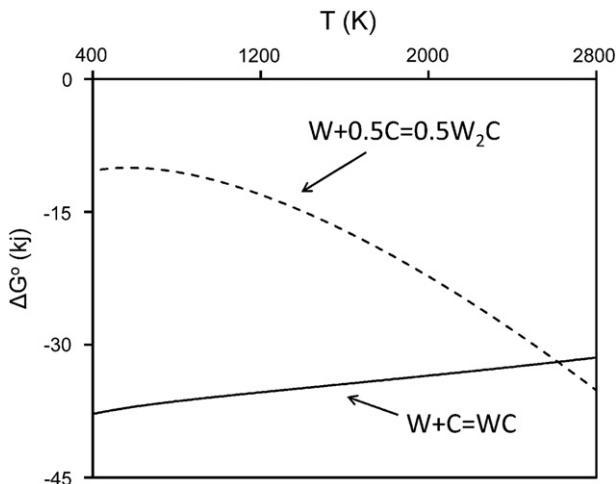


Fig. 5. Comparison between thermodynamic stability of WC and W_2C over a wide range of temperature.

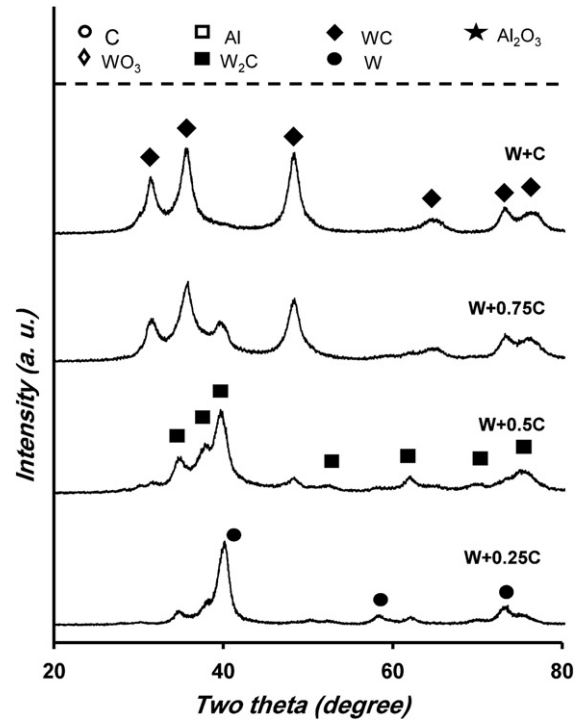


Fig. 6. XRD patterns of W-yC ($y = 0.25, 0.5, 0.75$ and 1) mixtures after 480 min of milling.

previously formed W_2C with unconsumed carbon in the mixture [35]. Presence of W_2C peaks in Fig. 3-e reveals the insufficiency of carbon left in the mixture for the completion of reaction 4. Increase of WC amount after a long time of milling, is also presented in Fig. 4 ($WO_3-2Al-1.8C$ mixture). XRD patterns of this case reveal that W_2C phase has been eliminated after 360 min of milling indicating that excess carbon in the mixture has been enough for the completion of reaction 4. Gradual changes of XRD patterns together with slow rises of pots outside temperatures during the conversion reaction of W_2C phase to WC (reaction 4) reveal that the type of this exothermic reaction ($\Delta H_{298}^0 = -54$ kJ) is gradual.

BF-TEM images of produced WC- Al_2O_3 powder are shown in Fig. 8. This figure shows that the powder contains large agglomerates

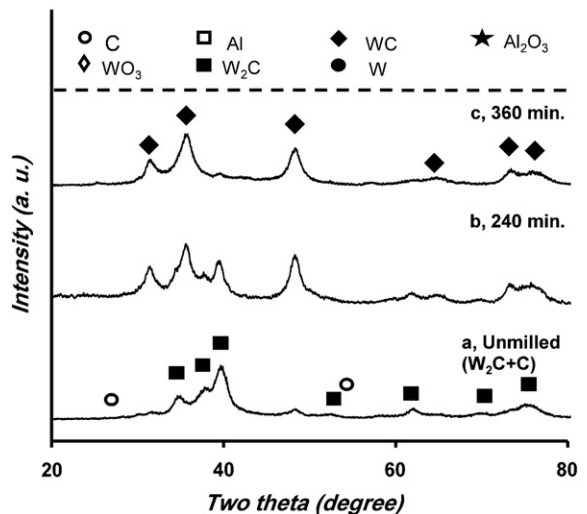


Fig. 7. XRD patterns of W_2C-C mixtures after different times of milling. Indicated milling time is a cumulative value. W_2C phase, used here, was first mechano-chemically synthesized from W-0.5C mixture (see Fig. 6).

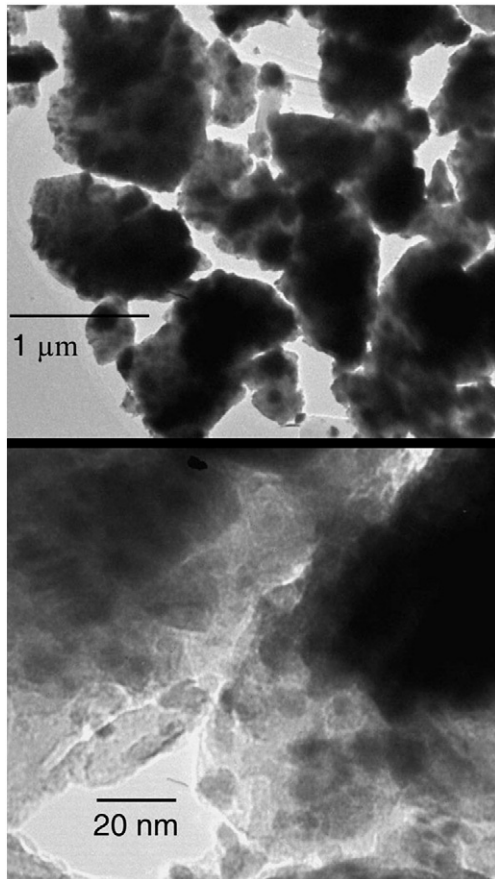


Fig. 8. BF-TEM images of WC–Al₂O₃ powder produced via 360 min milling of WO₃–2Al–1.8C mixture.

while each agglomerate consists of nano-size particles. Fig. 8 also shows that the produced composite powder has a good homogeneity.

The Williamson–Hall plot of WC–Al₂O₃ powder produced via 360 min milling of WO₃–2Al–1.8C is presented in Fig. 9. Since the intensity of alumina peaks in the XRD patterns is low, calculations are not accurate for this compound. It may be assumed that values of crystallite size and lattice distortion of Al₂O₃ phase are around those of WC phase. Fig. 9 shows that the calculated values of crystallite size and lattice distortion of WC phase are 16 nm and 0.2%,

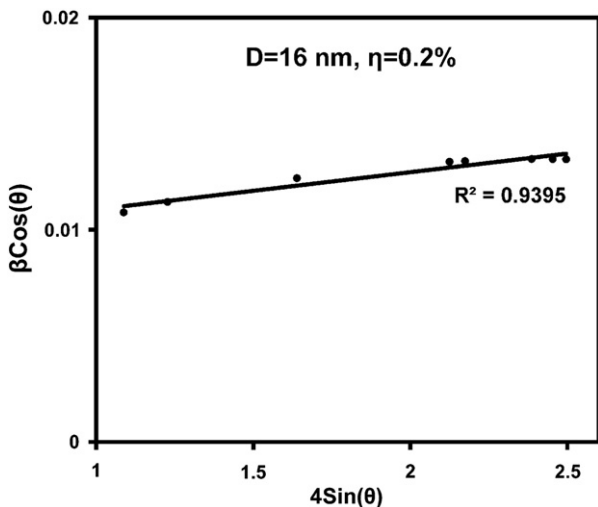


Fig. 9. Williamson–Hall plot for WC–Al₂O₃ powder obtained via 360 min milling of WO₃–2Al–1.8C mixture.

respectively. These amounts verify the TEM observations and show that the product contains nano-size phases.

4. Conclusion

Formation of W₂C compound during mechano-chemical synthesis of WC phase has been reported by various researchers. Since the properties of W₂C phase are inferior to WC, in this research work the effect of excess carbon addition to WO₃–2Al–C mixture on the conversion of W₂C to WC phase during mechano-chemical synthesis of nano-size WC–Al₂O₃ composite powder has been investigated. Supplementary tests on W–yC and W₂C–C systems have also been performed to clarify the reaction mechanism.

Experimental results showed that the types of occurred reactions in the WO₃–2Al–(1+x)C mixtures are MSR. The observed evolution of CO gas during the reactions is related to the activation of carbothermic reduction reaction of WO₃ at high temperatures resulted from the large amount of heat released by aluminothermic reduction reaction. It has been concluded that the excess carbon promotes the WC formation through the following routes:

- Excess carbon might decrease the intensity of heat release in the mixture through the absorption of some heat of aluminothermic reduction reaction. This phenomenon would decrease the mixture maximum temperature and hence, increases the thermodynamic stability of WC phase.
- Excess carbon compensates the carbon loss resulted from the side carbothermic reduction reaction of WO₃ in the mixture. Hence, the amount of carbon in the system would be enough to yield WC phase.

The obtained results showed that a W₂C free product can be achieved when an initial mixture of WO₃–2Al–1.8C is used. BF-TEM images and Williamson–Hall calculation showed that the produced WC–Al₂O₃ powder contains nano-size phases. Crystallite size of WC phase has been estimated to be around 16 nm.

References

- [1] Lassner E, Schubert W. Tungsten: properties, chemistry, technology of the element, alloys, and chemical compounds. New York: Plenum Publishers; 1999.
- [2] Upadhyaya G. Cemented tungsten carbides: production, properties, and testing. New York: Noyes Publications; 1998.
- [3] Fang Z, Wang X, Ryu T, Hwang K, Sohn H. Synthesis, sintering, and mechanical properties of nanocrystalline cemented tungsten carbide—a review. Int J Refract Met Hard Mater 2009;27:288–99.
- [4] Yao Z, Stiglich JJ, Sudarshan T. Nano-grained Tungsten Carbide–Cobalt (WC/Co). http://www.matmod.com/publications/armor_1.pdf (accessed May 27 2012).
- [5] Vallance S. Microwave synthesis and mechanistic examination of the transition metal carbides. University of Nottingham; 2008.
- [6] Hewitt SA, Kibble KA. Effects of ball milling time on the synthesis and consolidation of nanostructured WC–Co composites. Int J Refract Met Hard Mater 2009;27:937–48.
- [7] El-Eskandarany M. Mechanical alloying for fabrication of advanced engineering materials. New York: Noyes Publications; 2001.
- [8] Suryanarayana C, Ivanov E, Boldyrev V. The science and technology of mechanical alloying. Mater Sci Eng A 2001;304:151–8.
- [9] Enayati M, Aryanpour G, Ebnonnasir A. Production of nanostructured WC–Co powder by ball milling. Int J Refract Met Hard Mater 2009;27:159–63.
- [10] El-Eskandarany M, Mahday A, Ahmed H, Amer A. Synthesis and characterizations of ball-milled nanocrystalline WC and nanocomposite WC–Co powders and subsequent consolidations. J Alloys Compd 2000;312:315–25.
- [11] Sherif El-Eskandarany M. Fabrication of nanocrystalline WC and nanocomposite WC–MgO refractory materials at room temperature. J Alloys Compd 2000;296:175–82.
- [12] El-Eskandarany M. Fabrication and characterizations of new nanocomposite WC/Al₂O₃ materials by room temperature ball milling and subsequent consolidation. J Alloys Compd 2005;391:228–35.
- [13] Zakeri M, Rahimpour M, Sadrnezhad S, Yazdanni-rad R. Preparation of alumina–tungsten carbide nanocomposite by mechano-chemical reduction of WO₃ with aluminum and graphite. J Alloys Compd 2010;491:203–8.
- [14] Sakaki M, Bafghi MS, Khaki JV, Zhang Q, Kano J, Saito F. Effect of the aluminum content on the behavior of mechanochemical reactions in the WO₃–C–Al system. J Alloys Compd 2009;480:824–9.

- [15] Sakaki M, Bafghi MS, Vahdati Khaki J, Zhang Q, Saito F. Control of carbon loss during synthesis of WC powder through ball milling of WO_3 -C-2Al mixture. *J Alloys Compd* 2009;486:486-91.
- [16] Welham N. Room temperature reduction of scheelite ($CaWO_4$). *J Mater Res* 1999;14:619-27.
- [17] Welham N. Novel route to submicrometer tungsten carbide. *AIChE J* 2000;46:68-71.
- [18] Zhao J, Yuan X, Zhou Y. Cutting performance and failure mechanisms of an Al_2O_3 /WC/TiC micro- nano-composite ceramic tool. *Int J Refract Met Hard Mater* 2010;28:330-7.
- [19] Zheng D, Li X, Ai X, Yang C, Li Y. Bulk WC- Al_2O_3 composites prepared by spark plasma sintering. *Int J Refract Met Hard Mater* 2012;30:51-6.
- [20] Qu H, Zhu S, Li Q, Ouyang C. Influence of sintering temperature and holding time on the densification, phase transformation, microstructure and properties of hot pressing WC-40 vol.% Al_2O_3 composites. *Ceram Int* 2012;38:1371-80.
- [21] Ouyang CX, Zhu SG, Ma J, Qu HX. Master sintering curve of nanocomposite WC-MgO powder compacts. *J Alloys Compd* 2012;518:27-31.
- [22] Ma J, Zhu S, Ouyang C. Two-step hot-pressing sintering of nanocomposite WC-MgO compacts. *J Eur Ceram Soc* 2011;31:1927-35.
- [23] Williamson G, Hall W. X-ray line broadening from filed aluminium and wolfram. *Acta Metall* 1953;1:22-31.
- [24] Takacs L. Self-sustaining reactions induced by ball milling. *Prog Mater Sci* 2002;47:355-414.
- [25] Takacs L, Baláz P, Torosyan A. Ball milling-induced reduction of MoS_2 with Al. *J Mater Sci* 2006;41:7033-9.
- [26] Mingliang M, Xinkuan L, Shengqi X, Donglang C, Jing'en Z. Effect of material characteristics on the ignition of the combustion reactions induced by ball milling. *J Mater Process Technol* 2001;116:124-7.
- [27] Mulas G, Monagheddu M, Doppiu S, Cocco G, Maglia F, Tamburini U Anselmi. Metal-metal oxides prepared by MSR and SHS techniques. *Solid State Ionics* 2001;141:649-56.
- [28] Kraus W, Nolze G. POWDER CELL—a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. *J Appl Crystallogr* 1996;29:301-3.
- [29] Lönnberg B. Characterization of milled Si_3N_4 powder using X-ray peak broadening and surface area analysis. *J Mater Sci* 1994;29:3224-30.
- [30] Caglioti G, Paoletti A, Ricci F. Choice of collimators for a crystal spectrometer for neutron diffraction. *Nucl Instrum* 1958;3:223-8.
- [31] Cullity B. Elements of X-ray diffraction. 2nd ed. Massachusetts: Addison Wesley; 1978.
- [32] Pallone E, Trombini V, Botta FW, Tomasi R. Synthesis of Al_2O_3 -NbC by reactive milling and production of nanocomposites. *J Mater Process Technol* 2003;143:185-90.
- [33] Tan G, Wu X, Zhao M, Zhang H. Synthesis of nanocrystalline cubic substoichiometric WC_{1-z} powders by mechanochemical technology. *J Mater Sci* 2000;35:3151-4.
- [34] Zhang J, Lee J, Won C, Cho S, Chun B. Synthesis of Al_2O_3 -WC composite powder by SHS process. *J Mater Sci* 1999;34:5211-4.
- [35] Bolokang S, Banganayi C, Phasha M. Effect of C and milling parameters on the synthesis of WC powders by mechanical alloying. *Int J Refract Met Hard Mater* 2010;28:211-6.
- [36] Tan G. Synthesis of metastable tungsten carbide nanoparticles by mechanochemical alloying process. *Adv Mater Res* 2009;66:135-8.