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Effect of C and milling parameters on the synthesis of WC powders by mechanical alloying

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ABSTRACT

In the current study, the amount of carbon and the effects of milling parameters in production of tungsten-carbide (WC) powder were evaluated. Mechanical alloying (MA) of elemental W and C powders at different carbon-rich and carbon-deficient compositions was studied. XRD results showed that the higher the carbon content the longer the milling period for the formation of WC powder. We also report on the effect of milling parameters on the phase formation. In stoichiometric composition, WC was synthesized faster than in compositions with higher carbon amount. Furthermore, W_2C phase was observed in compositions with higher carbon content milled at low speed and ball-to-powder ratio (BPR), as well as in carbon-deficient composition milled for shorter period. The *ab initio* calculations were performed in attempt to explain the destabilization of W_2C on further milling.

1. Introduction

Carbon deficiency or tungsten excess in WC–Co promotes the formation of unwanted η-phase or M_6C [1,2], these carbides are in the form of Co_3W_3C and Co_6W_6C after sintering [3]. These phases are detrimental to the final mechanical properties and need to be avoided [1]. Although MA can produce a non-equilibrium, supersaturated and amorphous material [4], it is important to understand the synthesis of alloys at different starting compositions. Since W–C phase diagram (Fig. 1) shows a mixture of WC and graphite (C) on C-rich side [5], it is intriguing to study the extended solid solubility and metastable phases induced by MA in different composition range. There are limited studies done on the effect of milling parameters and carbon content on the formation of WC by MA. In the current paper, the effect of C content and milling parameters on the synthesis of tungsten-carbide (WC) powder by mechanical alloying is reported. It is significant to plan for the free C and W in the powder during sintering to improve mechanical properties. In our paper we report formation of equilibrium WC and its formation at different carbon content. The first-principles calculations were carried-out in attempt to explain the formation mechanism. Our results are based on MA, XRD analysis and *ab initio* predictions.

1.1. Experimental procedure

Both tungsten (W) and amorphous carbon (C) powders were supplied by Boart Longyear (South Africa), and both with purity of 99.99%. High energy ball milling was performed using a planetary milling machine (PM 400/2). Milling speeds of 250 and 300 revolutions per minute (rpm) were applied. Initially, a total powder charge of 50–60 g was used, and then it was reduced to 35 g to raise the ball-to-powder ratio (BPR). Milling was performed on W–C system with carbon contents of (4.2; 6.13; 17 and 23 wt.%) at (6.4:1; 7:1; and 10:1) ball-to-powder ratios. The ball milling was done in a 250 ml vials equipped with a lid designed for both normal and inert atmosphere, with 10 mm diameter balls. In this study, milling was conducted in argon atmosphere. Both the vials and balls were made of WC to avoid contamination. During milling experiments, small samples of approximately 2 g were taken at selected time intervals to study the phase evolution using Phillips PW 1830 X-ray diffraction (XRD) machine fitted with Cu Kα radiation, and 0.02 step size scanned from 20 to 90 (2θ). Scherrer formula (Eq. (1)) was used to calculate the crystallite size. The XRD peak broadening was calculated from the full width at half maximum (FWHM) of the most intense Bragg peak. The Scherrer formula used is:

$$D = 0.9\lambda/B\cos\theta \quad (1)$$

where θ is a diffraction angle, D is a crystallite size, λ is a X-ray wavelength and B is a full width at half maximum (FWHM).

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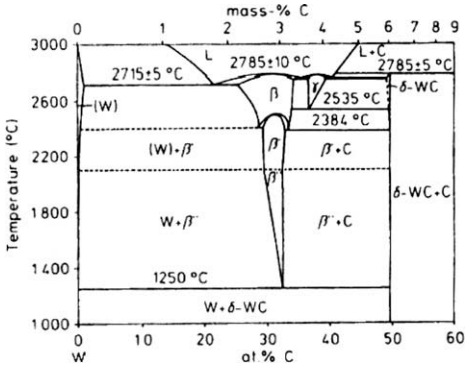

Fig. 1. W–C phase diagram [5].

1.2. First principles modelling procedure

Our *ab initio* calculations were performed using the well-established total energy code, CASTEP [8]. The CASTEP code is a first principles quantum mechanical programme for performing electronic structure calculations within the Hohenberg–Kohn–Sham density functional theory (DFT) [9] was used within the generalized gradient approximation (GGA) formalism [10] to describe the electronic exchange–correlation interactions. We used the recent Perdew–Burke–Ernzerhof (PBE) [11] form of GGA, which was designed to be more robust and accurate the density functional formalism and employs the plane-wave basis set to treat valence electrons and pseudopotentials to approximate the potential field of ion cores (including nuclei and tightly bond core electrons).

In CASTEP, maximum plane wave cut-off energy of 400 eV was employed on alloys, using Vanderbilt-type ultrasoft pseudopotentials (US) [12] to describe the electron–ion interaction. Geometry optimization was conducted using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method [13]. The integration in the Brillouin zone (BZ) is done on the special *k*-points determined from the Monkhorst–Pack scheme [14]. The calculations were performed using $13 \times 13 \times 12$ Monkhorst–Pack *k*-point grid for both B_h (space group #187) and C6 (space group #164) crystal structures representing WC and W_2C, respectively. The energy cut-off as well as the number of *k*-points was converged to within 1 meV per atom. For each phase of interest, the geometry optimization is first performed to find its ground state, as well as to obtain the structural properties. The hydrostatic pressures of up to 150 GPa were applied on the optimized structures with lowest heat of formation as well as on the constituent metals, W and C, in bcc and diamond phases, respectively.

2. Results and discussion

2.1. Mechanical alloying of W–6.13 wt.% C (stoichiometric) at 10:1 BPR, 300 rpm

In Fig. 2, the XRD patterns of milled stoichiometric WC powders at different milling times are shown. After 4 h of high energy ball milling, the new peaks of WC become well pronounced. The presence of unreacted W after 4 h shows the inhomogeneity of powders in early stages of milling as a consequence of high energy ball milling. The Bragg peaks of W have decreased indicating occurrence of alloying to form WC and disappeared completely after 8 h of MA resulting to increased WC peak intensity. Milling for further 12 h did not yield any structural changes.

The corresponding structural parameters of phases obtained during MA by XRD analysis are presented in Table 1.

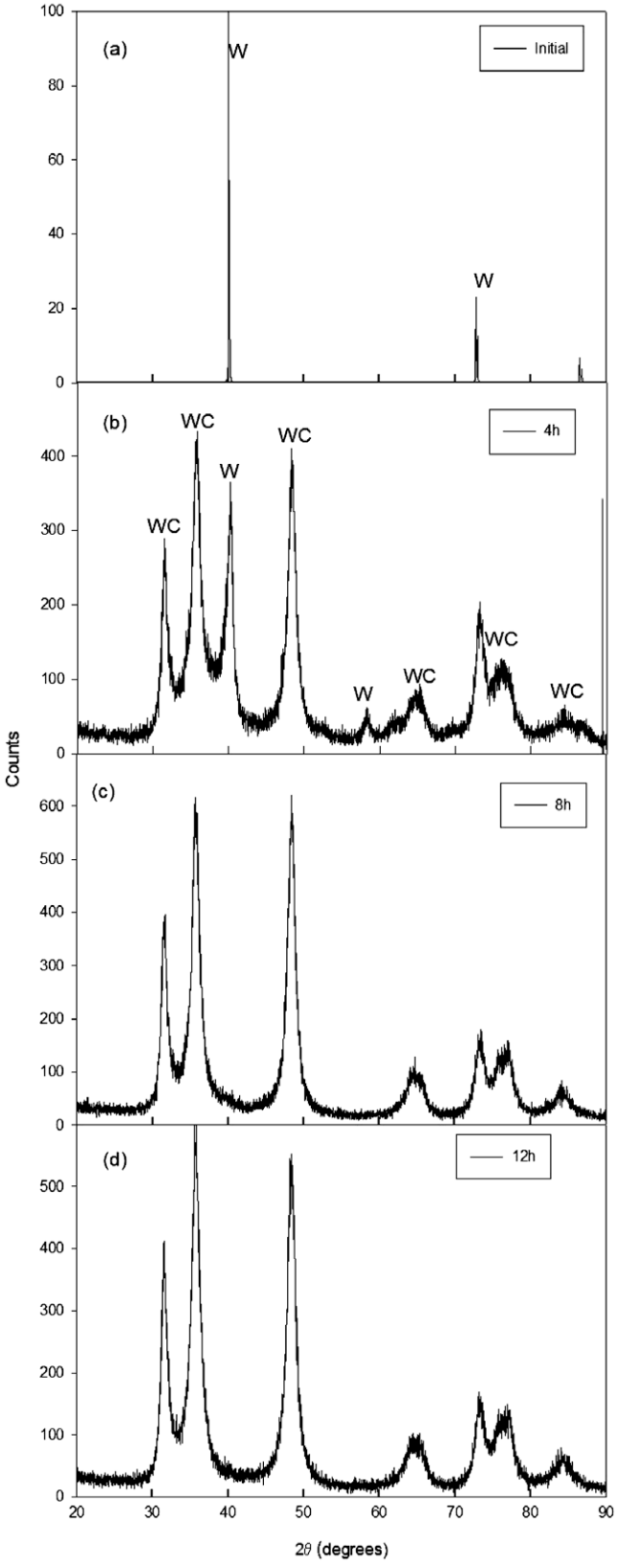

Fig. 2. XRD pattern for the production of WC from interrupted high energy ball milling of W and C, corresponding to (a) initial mixture, (b) 4 h, (c) 8 h and (d) 12 h of milling, at BPR of 10:1 and milling speed of 300 rpm, respectively.

Fig. 3 shows a decrease in powder crystallite size with increasing milling times. After 12 h milling time, 11 nm WC crystallite size was obtained.

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Table 1
Phases obtained from mechanical alloying of W 6.13 wt.% C powders.

Milling time (h)	Phases	Lattice constant (Å)	Lattice volume (Å^3)
4	W	a = 3.165	31.71
	WC	a = 2.906	
		c = 2.837	20.75
8	WC	a = 2.908	20.66
		c = 2.822	
12	WC	a = 2.906	20.75
		c = 2.837	

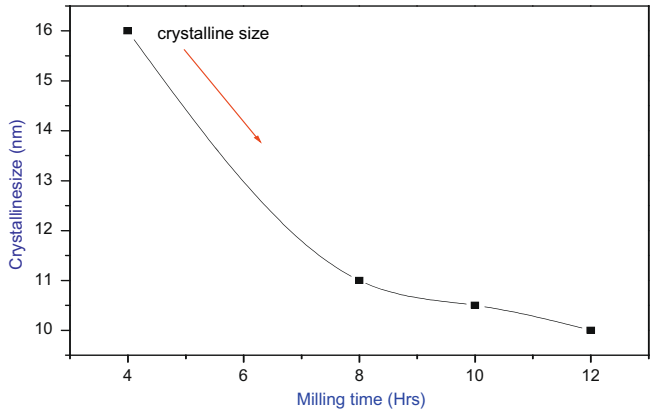

Fig. 3. Decrease in crystalline size as a function of milling time in stoichiometric WC composition.

2.2. Mechanical alloying of carbon deficient W–4.2 wt.% C

In this experiment 4.2 wt.% C was milled with equal amount of W used in stoichiometric composition presented in Section 2.1. Fig. 4 shows the XRD patterns of the milled W–4.2 wt.% C. The peaks of W, WC and W_2C were observed after 4 h. The dominating W peak indicates that at this stage most of W had not reacted. W_2C which is a hexagonal-close-packed (hcp) W-rich phase was formed. Thermodynamically, W_2C is a high temperature phase forming at low carbon amount and unstable at low temperature [6,7]. This phase might have formed due to the temperature rise inside the milling container although the temperature was not measured. We used *ab initio* calculations to investigate the possibility of forming W_2C at high pressure at 0 K, it may not be possible by since MA to reach the necessary temperature for the formation of W_2C. Firstly, using *ab initio* calculations we calculated the heat of formation for WC equal to −217 meV/atom while for W_2C is −2 meV/atom, as shown in Fig. 5. The predictions confirm that the formation of WC is thermodynamically favourable than W_2C formation.

On further milling to 8 h, only intense WC peaks are observed. This might be due to the reaction between unreacted W and available C rather than that of W_2C and C, since the C affinity to W is higher than to W_2C. Because the system is C deficient, there might not be enough C to transform W_2C to WC. The disappearance of W_2C peaks is thought to be as a result of amorphization, it has been reported that metastable phases turn amorphous easier during milling [15]. The *ab initio* pressure studies shown in Fig. 5 indicates the possibility of destabilization of W_2C due to high pressure ~(30 GPa), while WC stability increases with pressure. Surprisingly, W_2C re-stabilize above 70 GPa. This might sug-

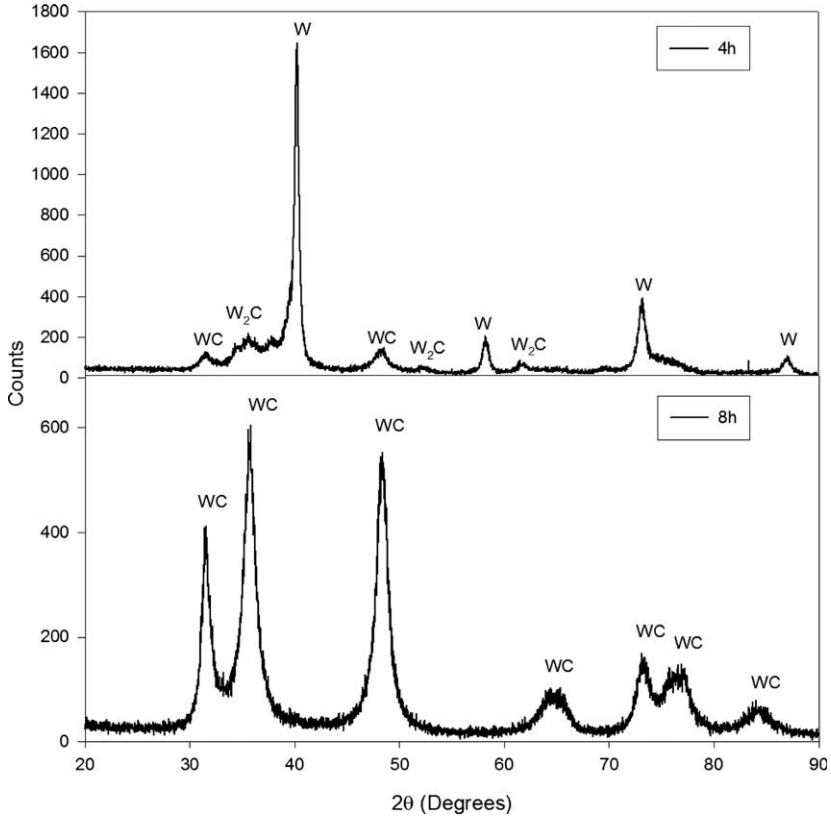

Fig. 4. XRD patterns of high energy ball milled W 4.2 wt.% C for 4 h at 10:1 BPR and milling speed of 300 rpm.

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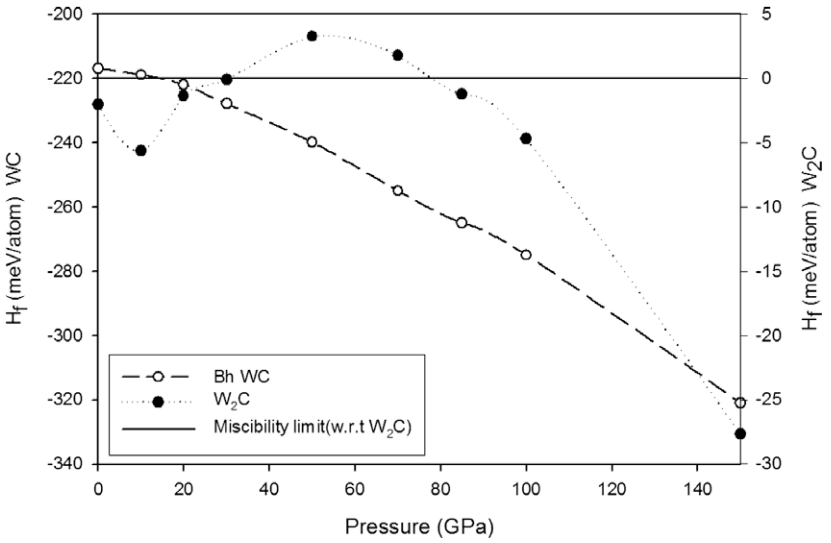

Fig. 5. The *ab initio* predicted heats of formation of WC (left *y*-axis) and W_2C (right *y*-axis) as a function of pressure.

gest recrystallization if milling is prolonged for much loner periods.

In Fig. 5, the heats of formation (H_f) of WC and W_2C phases at various pressures are plotted. As shown on the left *y*-axis, the H_f of WC increases with increasing pressure indicating increased stability. The H_f of W_2C shown on the right *y*-axis start by increasing slightly to a maximum at 10 GPa, after which begin decreasing to above miscibility limit at pressures higher than 30 GPa.

2.3. Mechanical alloying of W–17 wt.% C milled at the speed of 250 rpm and 6.4:1 and 7:1 BPR

The XRD pattern of high energy milled W–17wt.% C powder at 6.4:1 BPR and milling speed of 250 rpm is shown in Fig. 6a. The W_2C phase has formed due to lower milling parameters (speed, and BPR) during MA after 30 h. The most intense XRD peak belongs to unreacted W, appearing along side weak WC

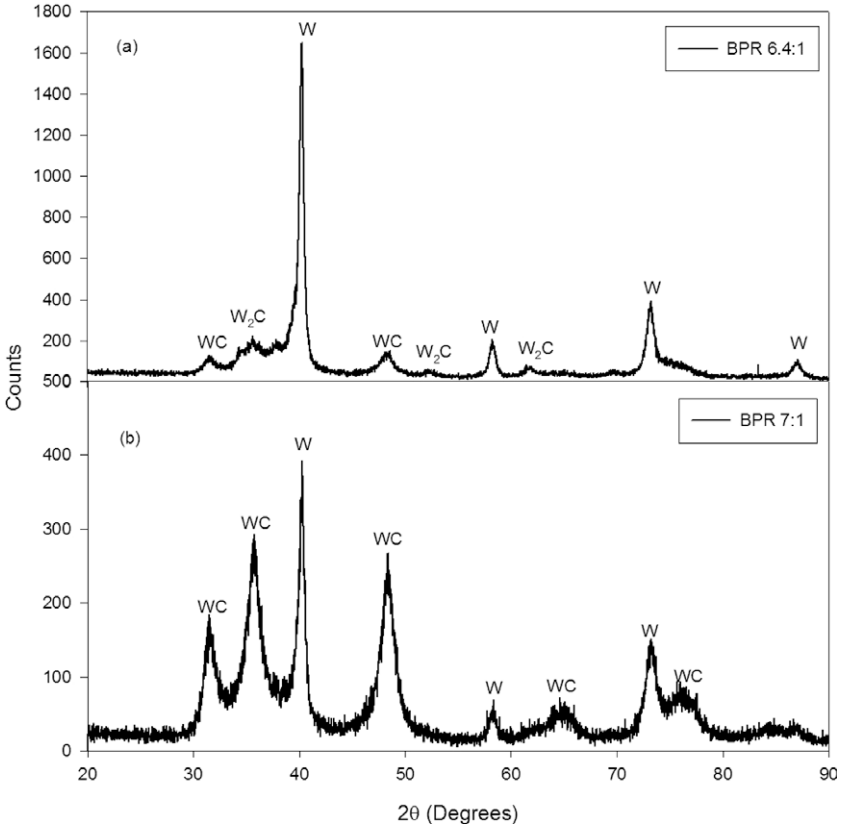

Fig. 6. XRD pattern of milled W 17 wt.% C for 30 h uninterrupted at milling speed of 250 rpm and (a) 6.4:1 BPR and (b) 7:1 BPR.

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and W_2C peaks. In this experiment it was evident that the kinetics did not favour a full WC synthesis after 30 h of milling. Although milled for 30 h, the milling intensity was low to can amorphize W_2C phase as in Section 2.2. The W_2C phase formed due to both low milling speed and BPR. Although the charge contains high amount of C, the selected milling parameters did not provide adequate energy or pressure to react $W_2C + C$ to form WC. As a result, the BPR was increased to 7:1 and the results are shown in Fig. 6b.

As shown in Fig. 6, an increase in BPR by 0.6 to 7:1 promoted the formation of WC. The W_2C Bragg peaks disappeared after BPR was increased. The increased kinetics promoted the formation of WC either from $W_2C + C$ reaction, or directly form W + C to form WC. This is possible since carbon is available and the required energy is provided. The XRD pattern indicates the presence of unreacted W due to inhomogeneity in the current milling conditions.

2.4. Mechanical alloying of W–17 wt.% C at 10:1 BPR and milling speed of 300 rpm

The presence of unreacted W in the experiments in Section 2.3 indicated the incompletion of the reaction. We therefore increased the milling parameters to 300 rpm and 10:1 BPR. An almost complete synthesis of WC was attained, as shown in Fig. 7. The amount of unreacted W was quite small and its peak was drastically decreased and negligible in size. The result indicates that higher BPR and speed provide sufficient kinetic energy, hence the improved synthesis during milling [4]. The WC peaks are more pronounced in the present conditions. Due to available C and suitable milling parameters $W_2C + C$ reaction occurs instead of W_2C amorphization.

From the results discussed, it was shown that at 17 wt.% C longer milling period is required to form WC than in both C deficient and stoichiometric compositions. To investigate this observation further, the amount of C was then increased to 23 wt.% and the results are presented in Section 2.5 below.

2.5. Mechanical alloying of W–23 wt.% C at 10:1 BPR and 300 rpm milling speed

The milling conditions used in Section 2.4 were kept the same. The only change was in carbon content which was increased to 23 wt.%. The XRD pattern of the results is shown in Fig. 8. A full synthesis of WC was not achieved in 30 h of MA. The results show that the W peak intensity is higher than the one shown in Fig. 7. Further milling resulted in decrease of W peak intensity after 40 h. The results indicate that the WC formed after 30 h in Section 2.4 is achieved after 40 h under current milling conditions. The complete synthesis of WC was attained after 50 h of milling.

All milling experiments show that the higher the C content the longer the milling period required for complete WC formation, as shown in Fig. 9. The more carbon on the system the slower the kinetics due to formed WC impeding the probability of W atoms to be in contact with C atoms to form WC and as a result delays the reaction. The results in Fig. 9 indicate that WC formation during MA is both time and carbon content dependent.

Although MA can produce non-equilibrium phases, it forms the thermodynamically more feasible phase first, and later begins to form metastable structures as well.

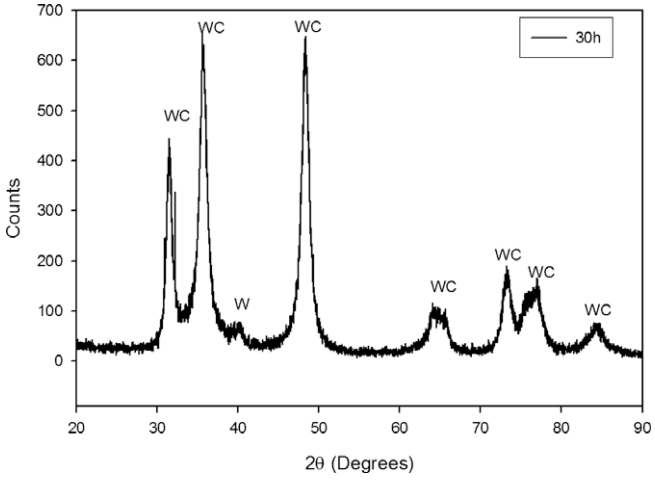

Fig. 7. XRD pattern of W–17 wt.% C milled for 30 h uninterruptedly at 10:1 BPR and milling speed of 300 rpm.

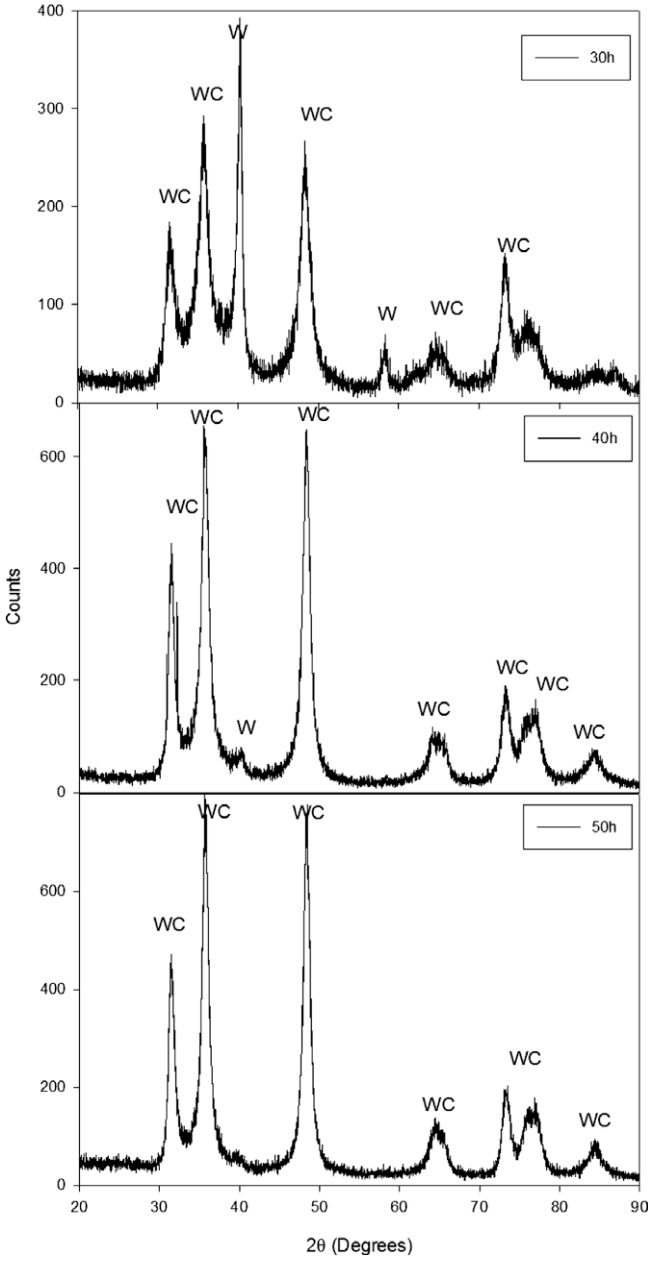

Fig. 8. XRD patterns of W–23 wt.% C milled for 30, 40, and 50 h at 10:1 BPR and milling speed of 300 rpm.

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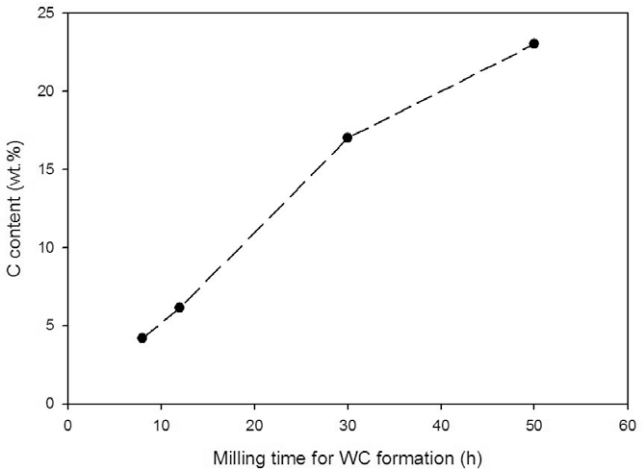

Fig. 9. Time required for producing WC at various C content.

3. Conclusions

The complete synthesis of homogeneous WC by MA is affected by the milling parameters and carbon content. Our milling experiments indicate that the higher the C content the longer the milling period required for complete WC formation. W_2C phase was observed after 4 h in carbon-deficient composition and after 30 h in carbon-rich composition but lower milling parameters. The *ab initio* calculations at high pressures predict destabilization of W_2C around 30 GPa.

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