Preparation and Characterization of Amorphous W–B–C Alloy and Solid Solutions of C in Tungsten Borides

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Abstract Mixtures of W and $B_{13}C_2$ powders were mechanically milled and subsequently annealed at 900–1200 °C. It is found that amorphous W–B–C alloy formed as the mixtures were milled for 20–80 h. After annealing the 80 h-milled mixtures at 900–950 °C, solid solutions of C and/or B in tungsten [W(B, C)], C in tungsten boride [$W_2B(C)$ or $WB(C)$] formed by the crystallization of amorphous W–B–C. The formation temperature of $W_2B(C)$ and $WB(C)$ is lower than that of W_2B and WB reported previously. As the 80 h-milled mixtures were annealed at 1200 °C, W reacted with amorphous W–B–C completely to form WB and W_2B_5 or W_2B_5 instead of the solid solutions of C in tungsten borides, which is determined by the mole ratio of W to $B_{13}C_2$. The formation mechanisms of the $W_2B(C)$ and $WB(C)$ solid solutions as well as phase transition rules of the mixtures at annealing temperature and mole ratio were also investigated using first-principle calculation.

KEY WORDS: Ball milling; Annealing; Tungsten borides; Amorphous alloy

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1 Introduction

Tungsten borides have high hardness values, chemical inertness and conductivity, as well as industrial applications as abrasive, corrosion-resistant and electrode materials used under extreme conditions [1, 2]. In the past 30 years, various approaches, including solid-state reactions, molten salt electrolysis, chemical vapor deposition, mechanical alloying (MA), and self-propagating high-temperature synthesis (SHS) [3–11], were used for preparing various types of tungsten borides by using amorphous boron (B) or B_4C as B source and W, WC or WO_2 as W source. Up to now, six types of tungsten borides, WB , W_2B , W_2B_5 , WB_2 , WB_4 and WB_{12} , have been obtained and an equilibrium thermodynamic W–B phase diagram has been established in high-temperature range (> 1800 °C) [12]. Among these tungsten borides, WB_4 is a kind of superhard material (32–46 GPa) [13–15]; its hardness is much lower than that of other materials: For example, WB and W_2B_5 only have hardness of 25–27 GPa. However, WB_4 is metastable and is very difficultly to be

prepared, while WB and W_2B_5 are easily to be prepared and applied extensively. Therefore, it becomes the focus to improve hardness and conductivity of WB and W_2B_5 for their application in superhard and electrode material fields.

It is known that incorporation of C into some materials can improve the hardness. Carbon is adjacent to boron in periodic table of elements and has one more valence electron than boron. If C substitutes for B, it may provide one more electron than B and increase conductivity of tungsten borides. Therefore, it is expected that both the hardness and conductivity of tungsten borides can be improved by incorporation of C into tungsten borides. However, it is noted that high temperature (above 1200 °C) is always needed when tungsten borides are synthesized by the solid-state reaction of B_4C with W [8, 9, 13, 16]. C cannot incorporate into tungsten borides at high temperature, implying that solid solution of C in tungsten borides cannot form in a solid-state reaction. It is known that thermodynamic reaction process is related to temperature and reactants. So, it may be an effective approach to prepare solid solution of C in tungsten borides or tungsten carbon borides by solid-state reaction of W (or compounds of W) and carbon borides at low temperature. Thus, how to decrease reaction temperature is a key problem.

Ball milling can refine particle size and decrease interatomic diffusion distance of two materials, which can increase reaction activity and decrease reaction temperature [17, 18]. Therefore, we carried out research work on preparation of solid solution of C in tungsten borides or tungsten borides by ball milling and subsequent annealing, investigated the effects of milling time and annealing temperature on structures of tungsten borides and incorporation of C in tungsten borides, and suggested the thermodynamics mechanism of formation of the tungsten boride solid solutions by first-principle calculation.

2 Experimental

2.1 Materials and Synthesis

The raw materials used in present work were 99% pure tungsten (W) powder and 99% pure $B_{13}C_2$ powder, since the $B_{13}C_2$ is much cheaper than pure B powders and B_4C . Considering preparation of boron-rich tungsten borides, two mixtures with excessive B content were prepared by mixing the W and $B_{13}C_2$ powders in the nominal mole ratio of W to $B_{13}C_2$ of 1:2 and 1:5, respectively, and then loaded in a stainless steel vial together with stainless steel balls inside an argon-filled glove box. The diameters of the balls are 5–12 mm, and ball-to-mixture weight ratio was approximately 5:1. The mixtures were high-energy ball milled for 80 h. To investigate phase transition of the

mixtures during the milling process, some powders were taken out of the vial every 20 h for characterization of structure. In order to study the effect of temperature on phase transition of the milled mixtures, two mixtures milled for 80 h were pressed to cylinders with 6 mm in diameter and 2 mm in height and then annealed for 1 h at 10^{-3} Pa in a temperature ranging from 900 to 1200 °C.

2.2 Characterization

The crystal structures of the samples were characterized by using an X-ray diffractometer (XRD) with CuK_α radiation ($\lambda = 1.5406$ Å). Selected zone electron diffraction pattern and micromorphology of the samples were measured by high-resolution transmission electron microscopy (HRTEM). The elemental microanalysis of the sample was performed with energy-dispersive spectrometer equipped in the HRTEM.

2.3 Calculation

In order to study formation mechanism of the tungsten borides and their solid solutions, the formation energy and lattice constants of tungsten borides and their solid solutions were calculated by first-principles calculation, which was based on density functional theory (DFT) implemented in the VASP program with projector augmented wave (PAW) potentials, and Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) was adopted in calculation. And 500 eV plane wave energy cutoff was used, which was verified enough for absolute energy convergence.

3 Results and Discussion

3.1 Synthesis and Characterization of Amorphous W–B–C Alloy

Figure 1a–e shows XRD patterns of the mixture of W and $B_{13}C_2$ powders with nominal mole ratio of W to $B_{13}C_2$ of 1:2 [denoted as mixture (1:2)] unmilled and milled for 20, 40, 60 and 80 h, respectively. It is found that the XRD peak intensity of the $B_{13}C_2$ decreases drastically with increasing milling time and disappears completely as milling time is 20 h, as shown in Fig. 1b. At the same time, two typical diffraction peaks of amorphous alloy are observed: The strong one is in the diffraction angle ranging from 25° to 55°, and its peak position is somewhat smaller than that of (110) peak of W; and the weak one is in the range of 60°–80°. The peak intensity of the amorphous alloy increases with increasing milling time, while the peak intensity of the W decreases. Moreover, the intensity ratio of the strong

Fig. 1 XRD patterns of the mixture (1:2) unground **a** and milled for 20 **b**, 40 **c**, 60 **d**, 80 h **e**, respectively

peak of the amorphous alloy to the (110) peak of the W, that is, area ratio of the two peaks, increases with increasing milling time, as shown in Fig. 2. These results indicate that an amorphous alloy begins to form at milling time of near 20 h and its volume fraction increases with increasing milling time. In order to confirm the phase composition of the milled mixture (1:2), HRTEM was employed to characterize the structure of the 80 h-milled mixture (1:2). Figure 3a shows the HRTEM image of the 80 h-milled mixture (1:2), which demonstrates that the milled mixture (1:2) consists of amorphous and crystal phases. Figure 3b shows the selected-area electron diffraction pattern corresponding to the HRTEM image, which has two types of diffraction patterns: One consists of

Fig. 2 Plots of change of XRD peak intensity of (110) plane of W and amorphous W-B-C(I), and of intensity ratio of W(110) to amorphous W-B-C in mixture (1:2) and mixture (1:5) with milling time

dots and the other consists of circular ring (marked by a red arrow). The radius of the ring is somewhat smaller than distance from (110) dot to diffraction center, in agreement with XRD results of Fig. 1, where the peak position of the amorphous alloy is somewhat smaller than that of (110) peak position. So, it is concluded that Fig. 3a and (b) come from the W and amorphous alloy in the 80 h-milled mixture (1:2). The dots are due to diffraction of W along (111) crystallographic axis, and the circular ring to diffraction of the amorphous alloy.

In order to understand the composition and formation mechanism of the amorphous alloy, metal W and $B_{13}C_2$ powders were milled for 80 h. No phase transition was observed during 80 h milling, indicating that the amorphous alloy is neither amorphous W nor amorphous $B_{13}C_2$, but consists of W, B and C atoms. To further confirm this deduction, we carried out elemental microanalysis on the selected zone corresponding to the electron diffraction pattern by EDS, as shown in Fig. 4. W, B, Cu, V and C peaks are observed in Fig. 4, where the Cu and V are from specimen holder while the W, B and C come from the sample. This result implies that the amorphous alloy consists of W, B and a small amount of C, which will be demonstrated by experimental results of the milled mixture annealed latter. Hereinafter, we denote the amorphous alloy formed by milling of the mixture (1:2) as amorphous W-B-C(I). Based on above analysis, it is concluded that the mixture (1:2) milled for 20–80 h consists of crystalline W and the amorphous W-B-C(I) alloy.

Since W has much higher atomic scattering factor than B and C, the results of Fig. 2 imply that the W content in the amorphous W-B-C(I) and volume fraction of the amorphous W-B-C(I) in the milled mixture increase with increasing milling time. Therefore, the formation mechanism of the amorphous W-B-C(I) is suggested as follows: The $B_{13}C_2$ reacts with the W at interface of the $B_{13}C_2$ /W particles by interdiffusion to form amorphous W-B-C(I) during milling process, and all $B_{13}C_2$ reacts with partial W to form the amorphous W-B-C(I) upon milling for 20 h. Further milling the mixture, the W incorporates into the amorphous W-B-C(I), leading to that the W content in the mixture decreases but the volume fraction of the amorphous W-B-C(I) in the mixture and the W content in the amorphous W-B-C(I) increase, as shown in Fig. 2. This formation mechanism was demonstrated in the work of preparation of amorphous Fe-N alloy by ball milling Fe and BN powders [19, 20].

Figure 5a–e shows XRD patterns of the mixture of W and $B_{13}C_2$ with nominal mole ratio of W to $B_{13}C_2$ of 1:5 [denoted as mixture (1:5)] unground and milled for 20, 40, 60 and 80 h, respectively. Being similar to the milled mixture (1:2), the XRD peak intensities of W and $B_{13}C_2$

Fig. 3 HRTEM image **a** and electron diffraction patterns of W along [111] direction and of amorphous W–B–C(I) **b** for the 80 h-milled mixture (1:2)

Fig. 4 EDS of the selected zone corresponding to electron diffraction pattern of Fig. 3

decrease with increasing milling time, and two typical amorphous alloy peaks begin to appear as milling time reaches approximately 20 h and the peak intensity of the amorphous alloy increases with increasing milling time, as shown in Fig. 5. In order to confirm the results of Fig. 5 and formation mechanism of the amorphous W-B-C

suggested above, HRTEM measurement was employed. Figure 6a shows HRTEM image of the 80 h-milled mixture (1:5), indicating that the mixture consists of crystalline W and amorphous alloy, which is also confirmed by electron diffraction pattern, as shown in Fig. 6b. Figure 7 shows the EDS of the selected zone corresponding to

Fig. 6b, indicating that the amorphous alloy consists of W, B and C (as discussed in Fig. 4). We denoted it as amorphous W–B–C(II) here. It can be seen clearly that there are disorder atomic layers at interfaces of W/amorphous alloy, confirming that the formation of the amorphous alloy is attributed to diffusion reaction between W and $B_{13}C_2$, as suggested above.

It is noted that there are some differences in Figs. 1 and 5. The first one is that the diffraction peaks of $B_{13}C_2$ still can be observed in the 80 h-milled mixture (1:5), implying that $B_{13}C_2$ does not react with W completely to form W–B–C(II); another is that the XRD intensity ratio of amorphous W–B–C(II) to W of the milled mixture (1:5) is always smaller than that of mixture (1:2). Moreover, the

ratios difference increases with increasing milling time (shown in Fig. 2), implying that the volume fraction and W content of the amorphous W–B–C(II) are smaller than those of amorphous W–B–C(I). The results of Figs. 1 and 5 imply that formation ability of the amorphous W–B–C is related to mole ratio of W to $B_{13}C_2$ and the compositions of the two amorphous W–B–C are different. Obviously, formation of the amorphous W–B–C alloy is much easier in the mixture (1:2) than that in the mixture (1:5), and the W content in the amorphous W–B–C(I) is higher than that in the amorphous W–B–C (II).

3.2 Crystallization of Amorphous W–B–C Alloy

In order to study the effect of temperature and composition on structure of W–B–C system, the 80 h-milled mixtures (1:2) and (1:5) were annealed for 1 h under vacuum in temperature ranging from 900 to 1200 °C, respectively. Figure 8a–d shows XRD patterns of the 80 h-milled mixture (1:2) unannealed and annealed at 900, 950 and 1200 °C, respectively. By analyzing XRD data of Fig. 8a, b, it is found that the amorphous W–B–C(I) crystallizes partially as annealed at 900 °C and some additional XRD peaks appear near diffraction angles of W_2B and WB reported in the previous literatures (PDF No. 73-1767, 35-0738). However, compared to diffraction angles of the W_2B and WB, the additional peaks shift toward high diffraction angle direction obviously, as shown in Fig. 9b, where the angles marked by the red solid and dot lines are diffraction angles of (202) plane of the W_2B and (200) plane of the WB measured with CuK_α radiation, respectively. These results indicate that the diffraction peaks come from contributions of solid solutions of W_2B and WB, respectively, and the lattice constants of the W_2B and

Fig. 5 XRD patterns of the mixture (1:5) unground **a** and milled for 20 h **b**, 40 h **c**, 60 h **d**, 80 h **e**

Fig. 6 HRTEM image **a** and electron diffraction pattern of amorphous W–B–C(II) and W along [113] direction **b** of the 80 h-milled mixture (1:5)

Fig. 7 EDS of the selected zone corresponding to electron diffraction pattern of Fig. 6

Fig. 8 XRD patterns of the 80 h-milled mixture (1:2) unannealed **a** and annealed at 900 °C **b**, 950 °C **c**, 1200 °C **d**

WB solid solutions are smaller than those of W_2B and WB, respectively. Since atomic covalent radius of C (0.77 Å) is smaller than that of B (0.88 Å), the decrease in lattice constants implies that some C atoms substitute for B in the

Fig. 9 Partial XRD patterns of the mixture (1:2) unannealed **a** and annealed at 900 °C **b**, 950 °C **c**, 1200 °C **d**

W_2B and WB, respectively, forming solid solutions of C in W_2B and WB, which are denoted as $W_2B(C)$ and $WB(C)$, respectively. Based on above discussion, it is concluded that the amorphous W–B–C(I) crystallizes partially into

W₂B(C) and WB(C) solid solutions, respectively, as annealed at 900 °C, which also demonstrates that the W–B–C(I) consists of W, B and C.

In order to confirm that C can incorporate into WB at low temperature from thermodynamics point of view, we calculated the Gibbs energy and lattice constants of WB and WB(C) by the first-principle calculate. To stimulate this process, about 6% B atoms in WB are randomly replaced by C atoms, and the calculation result reveals that Gibbs energy decreases from –163.769 eV per unit cell of WB to –164.008 eV per unit cell of WB(C) and the lattice constant (*a*) decreases from 3.139 Å of WB to 3.092 Å of WB(C), indicating that C can incorporate into WB to form WB(C) solid solution and make lattice constants of WB decrease, which support our experimental results.

Figure 8c shows XRD pattern of the 80 h-milled mixture (1:2) annealed at 950 °C, indicating that most of the amorphous W–B–C(I) has crystallized. However, different from Fig. 8b, additional XRD peaks are observed only near diffraction angles of W and WB (PDF No. 04-0806, 35-0738), and no diffraction peak is observed near diffraction angles of W₂B or other phases. All the diffraction peaks move toward high diffraction angle direction in comparison with W and WB, as shown in Fig. 9c, where the red dash-dot and dot lines show diffraction angles of (200) plane of W and (200) plane of WB, respectively. Moreover, the peak intensity of the W increases obviously compared to that as shown in Fig. 8b. Based on analysis mentioned above, it can be deduced that the amorphous W–B–C(I) crystallizes into W and WB(C) solid solutions as annealed at 950 °C.

Since atomic radii of both B and C are smaller than that of W, the diffraction angle shifting for (200) plane of the W in Fig. 9c implies that some B and/or C substitute for W atom to form the solid solution of C and/or B in W [denoted by W(B, C)]. Since the sample contains solid solutions of W and WB(C), we cannot distinguish that the W solid solution contains B or C or both B and C, and only can deduce from the XRD results using Vegard's law.

The solubility (*x*) of C and/or B in the W can be estimated by modified Vegard's law [21],

$$r = xr_s + (1 - x)r_m, \quad (1)$$

where *r*, *r_s* and *r_m* are the atomic radius of solid solution, solute and solvent, respectively. Here, W is solvent and has atomic radius of 1.37 Å. The average atomic radius of W in W(B, C) can be estimated to be 1.368 Å by using XRD data of Fig. 8b. If the solute is B or C, the solubility of B or C in the W can be estimated by using Eq. (1) to be 0.4% and 0.3%, respectively. If both B and C are solute, we suppose that the B and C incorporate randomly into W at the atomic ratio of 13:2 and adopt mixed radius of B and C at the atomic ratio as radius of the solute; as such, the mixed

radius of B and C should be 0.87 Å. Using Eq. (1), the solubility of B and C in the W is estimated to be 0.4%, which is the same as the solubility of B in the W. These results are different from those reported previously [12], where B or C cannot incorporate into W at high temperature (> 1600 °C). This difference may be that the W(B, C) solid solution comes from crystallization of amorphous W–B–C(I) alloy at low temperature, which leads to a result that a trace amount of B and/or C remain in W. Resembling to Fig. 8b, the WB solid solution observed in Fig. 8c is WB(C) solid solution. The results of Fig. 8c and 9c indicate that the amorphous W–B–C(I) crystallizes into W(B, C) and WB(C) solid solutions as being annealed at 950 °C.

When the 80 h-milled mixture (1:2) is annealed at 1200 °C, it can be found from Figs. 8d and 9d that most of diffraction peaks appear at diffraction angles of the WB and three weak peaks at diffraction angles of W₂B₅, but no diffraction peak of W, C and C-related compounds is observed. These results indicate that the W reacted with the amorphous W–B–C(I) completely at 1200 °C to form WB and a small amount of W₂B₅, and C cannot incorporate into WB and W₂B₅, which are similar to some literatures reported previously [3, 12].

Figure 10a–d shows XRD patterns of the 80 h-milled mixture (1:5) unannealed and annealed at 900, 950 and 1200 °C, respectively. In order to see diffraction angle shift clearly, the partial XRD patterns of Fig. 10a–d in a diffraction angles of 55° to 65° are shown in Fig. 11a–d. It is found from Fig. 10b that the additional peaks appear near diffraction angles of the WB besides diffraction peaks near diffraction angles of W. Being similar to Fig. 8b, all diffraction peaks in Fig. 10b shift toward high diffraction

Fig. 10 XRD patterns of the 80 h-milled mixture (1:5) unannealed **a** and annealed at 900 °C **b**, 950 °C **c**, 1200 °C **d**

Fig. 11 Partial XRD patterns of the mixture (1:5) unannealed **a** and annealed at 900 °C **b**, 950 °C **c**, 1200 °C **d**

angle direction compared to diffraction angles of W and WB, as shown in Fig. 11b, where the red dash-dot and dot lines represent diffraction angles of (200) plane of W and (200) plane of WB measured with $\text{CuK}\alpha$ radiation, respectively. Referring to discussion on results of Fig. 8b and 9b, it can be concluded from Figs. 10b and 11b that the amorphous W–B–C(II) crystallizes partially into W(B,C) and WB(C) solid solutions as the 80 h-milled mixture (1:5) is annealed at 900 °C, which is different from the crystallizing products [W₂B(C) and WB(C)] of the amorphous W–B–C(I) annealed at the same temperature, indicating that the composition of the amorphous W–B–C has influence on crystallizing product. As annealing temperature reaches 950 °C, it can be concluded from Figs. 10c and 11c that the amorphous W–B–C(II) crystallizes almost completely into W(B,C) and WB(C). It is found by comparison of Fig. 11a–c that the diffraction angles of W(B,C) and WB(C) increase with increasing annealing temperature, indicating that the contents of B and/or C in the W(B,C) and of C in the WB(C) increase with increasing annealing temperature.

The lattice constant (*a*) of the W(B,C) obtained by annealing amorphous W–B–C(II) at 950 °C is calculated to be 3.162 Å, which is the same as that of W(B,C) (3.162 Å) obtained by crystallization of the amorphous W–B–C(I) at 950 °C, implying that the solubility of B and/or C in the W(B,C) is the same and only related to temperature but not to composition of the amorphous W–B–C. However, as for WB(C)s obtained by crystallization of amorphous W–B–C(I) and W–B–C(II) at the same annealing temperature, for example, 950 °C, although their lattice constants in *c* axis (*c*) are almost the same, but the lattice constants in *a* axis

(*a*) are different. The lattice constant (*a*) is 3.0731 Å for the WB(C) obtained by crystallization of amorphous W–B–C(II) but 3.1032 Å for WB(C) obtained by crystallization of amorphous W–B–C(I), which indicate that the C content is different for in the two WB(C) solid solutions and is affected not only by the temperature but also the composition of the amorphous W–B–C.

When the 80 h-milled mixture (1:5) is annealed at 1200 °C, it is found from Figs. 10d and 11d that its XRD pattern is the same as that of W₂B₅ reported in the previous literature (PDF No. 38-1365), and no XRD peak related to carbon and B₁₃C₂ is observed. The results of Fig. 10d and 11d indicate that the W reacts completely with the amorphous W–B–C(II) and the small amount of B₁₃C₂ to form W₂B₅ as the 80 h-milled mixture (1:5) is annealed at 1200 °C, and that the carbon cannot incorporate into W₂B₅ and may exist in the grain boundaries of the W₂B₅ or in a form of amorphous carbon.

3.3 First-Principle Calculation to Confirm Experimental Results

Based on the phase analysis on the crystallization products of the amorphous W–B–C and reaction products of W and the amorphous alloy, it is found that no tungsten carbide is observed, though the mixtures contain C. In order to explain these results from thermodynamics point of view, formation energies of tungsten borides and tungsten carbides are calculated by using first-principle calculation for three possible reaction processes between B₁₃C₂ and W, as listed in Table I. The formation energy of a system at 0 K can be calculated as

$$E_f = E_{\text{resultant}} - E_{\text{reactant}} \quad (2)$$

where $E_{\text{resultant}}$ and E_{reactant} are total energy of the resultant of the reactant at 0 K, respectively. It is found from Table 1 that formation energies of all tungsten carbides obtained in reaction (3) are positive, indicating that reaction (3) is much more difficult to occur than reactions (1) and (2). While the formation energy of the each tungsten boride obtained in reaction (1) is smaller than that obtained in reaction (2). Moreover, as mentioned above, the Gibbs energy of the solid solution of C in the tungsten boride is smaller than that of tungsten boride, and therefore, reaction (1) is much easier to perform than reaction (2) at the same condition, and the reaction products of B₁₃C₂ and W or crystallization products of the amorphous W–B–C should be solid solution of C in tungsten borides or tungsten borides and carbon, which is in agreement with our experimental results.

It is noted that the formation energy of the tungsten borides obtained in the reaction (1) increases with increasing B content, which implies that B-rich tungsten

Table 1 Calculated formation energies of W_2B , WB , W_2B_5 , WB_4 , WC and W_2C in three different reactions

Reaction (1)		Reaction (2)		Reaction (3)	
$B_{13}C_2 + W \rightarrow W_xB_y + C$		$B_{13}C_2 + W \rightarrow W_xB_y + WC$		$B_{13}C_2 + W \rightarrow W_xC + B$	
Comp.	Formation energy (eV)	Comp.	Formation energy (eV)	Comp.	Formation energy (eV)
W_2B	− 0.74454	W_2B	− 0.73936	W_2C	1.9418
WB	− 0.67874	WB	− 0.67874	WC	0.56659
W_2B_5	1.9513	W_2B_5	1.9772		
WB_4	2.2964	WB_4	2.3171		

borides is fabricated more difficultly than B-poor tungsten borides at low temperature, consistent with the present results, where the temperatures of formation of the $W_2B(C)$, $WB(C)$ and W_2B_5 are 900, 950 and 1200 °C, respectively, that is, formation temperature of the tungsten borides increases with increasing B content.

4 Conclusions

Amorphous W–B–C alloy was prepared by ball milling the mixture of metal W and $B_{13}C_2$ powders with nominal mole ratios of W to $B_{13}C_2$ of 1:2 and 1:5 in the milling period of 20 to 80 h, respectively. Its formation ability is related to the mole ratio, while its composition and volume fraction change with the ratio and milling time.

The $W(B, C)$, $W_2B(C)$ and $WB(C)$ solid solutions can be obtained by crystallization of the amorphous W–B–C alloys annealed at temperatures of 900 to 950 °C, which is much lower than the temperature of formation of tungsten borides reported previously. The crystallization products are related to the composition of the amorphous W–B–C alloys and annealing temperature.

As the 80 h-milled mixtures are annealed 1200 °C, no solid solution of C in W and tungsten borides, but only tungsten borides (WB and/or W_2B_5) are formed by reaction of W and the amorphous W–B–C alloy and/or a small amount of $B_{13}C_2$ left in the mixture. The structures of the tungsten borides are determined by the mole ratio of the mixtures.

The present work indicates that ball milling can decrease the formation temperature of tungsten borides and realize incorporation of C into tungsten borides and C and/or B into W at low temperature, which are also supported by first-principle calculation results.

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