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X–RAY DIFFRACTION STUDY OF W–B ELEMENTAL POWDER MIXTURES AFTER HIGH–ENERGY BALL–MILLING[1]

MIRKO STUBIČAR, ANTUN TONEJC and NADA STUBIČAR

Faculty of Science, University of Zagreb, Bijenička c. 32, P.O. Box 162, 41001 Zagreb, Croatia

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Very high temperatures are needed to prepare W-B compounds. However, the results obtained in this study demonstrate a possibility of inducing the formation of W_2B, WB or WB_4 tungsten borides, in air and at room temperature, using the high-energy ball-mill treatment on appropriate compositions of the W-B elemental powder mixtures. The present results throw a new light on the synthesis of tungsten borides, and on the accuracy of the equilibrium W-B phase diagram.

1. *Introduction*

The results of investigations described in numerous recently published papers clearly demonstrate that technically useful materials with functional properties, including preparation of new metastable materials such as amorphous, nanocrystalline and supersaturated crystalline solids, can be synthesized by utilizing the features of the mechanical alloying preparation technique [1,2]. This processing

[1] The authors dedicate the paper to Prof. Dr. Josef Schurz, head of the Inst. f. Physikalische Chemie der Karl-Franzens-Universität Graz on the occasion of his 70th birthday.

route often offers a direct access to the very origin of the consolidated products by influencing their characteristics in the embryonic powder state. It is also known that refractory compounds such as tungsten borides possess very high hardness, chemical inertness and metallic electrical conductivity, and hence they could be exploited as abrasive, corrosion-resistant, and electrode materials that can be exposed to particular environments [3]. Moreover, the formation (at higher temperatures) of various tungsten boride phases in the manufacture of boron filaments for structural composites for spacecraft and aircraft, possible according to the equilibrium phase diagram, has recently been reported [4]. In the present communication, the results of our study on high-energy ball–milling of powder mixtures of the W-B system are described. The compositions chosen were based on the well established phase diagram shown in Fig. 1 [5]. In the course of milling the changes in structure were studied by X-ray diffraction (XRD) technique.

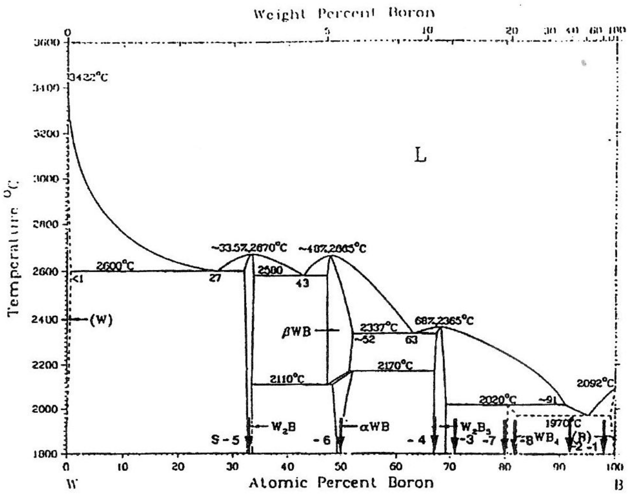

Fig. 1. The equilibrium W-B *phase diagram [5]. The arrows denote the compositions of elemental powder mixtures studied in the present work.*

2. Experimental

The starting materials for the preparation of tungsten boride powders were as follows: tungsten metal powder of about 1 μm mean particle size supplied by Korea Tungsten Mining Co.,Ltd., and boron powder, crystalline, with particle sizes smaller than 234 μm (60 mesh) from Alfa Products (Danvers, USA). The samples contained elemental boron and tungsten mixed at predetermined appropriate atomic ratios (Table 1) as shown in the phase diagram (Fig. 1). Mechanical alloying was carried out in a commercial planetary micro-mill (pulverisette 7) manufactured by Fritsch GmbH. Milling was done at room temperature and in air atmosphere, although some of the experiments were performed also in liquid ethanol medium.

The vessel and balls used for milling were made of sintered WC-Co material. A set of 10 balls of 10 mm in diameter and 4 balls of 12 mm in diameter were used. The weight ratio of balls to the amount of milled samples was kept constant and equal to about 20:1. After definite time intervals during milling, a small amount of powder was taken from the vessel to be used as a sample for XRD experiments. Structural changes in the prepared powder samples were followed by using a Philips PW 1820 diffractometer (graphite monochromatized CuK_α irradiation) in the appropriate region of Bragg's angles.

TABLE 1.
XRD identified crystalline phases coexisting in W-B powder mixtures during the high-energy ball-mill processing in air atmosphere.

Legend	W:B ratio	Milling times (min)							Cryst. phase
		10	30	60	90	150	210	300	
S-5(e)	2:1	s	s	s	s	m	m	m	W
			vw	vw	w	w	w	w	WC
						vw	w	vw	B_2O_3
S-6	1:1	s	s	s	m	w	w	vw	W
		vw	w	w	w	w	m	m	WC
			vw	vw	w	w	s	m	B_2O_3
						w	m	m	WB
S-4	1:2	s	s	m	w	w	vw	–	W
		vw	w	w	w	m	m	m	WC
			vw	w	w	m	w	vw	B_2O_3
				vw	vw	vw	vw	vw	WB
S-3	2:5	s	s	s	m	m	w	vw	W
		vw	vw	vw	w	w	w	w	WC
				vw	w	m	m	vw	B_2O_3
						vw	vw	w	WB
							vw	vw	WB_4
S-7	1:4	s	s	s	m	m	w	–	W
		vw	w	w	w	m	m	m	WC
			w	m	m	m	m	vw	B_2O_3
						vw	w	m	WB_4
S-8	2:9	s	s	s	m	w	vw	–	W
		vw	vw	vw	w	w	w	m	WC
				vw	w	w	w	m	B_2O_3
				vw	vw	w	w	m	WB_4
S-2	1:12	s	s	s	s	s	m	w	W
		w	w	w	w	w	w	w	WC
		vw	w	w	w	m	m	w	B_2O_3
						vw	vw	w	WB_4
S-1	2:98	s	s	s	s	m	m	w	W
		m	m	m	m	m	m	m	WC
		vw	w	m	m	m	s	m	B_2O_3
						vw	vw	w	WB_4

Remarks: (–) absent, (vw) *very weak,* (w) *weak,* (m) *medium,* (s) *strong,* (e) *milled up to 1020* min.

3. Results and discussion

Two series of experiments were performed. In the first, milling of samples was done in air atmosphere. Table 1 shows the structural changes, determined by XRD, which occurred during the milling process of the powder mixtures. For identification of the phases present in the samples, we used the data collected in the handbook [6]. At the early stage of milling, i.e. for milling times shorter than 10 minutes, samples showed similar XRD patterns. Namely, in this case XRD patterns exhibited peaks related to tungsten and/or boron components, depending on the mixture compositions. After 10 min of milling, WC peaks were observed in all samples, and B_2O_3 peaks in samples with higher content of boron. Figure 2 shows the changes in XRD patterns, taken from sample S-3, as a consequence of its milling in air. It is evident that after milling for 10 min, the presence of the WC phase was recorded. This means that the abrasion effect that occurred during milling is high. After 30 min of milling, the formation of cubic B_2O_3 and, in some cases, the presence of high-temperature WB was observed in XRD patterns. Further milling led to changes in XRD patterns, and new diffraction lines appeared for the same sample. We suppose that they belong to the WB_4 phase. Furthermore, a disappearance of W diffraction lines was observed only in some cases for prolonged milling times, while tungsten boride phases appeared as a consequence of the mechanical alloying process. Similar results were obtained for almost all mixtures; detailed results are shown in Table 1 and interesting XRD patterns are displayed in Fig. 3. Here, we would like to note that in the mixture denoted by S-5, the W_2B phase appeared only after prolonged milling (see comment to Table 1). Also, we were not able to synthesize the W_2B_5 phase. In this case (for mixture denoted by S-3), two coexisting phases were detected: WB and WB_4. The latter fact that WB and WB_4 were detected might be explained by the assumption that probably the W_2B_5 phase is a metastable phase. Thus, on the basis of the results shown in Table 1, and in Fig. 3, it follows that one can synthesize various tungsten boride phases, such as W_2B, WB or WB_4, from the appropriate elemental powder mixtures of the W-B system directly by applying the high-energy ball-mill processing in air atmosphere and at room temperature. Our results throw a new light on the synthesis of tungsten borides. Namely, it is well known that formation of these compounds is possible by applying a solid state reaction method. However, the processing temperature in that case has to be above 1000 °C [6,7]. Although the application of ball milling in our case seems to be very promising with regard to the possibility of saving high amounts of energy consumed for the preparation of tungsten borides, it is worth noting that we observed two inconvenient factors. The first relates to the excessive contamination of milled powders caused by the wear of balls and of the vial, and the second to the oxidation of boron. The second factor could be easily eliminated by applying a protective gas or liquid atmosphere. The first factor is inherent in the milling method, and its elimination requires designing of the milling equipment (both vial and balls) from an appropriate material. Finally, we would like to stress here that the analysis of the diffractometer patterns for the presence of various boride phases was not straightforward due to the presence of some additional milling products introduced into the milled samples by the abrasion and possibly by oxidation, which made the procedure applied for identification of all the coexisting phases difficult.

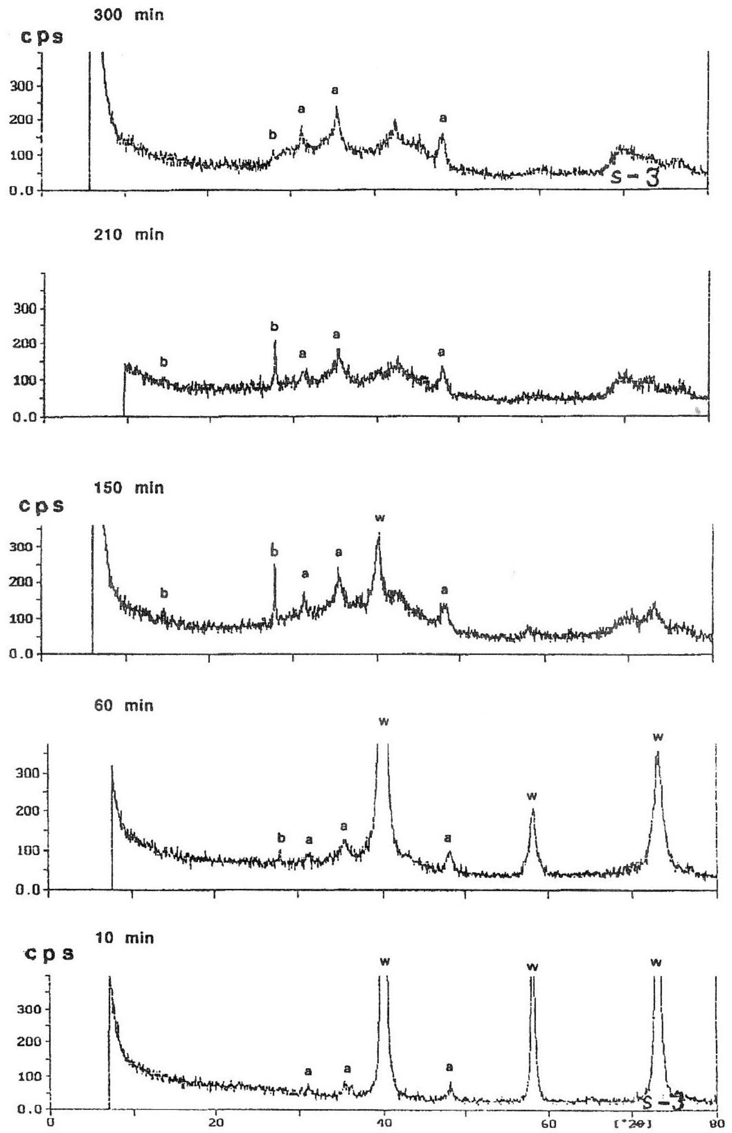

Fig. 2. Changes in the XRD pattern observed during the ball–mill processing of the powder mixture sample S-3, atomic ratio W:B=2:5 in air atmosphere and at room temperature. The numbers denote milling times, and the angular positions of observed diffraction lines belonging to the WC, cubic B_2O_3 and W phases that are marked with (a), (b) and (w), respectively.

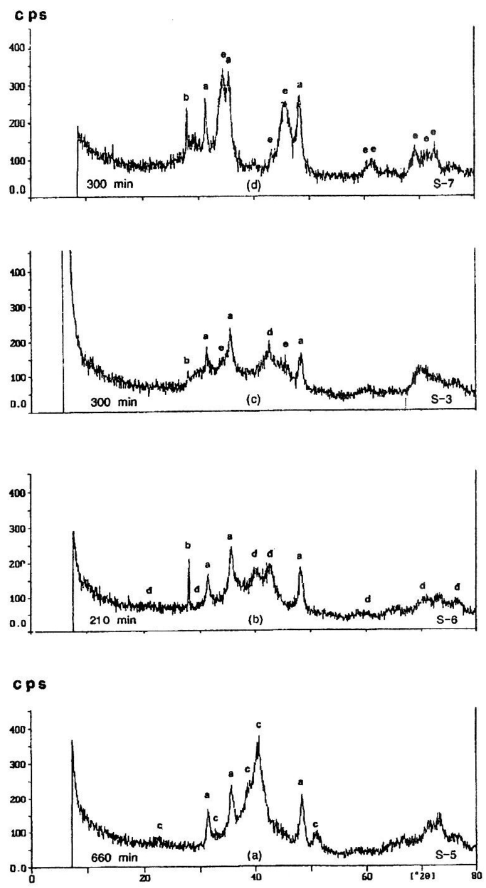

Fig. 3. XRD patterns taken from various powder mixtures milled in air atmosphere and at room temperature: (a) S-5 (W:B=2:1), (b) S-6 (W:B=1:1), (c) S-3 (W:B=2:5) and (d) S-7 (W:B=1:4). The numbers denote milling times; the angular positions of the observed diffraction lines belonging to the tungsten boride crystalline phases are marked as follows: (c) W_2B, (d) WB and (e) WB_4, while for those phases mentioned in Fig. 2 the same simbols are used.

4. Conclusions

Phase transformations that occur during high-energy ball milling of various W-B elemental powder mixtures were monitored by X-ray diffraction. In the scope of our results we emphasize the following:
(i) High-energy ball milling is a powerful processing method capable of inducing phase changes and involving the formation of W_2B, WB (high temperature) and/or WB_4 crystalline phases if powder mixtures have appropriate starting compositions.

(ii) For almost all mixtures studied, particularly in the early stage of milling, the oxidation of boron was registered. This oxidation can be avoided by using a gas or liquid protective atmosphere.
(iii) Excessive contamination of milled powders with WC was registered. This effect is inherent to the milling method. It is caused by the wear of balls and of the vial made with the same material.
(iv) It is interesting to note that the boron-enriched W-B milled powders showed a high chemical activity and a high self-compaction ability. Further studies of this system, including its processing in protective atmospheres, are now in progress.

Acknowledgement

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PROUČAVANJE METODOM RENDGENSKE DIFRAKCIJE SMJESA W–B SUSTAVA PRIPRAVLJENIH IZ TIH PRAHOVA NAKON INTENZIVNOG KUGLIČNOG MLJEVENJA

MIRKO STUBIČAR, ANTUN TONEJC i NADA STUBIČAR

Fizički odsjek, Prirodoslovno-matematički fakultet, Sveučilište u Zagrebu, Bijenička c. 32, Pošt. pret. 162, 41001 Zagreb, Hrvatska

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Vrlo visoke temperature potrebne su za sintezu W–B spojeva. Međutim, rezultati dobiveni u ovom radu ukazuju na mogućnost sinteze W_2B, WB ili WB_4 volframovih borida, na zraku i pri sobnoj temperaturi, pomoću procesa intenzivnog kugličnog mljevenja odgovarajućih W–B smjesa prethodno pripravljenih iz čistih prahova. Time je otkriven nov način sinteze volframovih borida, a istovremeno je i nešto utočnjen dijagram ravnotežnih stanja W–B sustava.