We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

4,800
Open access books available

122,000
International authors and editors

135M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

BOOK
CITATION
INDEX
CLARIVATE ANALYTICS
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter

Peculiarities of Refractory Borides Formation during Mechanical Alloying IV-V Group Transition Metals with Boron in Planetary Mill

Maria P. Savyak and Alex B. Melnick

Abstract

Mechanical alloying in the transition IV-V group metal-boron systems runs by the two following mechanisms: mechanically induced reaction of self-propagating synthesis determined by the enthalpy of refractory compound formation and capability to form substitutional solid solution through replacement of a metal atom by boron atoms; and diffusion-controlled process when a supersaturated interstitial solid solution prevails and its *bcc* lattice gradually transforms to the hexagonal lattice of the MeB_2 phase at a critical boron content. The domination of one of the above mechanisms is determined by capability of boron to form substitutional or interstitial solid solution. In the case of formation of combined (SSS and ISS) solid solutions, domination of a mechanism is determined by the interatomic bond strength as well as by the intensity of mechanical alloying. The method for calculation of the free Gibbs energy of the interstitial and substitutional solid solutions on the basis of the regular solution model was developed. It was shown that during milling tantalum and boron in a planetary mill, at first the formation of a combined solid solution occurs where two boron atoms replace one tantalum atom. Both the mechanisms of solid solution formation decrease the solution Gibbs energy. When a SSS dominates over the formation of an ISS, the Gibbs energy acquires a minimum value at a concentration of boron in tantalum of 50 at%, which leads to the solution decomposition.

Keywords: transition metals, refractory borides, Gibbs energy, solid solution, mechanical alloying, modeling

1. Introduction

Refractory metal borides have a high melting point, high thermal and electrical conductivity, low linear coefficient of thermal expansion, excellent corrosion resistance, and very high microhardness. Therefore, they attract much attention as promising materials for application. The potential application of such materials could be jet engine parts, armor plates, cutting tools, dies, etc. [1]. A large number of studies are devoted to these materials and in particular to methods for their preparation. As a rule, borides are obtained at high temperature and, therefore, the

grain size of the formed boride is big. However, high enthalpy of borides points that these compounds can be obtained at reduced temperature (for example, formation enthalpy ΔH (in kJ/mol) is 266 for TiB_2, 333 for HfB_2, 182–191 for TaB, 181–192 for TaB_2, 221 for NbB, 174 for NbB_2, 130 for VB, and 259 for VB_2 [2]). This can be performed with the help of a planetary mill where extremely high centrifugal forces appear under milling due to the disk and the vials rotation in the counter direction. Milling process of a solid state powder, where the powder particles are subjected to high energetic impacts by the balls in a vial, which involves repeated cold welding, fracturing, and rewelding of powder particles, is called mechanical alloying [3]. Numerous studies have been devoted to production of transition metal borides using a mechanical alloying [4–11]. This method allows one to obtain a nanocrystalline structure of these compounds, which helps to reduce the sintering temperature of borides to achieve a dense state of material. Ball milling can induce self-propagating reaction in such highly exothermic powder mixtures as boron and a transition metal. This process is called the self-propagating mechanically induced synthesis (SMS) [4]. SMS is characterized by ignition temperature T_i, at which the self-propagating reaction begins, and temperature T_m, to which the powder is heated between the ball collisions. The latter increases at the expense of the kinetic energy of the balls. As established experimentally, such an increase takes place up to 350°C, which is not enough to initiate the SMS process. In the standard SMS process $T_i > T_m$ and, hence, no ignition occurs. However, T_i decreases during the milling process under the action of several factors: the particles are refined, chemically active defects emerge, new dislocations and interfaces show up, etc. So when $T_i < T_m$, ignition does occur. Therefore the question arises: what initiates the SMS process in mechanical alloying of borides? One of the reasons is stresses arising in the metal due to various defects of dislocations and solid solutions induced in the metal during milling. Therefore, it is necessary to carefully study the structural changes in the metal after milling. The peculiarities of structure transformation under milling transition metals with boron have not clarified yet. The mechanisms of SMS during formation of the transition metal borides by mechanical alloying are still under discussion as well. It has been established that in the course of mechanical processing of Nb + B mixtures, formation of boron-in-niobium solid solution takes place followed by gradual precipitation of the NbB_2 phase [8]. However, questions concerning the influence of the structure and atom size on the peculiarities of boride formation during mechanical alloying have been scarcely considered so far. The transition metals of group IV Ti, Zr, and Hf have a *hexagonal close-packed* (*hcp*) structure while the transition metals of group V Nb and Ta have a *body-centered* (*bcc*) structure, which is characterized by a bigger free volume (space fill factors are 0.74 and 0.68, respectively). The group VI metals Cr, Mo, and W have a *bcc* structure as well, but their atoms are much smaller compared to group V metals and possess a stronger interatomic bond, which is confirmed by far higher Young modulus.

We selected the Ta-B system with different tantalum-to-boron ratios as a model to study the peculiarities of structure transformation under milling transition group V metals (*bcc* structure) with boron and Ti-B system as a model to study the peculiarities of structure transformation in the *hcp* structure.

The aim of the work was to study what phases can form during mechanical alloying of transition metals with different crystalline structures with boron in a planetary mill and how much the phase formation depends on the metal structure, the metal/boron atom size relationship, and the peculiarities of mechanical alloying process and to develop a model of solid solutions formation during milling using the Ta-B system as an example.

2. Experimental procedure

High purity tantalum and niobium powders with 10–60 μm particles were used. They were produced at the "Silmet" metallurgical plant by electrolytic reduction with hydrogenation and dehydrogenation for further purification. Titanium powder was produced at the Zaporizhzhya titanium-magnesium plant with a specific surface area of 0.1 m^2/g brand TG-T$_B$ (−2 + 1) mm, zirconium (Dneprodzerzhinsky PA "PCP") was obtained by the calcium thermal method, vanadium by thermal dissociation of vanadium iodide. Black amorphous boron powder (B-99 grade, as per 1-92-15490) with a specific surface area of 11.2 m^2/g was used. The brand of such black amorphous boron powder was obtained by gaseous boron halogenide reduction with hydrogen. The metal-to-boron atoms ratio depended on a specific metal-boron compound to be produced: MeB (1Me:1B), and MeB$_2$ (1Me:2B). Milling was performed in an argon medium in a planetary mill AIR 015 M, which provides an acceleration of 45 g at an rotation speeds of the disk and vials of 735 and 1840 rev/min, respectively. The balls-to-powder mass ratio was 20:1. XRD analysis was carried out on an installation DRON3 under copper Ka radiation. Broadening analysis of X-ray reflections estimated the coherent scattering domain (CSD) and the crystal lattice microdistortion ε. The microstructure was studied using a transmission electron microscopy (TEM) JEM-100CX. The steel balls were pre-milled with boron and tantalum at the same time as the process of milling was 50 min. Therefore, contamination of steel material was minimal. In the case of milling within 10 min, the contamination of iron was 0.4 mass%. The iron worn off from the milling balls was removed with HCl leaching under the effect of ultrasonic stirring.

## 3. Experimental results

3.1 Ti-B

Using titanium as an example, let us consider how borides are formed during milling *hcp* metals of group IV with boron. **Figure 1** demonstrates changes in XRD patterns of Ti-B (1:2) mixture depending on the milling time. The change in the crystal lattice volume of titanium after milling with boron, calculated by the Rietveld method, is shown in **Figure 2.** As seen, the lattice volume of titanium noticeably decreases after 5 min milling. Under milling, titanium undergoes significant plastic deformation, which is confirmed by the texture in the plane of the easiest slip (002) in **Figure 1b**. Boride phase nucleation occurs after 6 min of milling, therefore the lattice volume of titanium increases (**Figure 2**). Titanium completely transforms into titanium diboride TiB$_2$ after 7 min milling (**Figure 1d**). The electron microscopic studies showed that milling of powder mixtures Ti-B for 6 min leads to extraction of nanodisperse allocation no larger than 3–5 nm in the shells of particles. TEM microphotographs of obtained TiB$_2$ are shown in **Figure 3**. Flat, greatly loosened along the edges polycrystalline particles are the main components after 7 min milling. These particles consist of nanodisperse grains of titanium diboride. The main range of the grain sizes is 3–10 nm; however, there are also areas where they reach 15–20 nm. To estimate the effect of boron on the change in the crystal lattice volume of titanium after milling, we milled pure titanium powder in argon. We did not observe any formation of texture during milling of pure titanium; also, we did not reveal any changes in the size of the titanium crystalline lattice after 5 and 6 min milling.
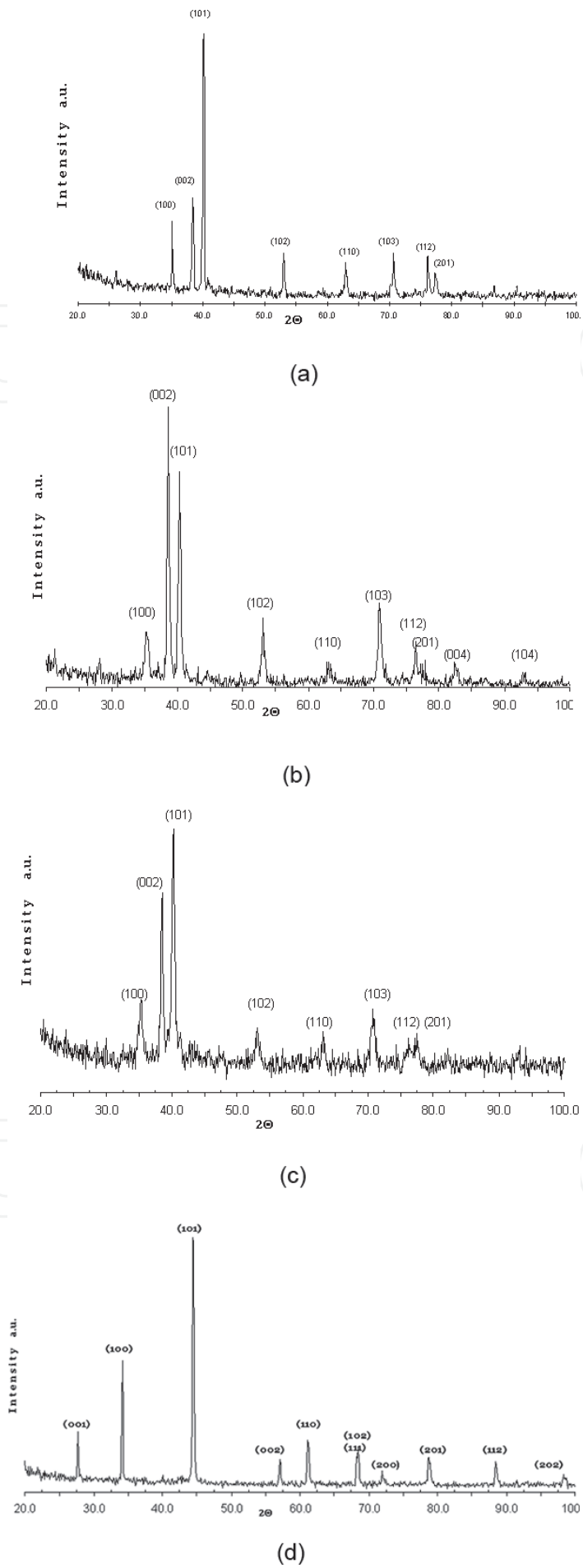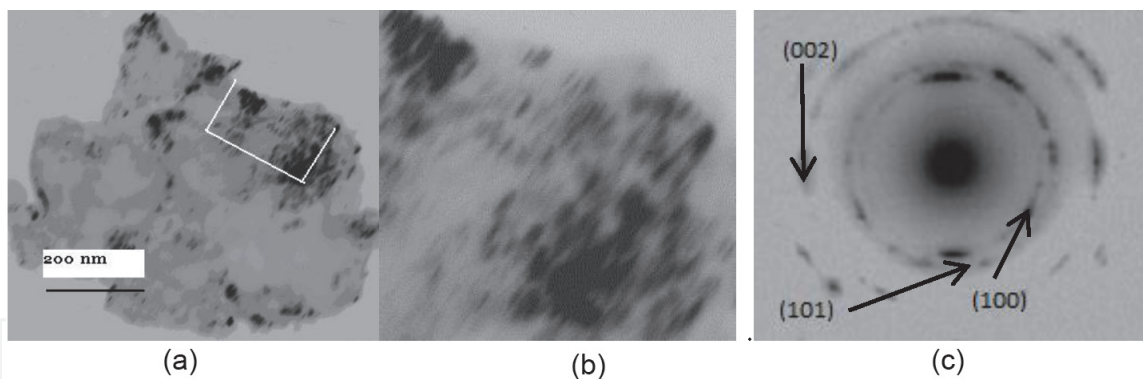
Figure 1.
XRD patterns of Ti-B mixture in the initial state (a), upon milling for (b) 5, (c) 6, and (d) 7 min (the indices a, b, c denote Ti, and d TiB$_2$).

3.2 Zr-B

Zirconium like titanium has the *hcp* structure. Zirconium diboride is formed in the same way as TiB$_2$. XRD patterns of ZrB$_2$ formed upon 6 min milling of Zr-B mixture are shown in **Figure 4**.
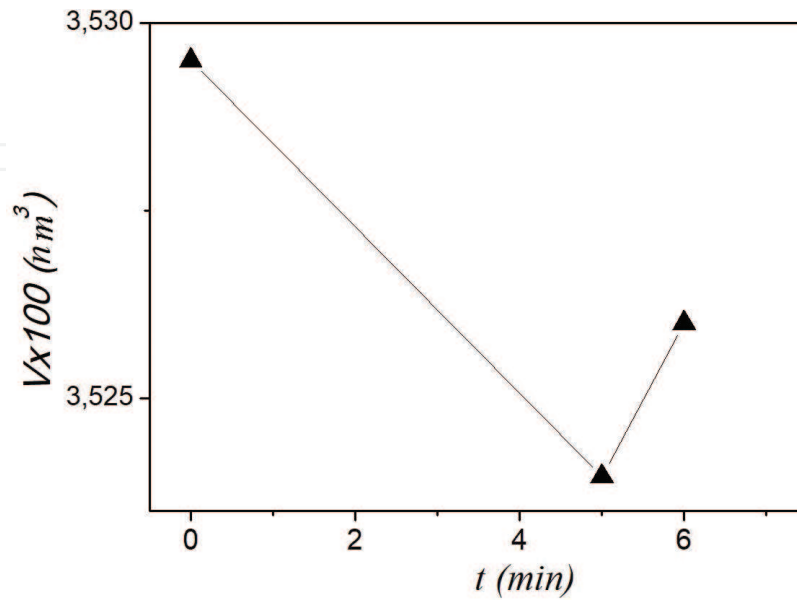
Figure 2.
Change in the crystal lattice volume of titanium after milling with boron calculated by the full-profile Rietveld method [9].

Figure 3.
TEM microphotograph of TiB$_2$ obtained upon milling Ti and B powders: (b) increased area accented in (a); (c) microelectron diffraction pattern.
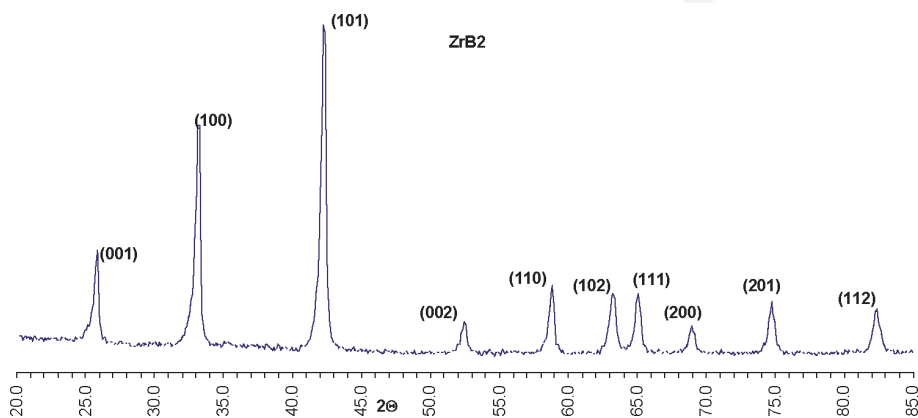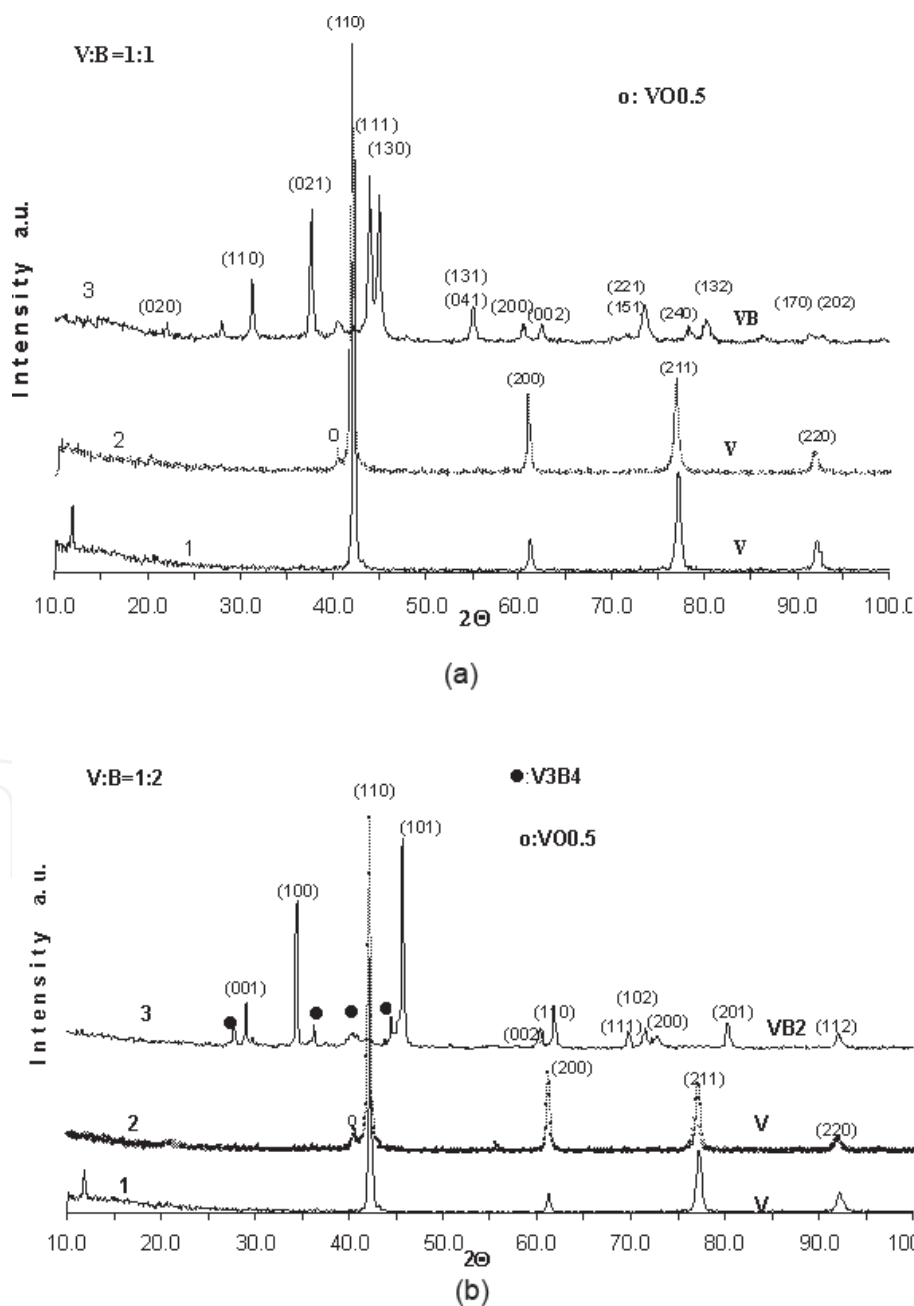

Figure 4.
XRD patterns of ZrB2 formed upon 6 min milling of Zr-B powders.

5

3.2.1 Milling of bcc group V metals with boron

A peculiarity of the group V transitions metals is that they have a *bcc* structure, in which there is much more free volume in comparison with the close-packed structures.

3.3 V-B

Figure 5 shows changes in the XRD patterns of V-B mixtures depending on the milling time at V:B ratios of 1:1 and 1:2. The diffraction lines shift toward smaller angles within 5 min milling, which indicates an increase in the lattice parameters at the both atomic ratios of the components. The vanadium lattice parameter (a = 0.3028 nm) for V:B = 1:1 after milling with boron for 5 min increases and is equal to 0.3034 nm. Within 20 min milling, the V:B = 1:1 mixture transforms into
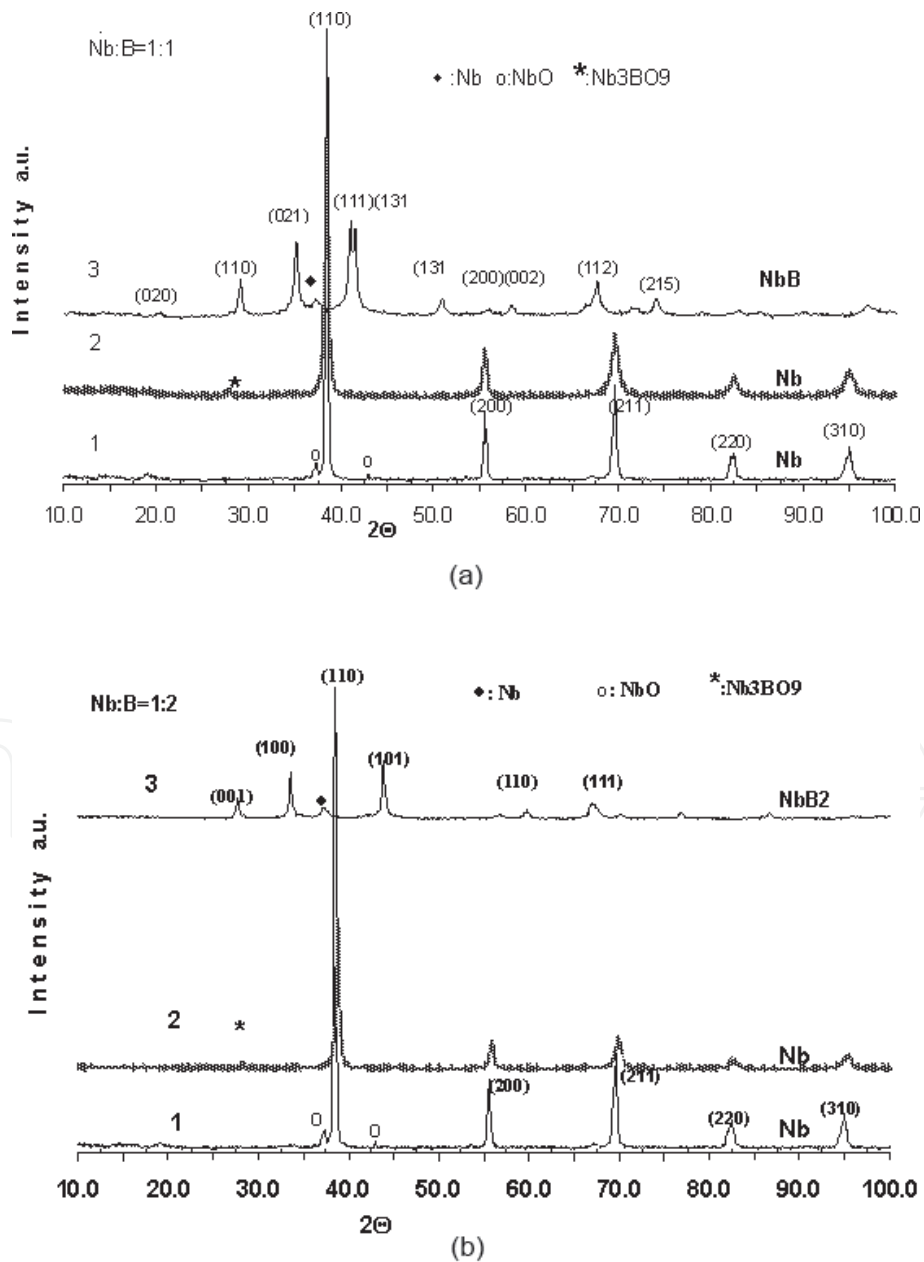

Figure 5.
XRD patterns of V-B powders upon milling for (a) (1) 0, (2) 5, (3) 20 min, (b) (1) 0, (2) 5, (3) 15 min [the indices on lines 2 denote V, on lines 3: (a) VB, (b) VB2].

the VB phase extremely rapidly, whereas the V:B = 1:2 mixture does into the VB_2 phase upon 15 min milling.

3.4 Nb-B

XRD patterns for the transformation of niobium into the borides NbB and NbB_2 under milling Nb-B mixtures are shown in **Figure 6**. Unlike vanadium characterized by increasing the lattice parameter within 5 min milling, in this case, at the ratio Nb:B = 1:1, the lattice parameter does not change, whereas at the ratio Nb:B = 1:2, it reduces and is equal to 0.3293 nm (a = 0.3300 nm for Nb), which indicates the formation of a substitutional solid solution. After niobium transformation into borides, in the XRD patterns, a strong niobium line (110) appears, shifted toward smaller angles, that is, the lattice parameter increases. This remaining niobium with an increased lattice parameter is evidence to the existence of parallel mechanisms of formation of boron-in-niobium solid solutions: on the one hand, a SSS is formed,

Figure 6.
XRD patterns of Nb-B mixture upon milling for (a) (1) 0, (2) 5, (3) 20 min, (b) (1) 0, (2) 5 and (3) 15 min [the indices on lines 1 denote Nb, on lines 3: (a) NbB, (b) NbB2].

which leads to a decrease in the lattice parameter; on the other hand, an ISS is formed, which leads to the lattice parameter increasing.

3.5 Ta-B

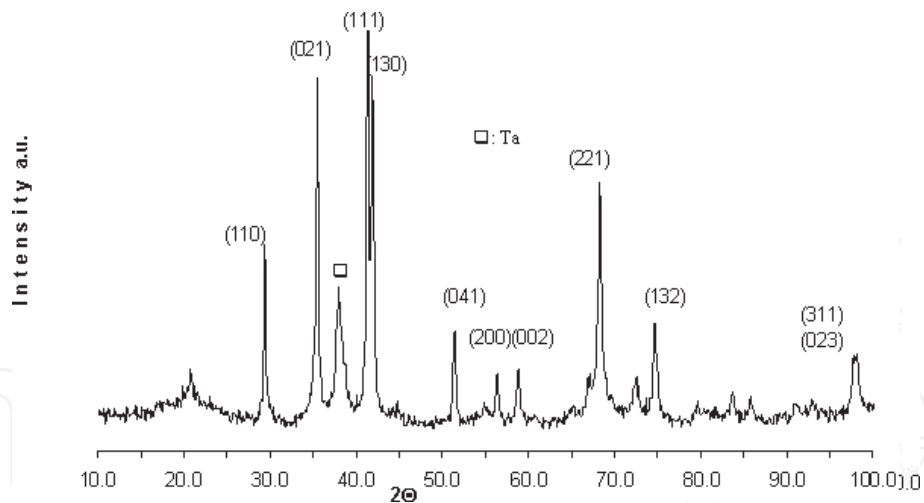### 3.5.1 Powder mixture at the atomic ratio Ta:B = 1:1

In the case of 5 min milling of the Ta:B = 1:1 mixture, the resulted structure is defective, which is confirmed by weakening and broadening X-ray lines with remaining their positions (**Figure 7**). After 8 min milling, the tantalum lines positions are still the same (**Figure 8**). The 10 min milling transforms the tantalum powder into TaB with residual tantalum, whose line (110) is shifted toward smaller angles (**Figure 9**), which indicates that the lattice parameter increases owing to the formation of an interstitial boron-in-tantalum solid solution under milling. The facts that the tantalum lattice parameter does not change after milling for 5 and 10 min and that there is residual tantalum with increased lattice parameter after 10 min milling may be indicative of running two processes in parallel which differently influence the lattice parameter. Therefore, it can be assumed that both interstitial and substitutional solid solutions of boron in tantalum can be formed under milling. The lattice parameter in the Ta:B = 1:1 mixture increases for ISS and decreases for SSS. The powder mixtures containing 50 at% B show no change in the lattice parameter.
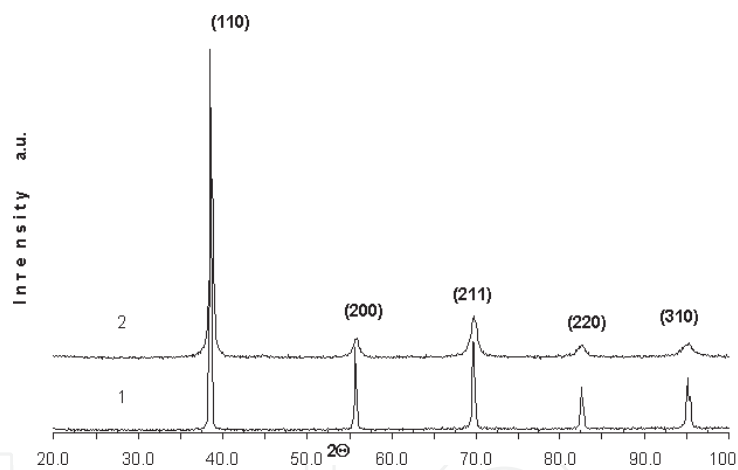
Figure 7.
XRD patterns of Ta:B = 1:1 powder mixture: before milling (1) upon milling for 5 min (2) (the indices in **Figures 7** *and 8 denote Ta).*
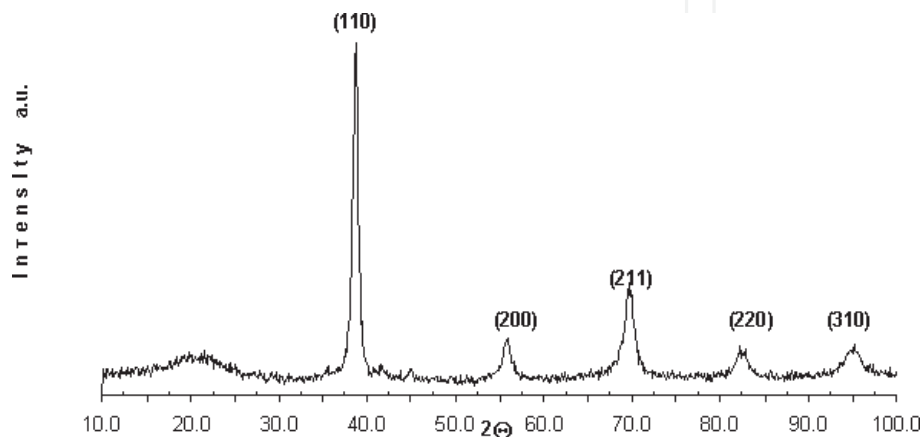
Figure 8.
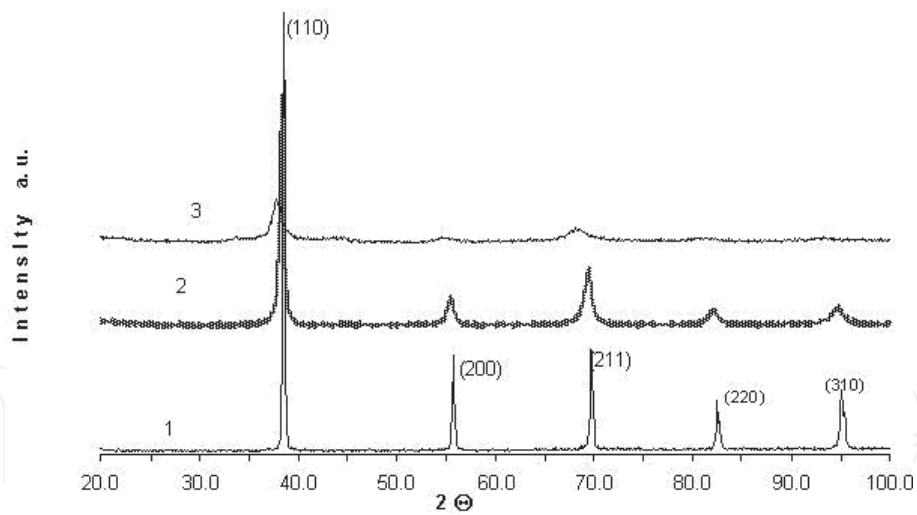*XRD patterns of Ta:B = 1:1 powder mixture upon 8 min milling.*

Figure 9.
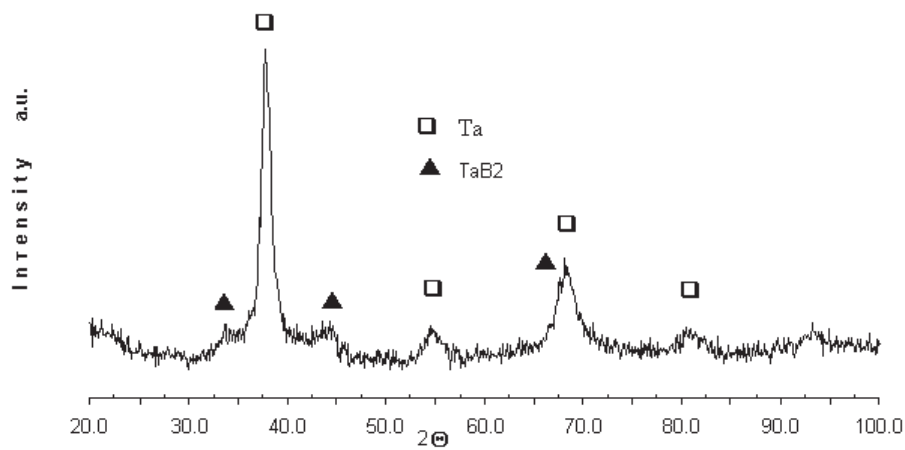*XRD patterns of Ta:B = 1:1 powder mixture upon milling for 10 min (the indices denote TaB).*

3.5.2 Powder mixture at the atomic ratio Ta:B = 1:2

Figure 10 compares XRD patterns recorded from powders milled during different periods of time. As low-intensity peaks for the mixture milled for 15 min are not seen in pattern 3 (**Figure 10a**) because of the scale factor, this pattern is enlarged in **Figure 10b**, where one can see the peaks corresponding to the TaB_2 phase. After milling for 5 min, the lines shift toward smaller angles and reveal that the lattice parameter changes from a = 0.3302 nm to a = 0.3315 nm, which indicates the fact of formation of an ISS. The intensive milling of the Ta:B = 1:2 powders for 5 min leads, like for Ta:B = 1:1 mixtures, to tantalum lattice distortion, which is confirmed by the broadening the X-ray lines and a lower intensity of reflection peaks under the impact of shock loads and shear deformation in the milling process. For the Ta:B = 1:2 mixture milled for 5 min, coherent scattering domain (CSD) size D is 28.91 nm and distortion ε is 0.004578. **Figure 11** shows XRD patterns from the Ta:B = 1:2 mixture milled for 15, 30, and 50 min. Milling for 15 min leads to an increase in *bcc* lattice distortion ε to 0.02394 with no significant change in the CSD size. The tantalum diboride lines appear as well. Therefore, the solvent metal lattice undergoes transformation (so-called concentration polymorphism) during the formation of a supersaturated solid solution. When milling time increases to 30 and 50 min, the tantalum diboride lines become more intensive. The results of performed calculations are the following: the lattice parameter *a* of the initial tantalum powder is 0.3303 nm and increases to 0.3314 nm after milling for 5 min, to 0.3364 nm for 15 min, and to 0.3368 nm for 50 min.

As established in [12], the change in the lattice parameter Δ*a* to 0.0018 nm corresponds to the dissolution of 10 at% B. In this work, Δ*a* is 0.0011 nm after 5 min milling, which corresponds to 7 at% B. The intensive milling of Ta and B powders can induce significant lattice distortion, which promotes diffusion of boron atoms into tetrahedral pores in the tantalum *bcc* lattice with the formation of an ISS, the decomposition of which leads to the appearance of hexagonal tantalum diboride (AlB_2 type). The diboride formed after 50 min milling is characterized by the following lattice parameters: *a* = 0.3086 nm and *c* = 0.3254 nm. The tantalum diboride has CSD D = 3.73 nm and distortion ε = 0.007851. In view of the above, one can conclude that occupation of tetrahedral pores in the tantalum *bcc* lattice becomes more preferable when boron concentration increases to 66 at%, which breaks the equilibrium between the SSS and ISS existing at 33 and 50 at% B. The lattice parameter increases after this mixture is milled for 5 min.
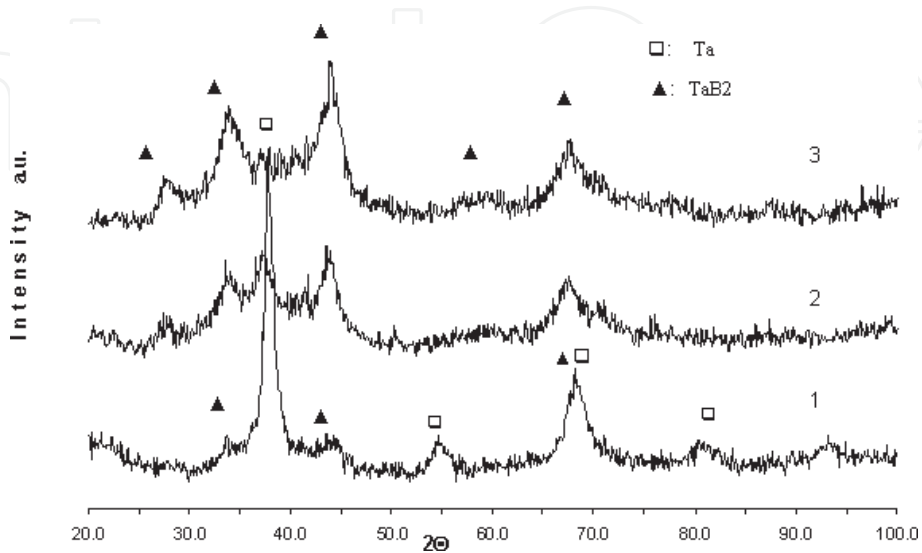
9

Figure 10.
XRD patterns of Ta:B = 1:2 powders in the initial state (1), upon milling for 5 (2), and 15 (3) min (the indices in a denote Ta). (b) Enlarged scale of above pattern 3 in (a).

Figure 11.
XRD patterns of Ta:B = 1:2 powders mixture upon milling for 15 (1), 30 (2), 50 (3) min.

3.6 Modeling for process of boron-in-tantalum solid solution formation

In order to produce stable solid solutions, the authors first estimated stability of boron-in-tantalum ISS and SSS through determination of their Gibbs energy with taking into account that the latter is formed by the elastic energy (owing to the distortions in solid solutions) and the enthalpy of the system milling. Then, the solid solutions were studied in the frame of the regular solution model [13], using the following formula for the enthalpy of mixing n component alloys [14]:

$$\Delta H_{mix} = \sum_{\substack{i,j=1 \\ i \neq j}}^{n} c_i c_j \Omega_{ij}, \tag{1}$$

where Ω_{ij} is a parameter characterizing the interaction between i and j elements in a regular solution; $\Omega_{ij} = 4\Delta H_{mix}^{ij}$, c_i is the atomic fraction of the ith element; ΔH_{mix}^{ij} is the enthalpy of mixing for binary equiatomic alloys.

According to the Boltzmann hypothesis, the entropy of mixing n elements in a regular solution can be expressed as follows:

$$\Delta S_{mix} = -k_B \sum_{i=1}^{n} c_i \ln (c_i), \tag{2}$$

where c_i is the atomic fraction of the ith element, and k_B is the Boltzmann constant.

The solid solutions are crystals with a distorted lattice because their atoms have different sizes. Elastic distortions, arising from size discrepancy, can affect the free energy of the alloy as well. It is important to take into consideration different factors that contribute to the total enthalpy, such as the elastic energy ΔH_{el} and mixing enthalpy ΔH_{mix}:

$$\Delta H = \Delta H_{mix} + \Delta H_{el}, \tag{3}$$

We consider that the atomic volumes and local bulk moduli for solid solutions correspond to those for single-component systems. Since the components have different sizes, the lattice becomes distorted. Taking $\overline{V}$ as an average atomic volume of the solid solution, we will write equations for distortion of different atoms: $\varepsilon_1 = (V_{Ta} - \overline{V})/\overline{V}$ is the tantalum atom distortion in the absence of interstitial atoms nearby, $\varepsilon_2 = (2V_B - \overline{V})/\overline{V}$ is the distortion of two boron atoms when they replacing one tantalum atom in the *bcc* lattice in the absence of interstitial atoms nearby and V_{Ta} and V_B are the atomic volumes of tantalum and boron, respectively. Since two boron atoms and one replaced tantalum atom are commensurable in volume, it can be assumed that boron causes minimum distortion. It can penetrate into octahedral and tetrahedral pores of the *bcc* lattice. Then distortion of the interstitial boron atom will be $\varepsilon_3 = (V_B - Vp)/Vp$ (V_p is the pore volume). Finally, distortion of the tantalum and boron atoms that replace them in the presence of m interstitial atoms nearby will become $\varepsilon_4(m) = (V_{Ta} - (\overline{V} - m\alpha Vp))/(\overline{V} - m\alpha Vp)$ and $\varepsilon_5(m) = (2V_B - (\overline{V} - m\alpha Vp))/(\overline{V} - m\alpha Vp)$, respectively.

Here α is the parameter that characterizes the pore volume fraction corresponding to one tantalum atom. We take into account that $V_p = \frac{2}{3}\overline{V}$ and

$\alpha = 1/6$ in case of an octahedral pore and $V_p = \frac{1}{6}\overline{V}$ and $\alpha = 1/4$ in case of a tetrahedral pore. If the lattice is stable, its stresses are compensated and the following equation is valid:

$$c_1 B_{Ta}\varepsilon_4(m-1)\big(\overline{V}-(m-1)\alpha V_P\big)+c_2 B_B\varepsilon_2\overline{V}+c_3 B_B\varepsilon_5(m-1)\big(\overline{V}-(m-1)\alpha V_P\big)$$
$$+\,c_4 B_{Ta}\varepsilon_4(m)\big(\overline{V}-m\alpha V_P\big)+c_5 B_B\varepsilon_5(m)\big(\overline{V}-m\alpha V_P\big)=0$$

$$(4)$$

where B_{Ta} and B_B are the bulk moduli for tantalum and boron. If c_{Ta} is the atomic fraction of tantalum in the solution and c_{Bs} and c_{Bi} are the atomic fractions of boron in substitutional and interstitial states, then the concentration coefficients for SSS and ISS with boron in octahedral pores will be as follows:

$$c_1 = c_{Ta}\left(1-\frac{6c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}+INT\left[\frac{6c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}\right]\right);$$

$$c_2 = \frac{c_{Bs}}{2}\left(1-\frac{6c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}+INT\left[\frac{6c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}\right]\right);$$

$$c_3 = c_{Bi};$$

$$c_4 = c_{Ta}\left[\frac{6c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}-INT\left[\frac{6c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}\right]\right];$$

$$c_5 = \frac{c_{Bs}}{2}\left(\frac{6c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}-INT\left[\frac{6c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}\right]\right);$$

And for SSS and ISS with boron in tetrahedral pores:

$$c_1 = c_{Ta}\left(1-\frac{4c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}+INT\left[\frac{4c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}\right]\right);$$

$$c_2 = \frac{c_{Bs}}{2}\left(1-\frac{4c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}+INT\left[\frac{4c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}\right]\right);$$

$$c_3 = c_{Bi};$$

$$c_4 = c_{Ta}\left[\frac{4c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}-INT\left[\frac{4c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}\right]\right];$$

$$c_5 = \frac{c_{Bs}}{2}\left(\frac{4c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}-INT\left[\frac{4c_{Bi}}{c_{Ta}+\frac{c_{Bs}}{2}}\right]\right);$$

Function $INT[x]$ specifies the integer part of x.

Eq. (4) can be used to obtain the expression for average atomic volume V of the solution and calculate distortion energy H_{el}:

$$H_{el} = \frac{1}{2}\left(c_1 B_{Ta}\varepsilon_1^2\overline{V}+c_2 B_B\varepsilon_2^2\overline{V}+c_3 B_B\varepsilon_3^2 Vp+c_4 B_{Ta}\varepsilon_4^2\big(\overline{V}-m\alpha Vp\big)+c_5 B_B\varepsilon_5\varepsilon_5^2\big(\overline{V}-m\alpha Vp\big)\right)$$

$$(5)$$

In this case, the equation allowing for change in the free Gibbs energy in transition to the solid solution state is as follows:

$$\Delta G = 4c_{Ta}(c_{Bs}+c_{Bi})\Delta H_{mix}^{TaB}+H_{el}-k_B T\big((c_{Bs}+c_{Bi})\ln(c_{Ta})+c_{Ta}\ln(c_{Bs}+c_{Bi})\big).$$

$$(6)$$

To calculate the composition dependences of ΔG for the substitutional and interstitial solid solutions with boron in octahedral and tetrahedral pores, the bulk moduli and atomic volumes of elements were taken from [15] and the mixing enthalpy ΔH_{mix}^{TaB} for the Ta-B equiatomic alloy from [16]. **Figure 12** demonstrates the change in the Gibbs energy for boron-in-tantalum solid solution. The deviation in the lattice parameter a of the solution relative to the lattice parameter a_{Ta} of pure tantalum is determined as

$$\chi = \frac{a}{a_{Ta}} = \sqrt[3]{\frac{\overline{V}}{V_{Ta}}}.$$

The concentration dependence for χ is presented in **Figure 13**. As shown in **Figure 12**, both mechanisms decrease the solution energy. The SSS reaches minimum ΔG at 50 at% B, while the ISS at 33 at% B. Consequently, a combined solid solution may be stable at <50 at% B. The ISS with boron in octahedral pores can be formed only in the presence of the SSS (**Figure 12b**), but the ISS with boron in tetrahedral pores is more likely to appear.
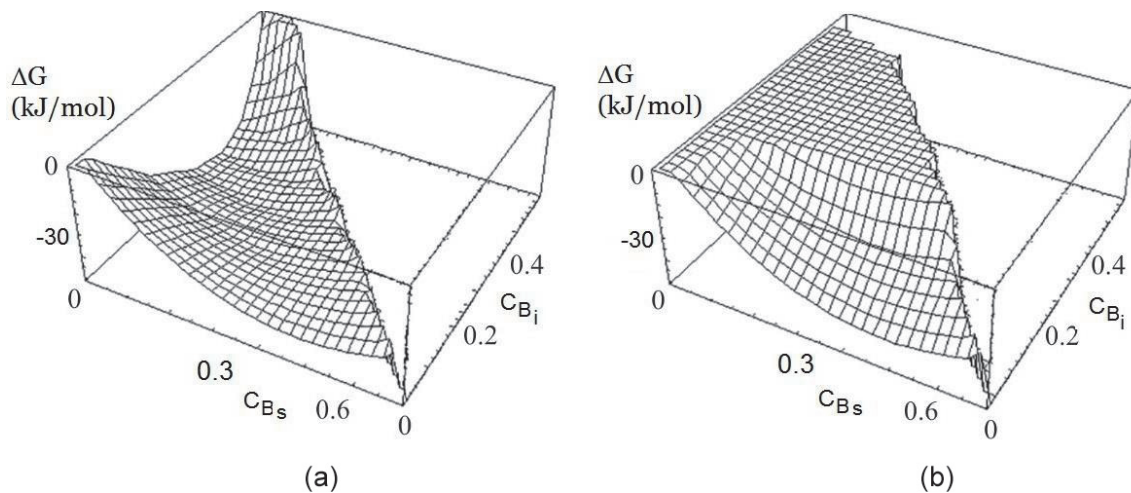
Figure 12.
The calculated Gibbs free energy of solid solutions (ΔG) for combined Ta-B solid solution with boron in tetrahedral (a) and octahedral (b) pores in the bcc lattice of Ta (c_{Bs} and c_{Bi} are the concentrations of substitutional and interstitial boron atoms, respectively).
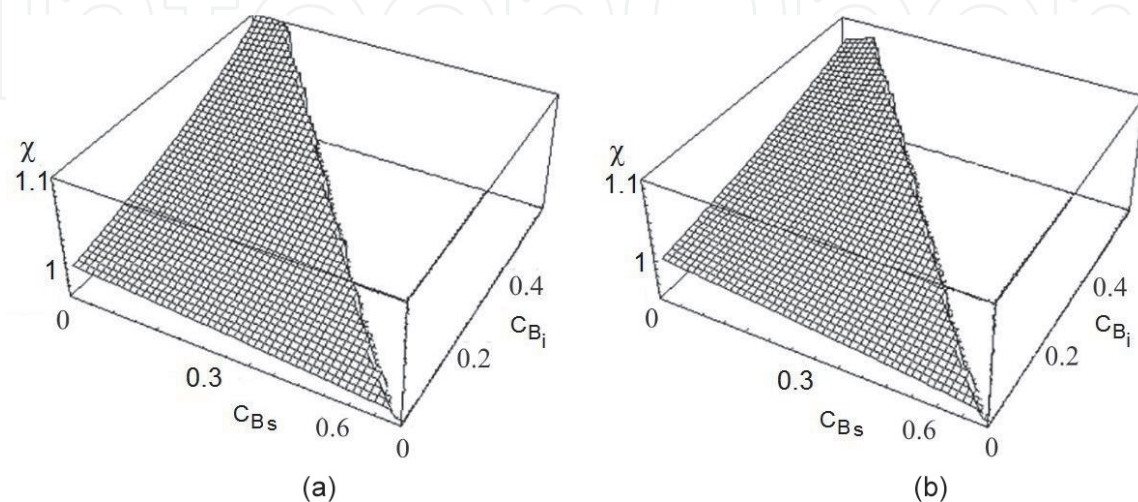
Figure 13.
Change in the parameter χ of the combined (substitutional and interstitial) Ta-B solid solution with boron in tetrahedral (a) and octahedral (b) pores in the bcc lattice of Ta (c_{Bs} and c_{Bi} are the concentrations of substitutional and interstitial boron atoms, respectively).

The parameter χ decreases for the substitutional mechanism and increases for the interstitial mechanism. A greater its increase is observed when boron atoms occupy tetrahedral pores.

3.7 Discussion of results

Modeling for process of formation of boron-in-tantalum solid solutions allows a supposition that the formation of SSS under intense milling of Me-B mixtures in a planetary mill takes place owing to replacement of a metal atom by two (or three for zirconium and hafnium) boron atoms. The possibility of SSS formation through replacement of a metal atom by two boron atoms is due to their close sizes [so-called Goldschmidt criterion (G.c.)]. G.c. was calculated if suppose that two or three boron atoms take place a metal atom knocked out of the crystal lattice under milling according to the formula.

$$G.c. = \frac{2at.v.B - at.v.Me}{at.v.Me} \; x \; 100\% \leq 15\%,$$

where (*at.v.*) is atom volumes for transition metals (*at.v. Me*) and boron (*at.v. B*).

The G.c., atom volumes, and Young moduli for transition metals of IV–VI groups are presented in **Table 1**. G.c. is valid for all of the transition metals except Gr. As for the Young modulus, it is very high for tungsten and molybdenum. That is why those atoms cannot be knocked out of the crystal lattice under milling. Also, a marked difference in the niobium and tantalum Young moduli explains the domination of SSS over ISS in the Nb + 2B mixture in our case. However, under the conditions of less intense milling, ISS prevails [10].

Taking into account the atom volumes for transition metals and boron, one can reveal that replacement of a vanadium atom by two boron atoms results in some increase in the lattice parameter, whereas replacement of a tantalum (as well as niobium and titanium) atom by two boron atoms results in decreasing lattice parameter (**Table 1**). Hagg's rule (rB/rMe ≤ 0.59) for the ISS formation is fair for tantalum and niobium; therefore, in the Ta-B and Nb-B systems, there are also observed ISS, in addition to SSS. For the V-B system, rB/rMe = 0.63, that is, Hagg's rule is not obeyed, so here only SSS can be formed. As the transition metals of group IV Ti and Zr have a *hcp* structure, there cannot be formed ISS. That is why we observed decreasing lattice volume of titanium after 5 min milling with boron. It is min that in this cause only SSS is formed.

In addition, the modeling has showed that at 50 at% B in Ta, the Gibbs energy is minimal. Perhaps at the same boron concentration, an abrupt formation of the TiB_2, VB, VB_2, NbB, NbB_2, and TaB phases occurs due to the minimal SSS stability. The presence of lattice sites replaced by two or three boron atoms in the *bcc* or *hcp* metal lattice facilitates the further transformation of the solid solution into the borides MeB and MeB_2 by cooperative mechanisms under the action of internal strains. This

Group	B	IV			V			VI		
Me		Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W
Young modulus, GPa		120	98	141	131	105	186	279	325	415
Atomic volume, cm³/g-atom	4.6	10.6	14.1	13.4	8.3	10.3	10.9	7.3	9.4	9.5
G.c.		13%	2%	+3%	+11%	11%	15%	21%	2%	3%

Table 1.
Young's modulus, atom volumes for boron and transition metals, and Goldschmidt criterion for SSS formation.

is conditioned by the facts that a prototype of chain and ring structures of borides is formed yet in the solid solution, and the significant heat release connected with high enthalpy promotes a reaction running in the regime of mechanically induced self-propagating synthesis. When the fraction of boron atoms incorporated into tetrahedron voids overcomes that taking part in replacement of metal atoms, gradual decomposition of ISS, and the appearance of the TaB_2 take place.

4. Conclusions

The formation of a particular phase under milling in a planetary mill of *hcp* metals (Ti and Zr) and *bcc* metals (V, Nb, and Ta) with boron depends on the physical-chemical properties of starting powders, enthalpy of formation of the final product, and on the intensity of milling process. Depending on these conditions, processes of mechanical alloying in the Me-B system run by the two following mechanisms: mechanically induced reaction of self-propagating synthesis determined by both the enthalpy of refractory compound formation and the capability to form a substitutional solid solution through replacement of a metal atom by boron atoms, and diffusion-controlled process when a supersaturated interstitial solid solution prevails and its *bcc* lattice gradually transforms to the hexagonal lattice of the MeB_2 phase at a critical boron content. The domination of one of the above mechanisms is determined by capability of boron to form substitutional or interstitial solid solution. In the case of formation of combined (ISS and SSS) solid solutions (Ta-B and Nb-B), domination of one of the above mechanisms is determined by the interatomic bond strength, that is, by the Young modulus, as well as by the intensity of milling. The method for calculation the free Gibbs energy of the interstitial and substitutional solid solutions with the regular solution model was developed. It was shown that during milling tantalum and boron powders mixture in a planetary mill, at first the formation of a combined (interstitial and substitutional) solid solution occurs where two boron atoms substitute one tantalum atom. Both the mechanisms of solid solution formation decrease the solution Gibbs energy. When a substitutional solid solution dominates over the formation of an interstitial solid solution, the Gibbs energy acquires a minimum value at a concentration of boron in tantalum of 50 at%, which leads to the solution decomposition and to formation of TaB compound.

Author details

Maria P. Savyak[1*] and Alex B. Melnick[2]

1 Frantsevich Institute for Problems of Materials Sciences, National Academy of Sciences of Ukraine, Kyiv, Ukraine

2 G.V. Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine

*Address all correspondence to: mari_saviak@ukr.net

IntechOpen

References

[1] Gild J, Zhang Y, Harrington Y, et al. High-entropy metal diborides: A new class of high-entropy materials and a new type of ultrahigh temperature ceramics. Scientific Reports. 2016;**6**: Article number: 37946

[2] Moiseev GK, Ivanovsky AL. Standard enthalpies of forming related compounds in the metal–boron systems. Izv. Chelyab. Nauch. Ts. 2005; **29**(3):5-9

[3] Suryanarayana C. Mechanical alloying: A novel technique to synthesize advanced materials. Research Official Journal of Cast. 2019. DOI: 10.34133/2019/4219812

[4] Takacs L. Self-sustaining reactions induced by ball milling. Progress in Materials Science. 2002;**47**:355-414

[5] Oghenevweta JE, Wexler D, Calka A. Sequence of phase evolution during mechanically induced self-propagating reaction synthesis of TiB and TiB_2 via magnetically controlled ball milling of titanium and boron powders. Journal of Alloys and Compounds. 2017;**701**(15): 380-391

[6] Jalaly M, Gotor FJ. A new combustion route for synthesis of TaB_2 nanoparticles. Ceramics International. 2018;**44**(1):1142-1146

[7] Gurcan K, Ayas E, Gaşan H. Formation of TaB_2 powders from high energy ball milling and borothermal reduction process. Materials Chemistry and Physics. 2019;**235**:121732. DOI: 10.1016/j.matchemphys.2019.121732

[8] Savyak MP, Melnick AB, Vasil'kivska MA, Timofeeva II, Ivchenko VI, Uvarova IV. Mechanical synthesis of tantalum borides and modeling of solid solutions of boron in tantalum. Powder Metallurgy and Metal Ceramics. 2018;**57**(7–8):373-383

[9] Savyak MP, Melnick AB, Solonin YM, Kotko AV, Timofeeva II, Uvarova IV. Mechanosynthesis of nanodispersed titanium diboride. Powder Metallurgy and Metal Ceramics. 2014;**53**(9–10):497-504

[10] Iizumi K, Sekiya C, Okad S, Kudou K, Shishido T. Mechanochemically assisted preparation of NbB_2 powder. Journal of the European Ceramic Society. 2006;**26**: 635-638

[11] Morris MA, Morris DG. Competition between amorphous or intermetallic phase formation during ball-milling. Journal de Physique Colloques. 1990;**51**(14):151-155

[12] Kiessling R. The borides of tantalum. Acta Chemica Scandinavica. 1949;**3**:603-615

[13] Zhang B, Liao S, Xie H, Yuan X, Shu X. A subregular model for calculating the mixing enthalpies in 10 binary IIB–IIIB alloy systems. Europhysics Letters. 2010;**89**(5): 56002-56016

[14] Takeuchi A, Inoue A. Calculations of mixing enthalpy and mismatch entropy for ternary amorphous alloys. Materials Transactions. 2000;**41**: 1372-1378

[15] Web Elements Periodic Table: The Periodic Table on the Web. Available from: http://www.webelements.com/

[16] Takeuchi A, Inoue A. Classification of bulk metallic glasses by atomic size difference, heat of mixing and period of constituent elements. Materials Transactions. 2005;**46**:2817-2829