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# Mechanical Activation of Ti-2B System: XRD Investigation of Structural Features

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## Abstract

XRD investigation of Ti-2B system was carried out with the purpose of determining of structural changes in this system during mechanical activation. The size of coherent-scattering region (CSR size) and kind II stresses (microstresses) were calculated by diffraction peaks profile analysis. It was determined that initiation of the synthesis reaction directly in mill is taking place at achievement the value of microstresses for titanium approximately equal to its yield point. Spontaneous reaction in a mill indicates that mechanical activation gives essential structural changes in Ti-2B system. So mechanical activation has essential influence on structural condition of Ti-2B system. Titanium diboride synthesized by high-temperature combustion and by mechanosynthesis have approximately equal crystallites size. These results could clarify the processes of materials structural condition after mechanical activation and have a matter for materials science.

## 1. Introduction

Mechanical activation (MA) and its influence on various materials is a popular field for investigation in present time [1–4]. The reason of that is the preliminary MA allows to realize combustion for low-exothermic systems. Mechanically activated powders are ignited at lower temperatures and have higher combustion velocity than non-activated ones. It is also known that some system can react directly in mill (mechanosynthesis) and there is an interest to material synthesis during activation [1, 5]. The main differences between classic combustion and mechanosynthesis are heat dissipation and materials deformation.

The Ti-2B system has been studying earlier and increasing of combustion velocity for mechanically activated samples was determined [6]. However, structural changes for MA of Ti-2B system are not presented in literature and it seems to be important part of this system studying. It is also supposed that product synthesized directly during MA will have essential structural differences from the product synthesized by combustion synthesis.

So the aim of the work is to determine the relationships in Ti-2B system structural features (size of coherent-scattering region and microstresses) depending on duration of MA. Another objective was to compare product ($TiB_2$) obtained by combustion synthesis and mechanosynthesis.

## 2. Experimental

Commercial powders of Ti (PTM) and amorphous (black) boron were used as initial materials. Ti + 2B powder mixtures were mechanically activated during various times in AGO-2 planetary mill (acceleration is 90 g, ball/mill ratio is 20/1). The samples were characterized by XRD on ARL X'TRA diffractometer (Cu-$K_\beta$ radiation) with time exposition of 5 sec and DRON-3M, Cu-$K_\alpha$ radiation. Instrumental factor for line broadening were found by using LaB6 (SRM 660A).

Diffractometer ARL X'TRA was used for XRD patterns recording; β-lines were investigated for more precision measurement without necessity approximating functions for $K_\alpha$ doublet.

The size of coherent-scattering region (CSR size) and microstresses were estimated by profile analysis of diffraction peaks by using BUREVESTNIK

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software. The following lines for titanium were used in calculations: (100), (002), (101), (102), (110). The separation of contributions from CSR size and micro-stressing into line broadening were carried out by Williamson-Hall method [7]. Using the Cauchy function for description of diffraction line profile, we obtain $\beta = n + m$, where $n$ and $m$ are the contributions of lattice distortion and particles dispersion to the line broadening. Using the known dependences of $n$ and $m$ on the diffraction angle $\theta$:

$$\mathbf{n} = 4\left\langle \frac{\Delta \mathbf{d}}{\mathbf{d}} \right\rangle \mathbf{tg}\theta, \qquad \mathbf{m} = \frac{\mathbf{K}\lambda}{\mathbf{D}\cos\theta}$$

where $\left\langle \frac{\Delta d}{d} \right\rangle$ is the lattice distortion, and **D** is the mean CSR size, and **K** is the form-factor (equal to 1). Thus we obtain the equation

$$\beta\cos\theta = \frac{\lambda}{\mathbf{D}} + 4\left\langle \frac{\Delta \mathbf{d}}{\mathbf{d}} \right\rangle \sin\theta$$

and plot the dependence βcosθ = φ(sinθ) for above-mentioned diffraction lines. Than we obtain values of the slope and intercept from received plots and finally values of CSR (D) and microstresses ($\sigma$) were obtained. The microstresses ($\sigma$) were calculated taking into account elastic modulus:

$$\sigma = E\left\langle \frac{\Delta d}{d} \right\rangle$$

In calculations, we used the tabulated values of elastic modulus: 112 GPa for Ti and 500 GPa for $TiB_2$. The contribution of CSR size for titanium is appeared to close to zero. So, we believe that a key role in broadening of the titanium diffraction lines is played by microstresses.

## 3. Results and discussion

XRD patterns (Cu-$K_\beta$ radiation) of Ti+2B mixtures obtained at various time of mechanical activation are presented in Fig. 1. Amorphous boron was used in mixtures so no diffraction reflexes of boron on XRD patterns. It is seen that half-width of titanium lines have increasing with MA time; intensity ratio is also has changes at increasing of MA time. Chemical reaction and formation of $TiB_2$ is taking place at 9 min of MA. Ti+2B reaction takes place simultaneously in all the volume of mill after achievement of some parameters limits. This is the reason of appearing of the XRD peaks not gradually.

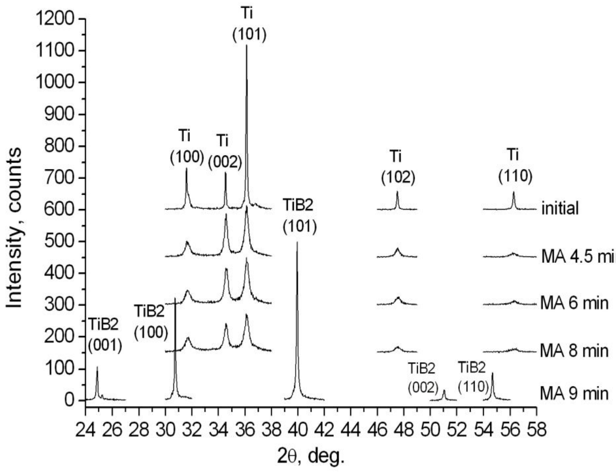

Fig. 1. XRD patterns of Ti+2B obtained at various time of MA.

Figure 2 shows micro-stresses in titanium as a function of MA time. We suggest that in this case a key role in broadening of the diffraction lines of titanium is played by kind II stress. The value of microstresses for titanium are increasing with MA time and reaches maximum of 500 MPa (at 8 min of MA).

Considering that titanium lines broadening are caused only by microstresses, one can suggest that crystallite size for titanium exceeds 1 micron. So there is no dispersion of titanium particles due to its high ductility. The value of microstresses in titanium attained 500 MPa before spontaneous reaction in a ball mill. This value is close to yield point of titanium (480–580 MPa). So the maximum of microstresses for titanium corresponds to its yield point, and after this value the reaction of titanium and boron occurred directly in mill.

It is known that MA of Ti+2B mixture results in formation of agglomerate particles consisting of interleaved titanium and boron layers [7]. Good contact between the components in these agglomerates yield to good reactivity.

Intensity decreasing of titanium lines (Fig. 1) with MA time increasing is provided by partially amorphization of titanium caused by growing of structure imperfection. This results to significant increasing of diffusion processes and accelerating of chemical interaction of titanium and boron.

Spontaneous interaction between titanium and boron directly in mill indicates on significant structural changes in Ti-2B system at mechanical activation. Ignition of Ti+2B mixture in a mode of thermal explosion occurs at 500–700 °C. There is no reaction at lower temperature because insufficiently diffusion mobility of atoms, but mechanical activation can improve it.

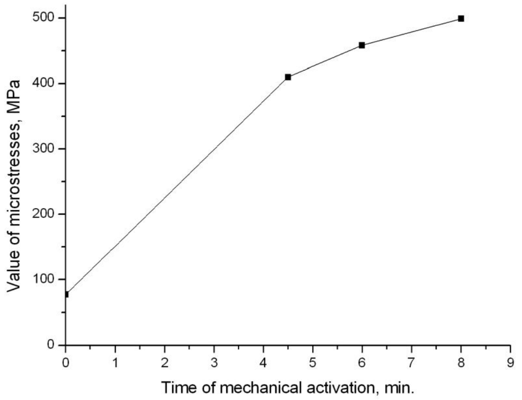

Fig. 2. Value of microstresses for titanium as a function of MA time.

Synthesis during MA (mechanosynthesis) could be considered as two-staged process: (1) intermixing of components on a cluster level and (2) chemical reaction with product formation [1]. In the system investigated a limiting factor is product formation that occurs at achievement of critical deficiency for titanium. Based on our results we can suggest the following reasons of chemical reaction during MA in Ti-2B system. The first one, it is essential increasing of contact area in activated compound. The second one, mechanical activation results to decreasing of titanium crystallinity rate during partially amorphization. The presence microstresses with value attained the yield point indicates to plastic deformation of titanium and thus significant increasing of structural deficiency. Structural defects and amorphization in titanium yield to accelerating of diffusive processes and overcoming of thermal barrier for chemical interacting between titanium and boron. Similar results were obtained for mechanical activation for another systems [2, 4]. So it is clear that during mechanical activation the amorphization and defects accumulation in compounds structure proceeds markedly faster.

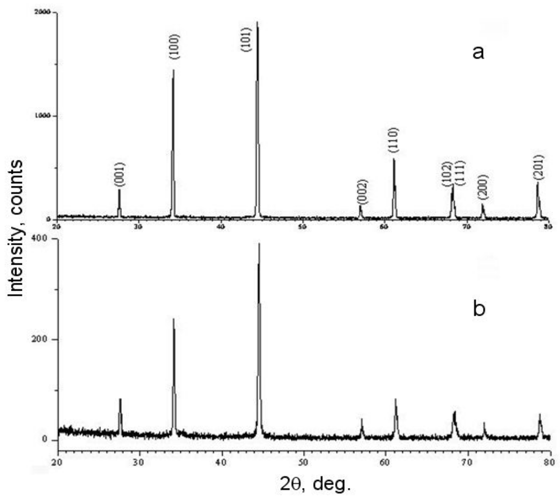

Fig. 3. XRD patterns of $TiB_2$ obtained by combustion synthesis (a) and mechanosynthesis (b).

XRD patterns of $TiB_2$ obtained by different methods (combustion synthesis and mechanosynthesis) are presented in Fig. 3.

Calculation results of CSR size and microstresses depending on synthesis mode are presented in Table 1.

These results indicate that CSR size for $TiB_2$ obtained by combustion synthesis and mechanosynthesis have approximately equal CSR size (crystallites size) – 200–300 nm.

**Table 1**

CSR size and microstresses for $TiB_2$ obtained by different methods

| $TiB_2$ synthesis mode | CSR size, nm | microstresses, MPa | CSR size*, nm |
|---|---|---|---|
| Mechanosynthesis | 300 ± 50 | 60 ± 30 | 220 ± 50 |
| Combustion synthesis | 180 ± 40 | 40 ± 30 | 160 ± 40 |
| * – calculation was carried out in the assumption of microstresses absence. | | | |

## 4. Conclusion

Mechanical activation has essential influence on structural condition of Ti-2B system. Initiation of the synthesis reaction directly in mill is taking place at achievement the value of microstresses for titanium approximately equal to its yield point. Titanium diboride synthesized by high-temperature combustion and by mechanosynthesis have approximately equal crystallites size. These results could clarify the processes of materials structural condition after mechanical activation and have a matter for materials science.

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