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Influence of Mechanical Activation on Synthesis of Compounds in the B/C - Mg/Al/Ca System

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Abstract

The possibility of mechanochemical synthesis and influence of mechanical activation on thermal synthesis of borides and boron carbides of mass-low metals is investigated. The opportunity of mechanochemical synthesis in the mill AGO-2 of such compounds as AlB_2 and CaC_2B_2 is established. Influence of mechanical activation in the mill SPEX 8000 on synthesis of such compound as $Mg_{0.5}Al_{0.5}B_2$ is shown. Mechanical activation also influences on the process of thermal synthesis: compound $Mg_{0.5}Al_{0.5}B_2$ is obtained in the conditions inaccessible to traditional thermal synthesis; formation of compound $Mg_{1-x}Al_xB_2$ in literature up to $x = 0.4$ was established on shifts of reflexes (002) and (110) pure MgB_2 aside the large corners; in our case $x = 0.5$ and as it was necessary to expect shifts of these reflexes exceeds shifts measured in literature only for $x \leq 0.4$.

Features of synthesis in systems containing metal magnesium are considered. The opportunity of application of crystalline boron for mechanochemical synthesis of borides and boron carbides of mass-low metals is established, that it was not represented probable to make in its ceramic synthesis. We revealed also that thermal analysis in conditions of helium results in crystallization almost all activated samples, and the analysis of received X-ray reflexes unambiguously allows to assert that mechanical activation accelerates synthesis of reaction products in the investigated systems in comparison with the traditional methods of its synthesis.

Introduction

Let's remind in brief of new materials on the basis of boron, synthesized and investigated during 1970-1990 years. Set of researchers (K. Spear, I. Higashi, M.Kh. Shorshorov, H. Werheit, M.S. Borovikova, P.S. Kisly, A. Guette, V.G. Aleshin, H.C. Ku, G.V. Samsonov, A.K. Niessen, J. Bauer, P. Rogl, F. Thevenot, C.N. Guy, A.A. Uraz, G. Bliznakov, Yu. B. Kuz'ma, W. Rodewald, H.M. VanNoort, H.M. VanNoort, H.M. VanNoort, I.D. Dragieva, B. Rauschenbach, D. Teneva, R. Pummer, R. Grossinger, S.Y.Jaang, M.Q. Huang, M. Jurczyk, K.H.J. Buschow, F.Pourarian, D. Mercurio-Lavaud, Z. Zakhariev, S. Motojima, F. Spada, E.K. Storms, V.S. Sinel'nikova, P. Peshev, L. Leyarovska, M.S. Koval'chenko, J.A. Avlokhashvili, R.A. Alfintseva, V.S. Postnikov, A.S. Bolgar, K. Nakano, T. Lundstrom and their co-authors) and published mainly in *Journal of Less Common Metals* ≡ *Journal of Alloys and Compounds* (see. also [1-3], their properties and scopes). The different modifications of elementary boron and numerous of its compounds belong to the group of materials called "boron-rich solids". They exhibit a close relationship in view of their crystal structures, because all of them contain B_{12} icosahedra or related aggregates of atoms as essential common structural elements. Since these icosahedra determine essentially the electronic structure and hence the chemical bonding of these solids, a large similarity of their chemical and physical properties can be expected. Because this assumption can be taken as proved, at least as far as such investigations have been performed, the generalization of properties determined on single representatives for the entire group of solids seems admittable to a certain extend. General properties of boron-rich solids: high melting points (2000 – 4000 K) - *e.g.* boron carbide about 2.900 K; great hardness - at ambient temperatures 2000 – 4500 kPa/mm^2 -β-rhombohedral boron is the hardest elementary crys-

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tal after diamond, and boron carbide is after diamond and cubic boron nitride the third hardest solid at all; low density; *e.g.* boron carbide 2.5 $g \cdot cm^{-3}$; small thermal extension coefficient - *e.g.* boron carbide $5.73 \cdot 10^{-6}$ K^{-1}; high resistance to chemical attack, hence low corrosivity; high neutron absorption cross section, caused by the ^{10}B isotope (enrichment in natural B about 20%); semiconducting behaviour. Some of these properties offer the prerequisites for technical use under extreme conditions, which are not admittable for most other materials. Moreover, the relationship of properties of this large group of structurally related solids allows the selection or tayloring of specific properties for particular uses. But this needs a detailed knowledge on the properties and their relation to the structural details. To gain this knowledge, is the objective of present investigations.

After opening of high-temperature superconductivity in MgB_2 at 39 K [4] and ferromagnetism in CaB_2C_2 up to 770 K [5], interest to connections of boron and carbon as to sources of new materials, has increased [6-8]. Besides considerably less appreciable has passed opening a new material with the record convertibility of hydrogen in a system of the easiest elements [9] (obviously, that alternative beryllium can be only boron).

On the other hand, technology of obtaining, say, nano-crystal abrasive or magnetic boron-rich solids, difficult enough [10]: synthesis in melts - high-speed quenching - crystallization of an amorphous product in vacuum furnaces - milling. Therefore the idea of mechanochemical synthesis of borides with obtaining of a ready material is not new [2], and was realized mainly at obtaining of borides of the transitive and heavy elements (borides of the groups of iron, manganese, chromium, vanadium, titanium, etc.). Mechanochemical synthesis of the borides of easy elements (such as Mg, Al, Ca, Sc, Si, C, N, P, S) has remained practically not investigated [11]. Moreover, exist preconditions of realization of synthesis of the such borides by means of mechanically stimulated reactions (MSR) in a regime of burning, as the thermal effect (-ΔH, in kcal/mole, see [12]) synthesis of such borides from elements makes, for example, for: MgB_2 (-ΔH = 22.0), AlB_{12} (48.0), NB and S_2B_3 (60.3) and their interval practically coincides with the heat of classical MSR synthesis [6 - p. 365] of Al_xNi_y (28.3 ÷ 67.5). Realization of MSR of synthesis under pressure of hydrogen with the purpose of synthesis of a complex hydrides of borides of mass-low elements will result in even more negative values ΔH [13]. Besides experimental researches MSR will serve in these systems essential help for the further theoretical research and modelling of MSR, begun recently [14-20].

Therefore, taking into account the available and again opened prospects of obtaining of the new materials [4-6] on a basis of borides of easy elements, the urgency of a problem of their synthesis and hydrogenation [9] by means of MSR [11,13] now does not cause doubts.

Experimental

Preliminary we shall specify known conditions of synthesis of these compounds: MgB_2 samples in [4] were prepared from powdered Mg and amorphous B, the powders were mixed, ground and pressed into pellets, the pellets were heated at 973 K under a high argon pressure (196 MPa) using a hot isostatic pressing furnace for 10 hours; $Mg_{1-x}Al_xB_2$ in [6] – the starting materials were bright Mg flakes, fine Al powder, and sub-micrometre amorphous B powder, materials were lightly mixed in half-gram batches, and pressed into pellets, the pellets were placed on Ta foil and fired in a tube furnace under a mixed gas of 95% Ar + 5% H_2, the samples were heated for 1 hour at 873 K, 1 hour at 1073 K, and 1 hour at 1173 K, after cooling, they were pressed into pellets and fired for an additional 2 hour at 1173 K, then quickly cooled to room temperature; CaC_2B_2 samples in [5] were prepared from Ca shot, amorphous powder B, and powder C, the starting materials were mixed in an argon glovebox, pressed into pellets, and placed in a wrapped Ta tube, the pellets were then heated in two ways – (i) at 1323 K for 20 hours in 2000 atm of an argon atmosphere in a hot isostatic pressing furnace, and (ii) at 1323 K for 30 hours in vacuum quartz tube, in both cases, reddish-brown powders of CaC_2B_2 were obtained.

In mechanochemical reactors P-T conditions [14-16] are close to specified [4-6], therefore we have studied an possibility of realization of synthesis of borides and boron carbides of easy metals in ball (steel, weight 0.253 g, radius R = 0.2 cm, a variation of number N = 100-424 and surface $S_b = 0.251N$ cm^2 of ball loading) steel two-drum-type (the cylinder, height h = 4.6 cm, radius l_2 = 3.1 cm, volume V = 140 cm^3, surface S_v = 150 cm^2) water-cooled (the charge of water 1 cm^3/s with the continuous control of temperature of water on an output) planetary-cen-

trifugal (l_1 = 5.3 cm is the distance between the rotation axes, ω_1 = 12 s^{-1} is the frequency of mill rotation, ω_2 = 29 s^{-1} is the frequency of opposite rotation of mill drum) mill AGO-2 with the following characteristics [15,21]: geometrical factor is $m = l_1/l_2$ = 1/7; kinematic factor is $k = \omega_2/\omega_1 = -2.4$; $cos\varphi = -(1+k)/m = 0.82$; relative velocity of the collision of the milling bodies is $W = 2\pi\omega_1 l_2[(k+1)^2 + m^2 - 2m(k-1)cos\varphi + (m+1)^2]^{0.5}$ = 11 m/s. All were applied to more uniform and effective processing of a samples 4 possible orientations of an axis drove mill: vertical, horizontal and ±15° to last.

For comparison and for exeption influence of the abrasive wear (rubbing) of iron we also used SPEX 8000 Mixer/Mill [18-20] with tungsten carbide vial set (size 2 $^1/_4$" × 2 $^1/_2$" or ~ 5.7 × 6.3 cm) and one tungsten carbide ball ($^7/_{16}$" or ~ 1.1 cm diameter). The relative rate of colliding milling bodies attainable in SPEX 8000 is W ≈ 400 cm/s [18-20] at $2\omega \approx 31$ s^{-1} (SPEX is in essence a vibrating mill with frequency ω of translation-rotation vibrations; this frequency determines the frequency of shock interactions between milling bodies per mill operation cycle [15], therefore $|\omega| = 2\omega$).

Various compositions of the B/C-Mg/Al/Ca system, containing in the appropriate mixtures always 1 g of boron were investigated. Time of the treatment in the mills varied in limits from 1.5 h till 21 h. Starting substances were as in [4-6] except the following: 1) in all compositions had excess of magnesium and aluminium ~ 3%, calcium ~ 5% from appropriate stoichiometry; 2) in experiences on AGO-2 the crystalline boron (fraction > 80 micron), and on SPEX 8000 - amorphous was applied only.

Differential thermal analysis (DTA) was performed on the milled powders. Samples of ~100 mg were loaded into an alumina or platinum crucible and heated up in an: (i) – inert argon atmosphere to 1173 K at 10°/min and cooled by usual image; (ii) - inert helium atmosphere to 1173 K at 10°/min and then to 1273 K at 0.5°/min and cooled.

Samples of milled powder were also isothermally annealed under flowing argon (~ 1 cm^3/s) for 2 h in Ta crucibles at ~ 1273 K with a Ti sponge on the inlet of heated quartz tube for clearing of argon from possible impurity of oxygen.

Powder X-ray diffraction was performed by a conventional X-ray spectrometer with a graphite monocromator (D8 Discover with GADDS, Bruker), intensity data were collected with CuK_α radiation over a 2 range from 8° to 80° at a step width of 0.04°.

Results and Discussion

On obtained products of mechanical activation (MA) in the mill AGO-2 it is possible to sum up the following:

1) in the system 2B-Mg within 1.5 hours of activation are formed practically amorphous and monodisperse granules in the size of ~ 1 mm, in similar conditions in the system 2B-Al it is formed also amorphous (see Fig. 1b) powder of particles of composition close to AlB_2;
2) in the systems 2B-2C-Mg and 2B-2C-Ca within 21 hours of activation are formed completely amorphous fine powders;
3) DTA in argon (see Fig. 2) results in crystallization only aluminium diboride (AlB_2, see Fig. 1c) with an impurity of a phase of Al_xFe_y (see Fig. 1c), caused by the iron rubbing (~ 3% according to the chemical analysis) at the presence of hard initial particles of the crystal boron (iron rubbing takes place and in other systems, however X-ray data do not always show reflexes of iron because iron reacts with other elements and it is distributed in various phases as, for example, in case of the system 2B-2C-Ca, see Fig. 3a).

Efficiency of the mill SPEX 8000 for comparable with the AGO-2 time of processing (2 hours) is insufficient: X-ray data show reflexes of starting materials in the all investigated systems (2B-Mg, 2B-Al, 4B-Mg-Al, 4B-4C-Mg-Al, 2B-2C-Mg, 2B-2C-Ca, and 4B-4C-Mg-Ca), moreover, even after annealing of these samples within 2 hours at 1273 K, alongside with reflexes of the reaction products, the reflexes of starting substances are found, see Fig. 3b – one of reflexes of Al.

Passing to discussion of the obtained results, first of all we shall touch features of synthesis of compounds in the systems containing magnesium. They are caused by the high volatility of magnesium at the increased temperatures. DTA data of the activated system 2B-Mg in AGO-2 mill show endothermic effects at 620 and 700°C which coincide with the beginning of gradual and fast losses of weight in TG of the sample (Fig. 4).

At annealing the systems containing Mg, on a cold part of a quartz tube a dark deposition is formed, the chemical analysis of its composition gives only magnesium. Therefore synthesis (in our case crystallization from an amorphous phase) in systems with Mg can be carried out only under a high pressure of argon [4].

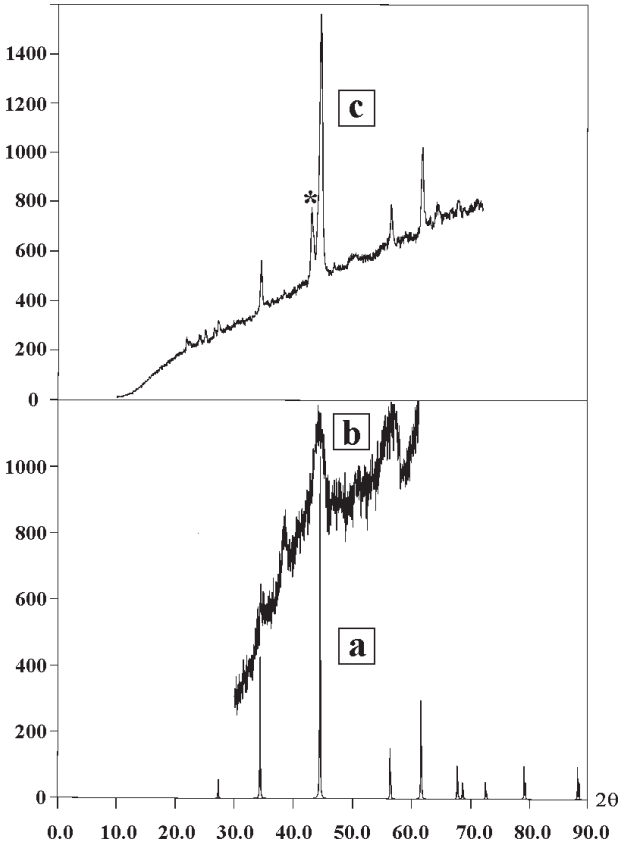

Fig. 1. X-ray data on the systems 2B-Al: a) standard AlB_2 (see PDF No 39-1483); b) a product of mechanical activation within 90 minutes in the mill AGO-2; c) the same product after the thermal analysis in an atmosphere of argon up to 900°C; the mark (*) answers the most intensive reflex of compounds Al_xFe_y, where the attitude $x/y \geq 2.5$.

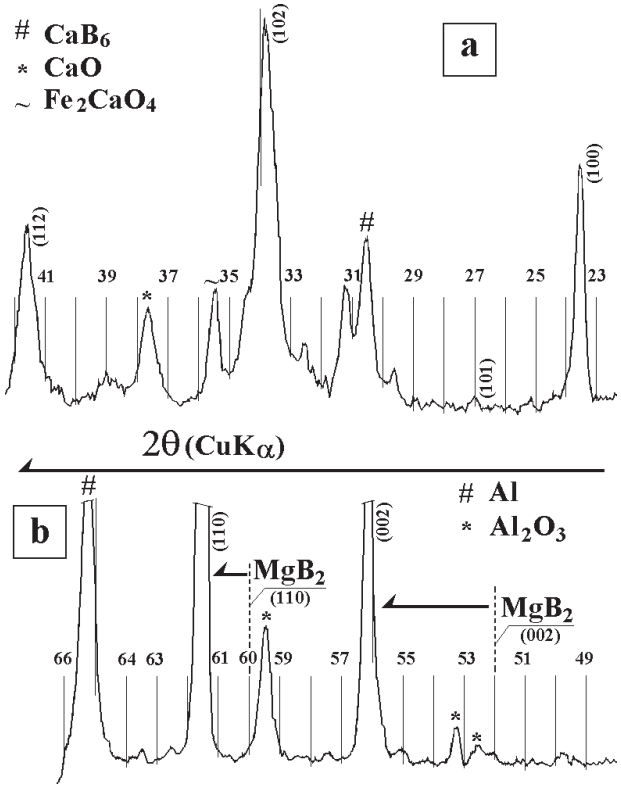

Fig. 3. X-ray data: a) system 2B-2C-Ca processed during 21 hours in mill –-2 after its annealing within 2 hours in a current atmosphere of argon at ~ 1000°C, see PDF 34-952; 83-515; 82-1691; 74-2136; b) processing 2 hours, SPEX 8000 mill, the system 2B-0.5Mg-0.5Al, annealing time 2 hours, an atmosphere of argon, ~ 1000°C, see PDF 8-263; 3-939; 12-539).

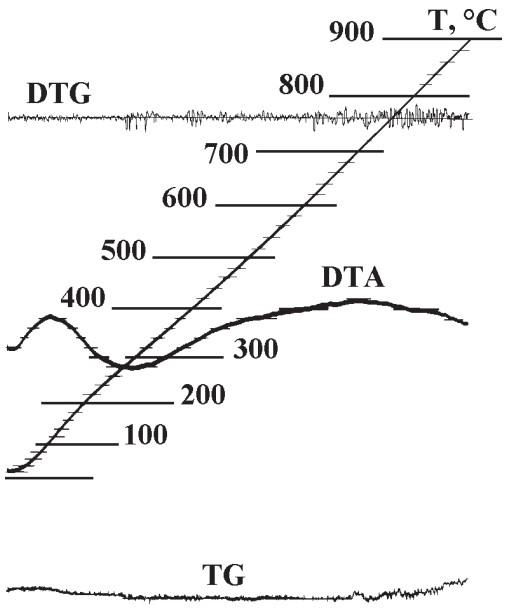

Fig. 2. Thermal analysis of mechanically activated system 2B-Al, processed during 90 min in mill AGO-2.

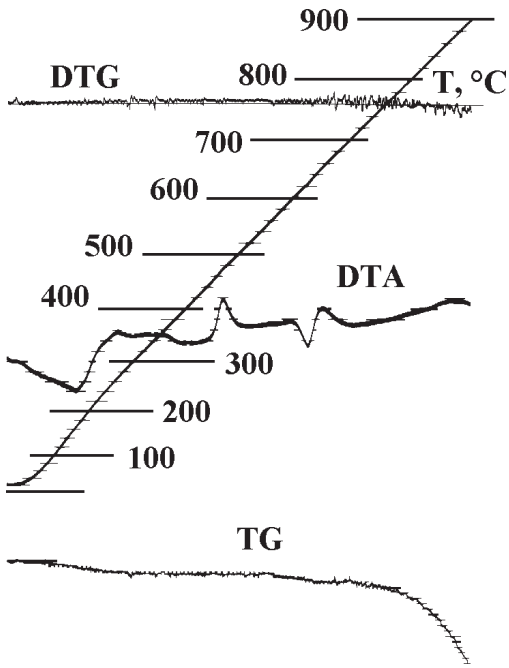

Fig. 4. Thermal analysis of mechanically activated system 2B-Mg, processed during 90 min in mill AGO-2.

The most important result consists in an opportunity direct mechanochemical synthesis of borides and boron carbides of mass-low metals in the mill AGO-2: AlB_2 (Fig. 1) and CaC_2B_2 (Fig. 2a; as confirmation [5]: at annealing initial black color of the powder varies on reddish-brown) are obtained. DTA data confirm this result also. For example, on curves DTA and TG of the activated system 2B-Al any features are not found out (see Fig. 2). Mechanical activation also influences on the process of thermal synthesis - compound $Mg_{0.5}Al_{0.5}B_2$ (see Fig. 2b) is obtained in the conditions inaccessible to traditional thermal synthesis. Formation of compound $Mg_{1-x}Al_xB_2$ in [6] up to x = 0.4 was established on shifts of reflexes (002) and (110) pure MgB_2 aside the large corners. In our case x = 0.5 and as it was necessary to expect, (see Fig. 3b) shifts of these reflexes exceeds shifts measured in [6] only for $x \leq 0.4$.

And, at last, see Fig. 1 and 3a, the opportunity of application of crystalline boron for synthesis of borides and boron carbides of mass-low metals is established, that it was not represented probable to make in [4-6]. In more detail see [6]. We revealed also that DTA in conditions of helium results in crystallization almost all activated samples, and the analysis of received X-ray reflexes unambiguously allows to assert that mechanical activation accelerates synthesis of reaction products in the investigated systems in comparison with the traditional methods of its synthesis.

Conclusions

Still the big prospects in creation of new materials in systems of mass-low elements are expected at mechanochemical synthesis in an atmosphere of the active gas environment (nitrogen, hydrogen etc. [2, 21]) and it is connected to an opportunity of obtaining boride-carbide-nitrides [22], for example as strong fibres [23], targets for magnetronic and ionic-plasma dispersion [24], and also complex hydrides with high convertibility of hydrogen [9,13].

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