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

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Abstract—**The possibility of mechano-chemical 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. Features of synthesis in systems containing metal magnesium are considered.**

I. INTRODUCTION

Proceedings of SMICS' 2004 Proceedings of SMICS' 2004 Proceedings of SMICS' 2004Let'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 determined essentially electronic structure and hence the chemical bonding of these solids, a large similarity of their chemical and physical properties could 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 crystal 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·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%); semiconductor behavior. 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.

Development for specific applications: For the tayloring of properties of boron-rich solids the following instruments are available: The crystal structures consisting of complicated three-dimensional networks of icosahedra or related aggregates contain holes, which are large enough to accommodate foreign atoms. These solid solutions exhibit properties, which are quantitatively or even qualitatively different from those of the pure structures. E.g. the mechanical properties can be modified considerably. This occupation of interstices by foreign atoms changes the electronic properties, too; e.g. the conductivity character of β-rhombohedral boron can be changed form p- to n-type, an indispensable requirement of many semiconductor applications, as thermoelectric equipments, too. The existence of many binary boron compounds is proved in principle, e.g. in the α-rhombohedral boron structure group compounds of the types $B_{12}X$, $B_{12}X_2$, and $B_{12}X_3$. But systematical investigations of physical properties have been performed only in very few cases, especially on boron carbide, and even in this case not in conclusion. It seems very probable that several of these compounds may have properties, which are much more favorable than those of compounds already known (e.g. boron carbide). Such binary boron compounds can have considerable homogeneity ranges. In the case of boron carbide it extends from $B_{4.3}C$ to about $B_{12}C$. The electronic

properties and the thermal conductivity change within the homogeneity range considerably. According to bond chemical considerations it seems probable that further binary homologous compounds with modified or modifiable properties can be synthesized. Ternary compounds, which can be obtained by interstitial or by substitutional introduction of a third partner are very favorable for the conditioning of materials properties. E.g. preliminary investigations on $B_{12}C_ySi_z$ and $B_{12}C_yAl_z$ have shown that the Seebeck coefficient can be considerably increased compared with boron carbide. Recent investigations on orthorhombic borides have shown, that this structure group allows an extended choice of metals for doping of icosahedral structures. In particular n-type conductivity and extraordinary high Seebeck coefficients (6000 V/K or even more) have been found. A further way to taylor boron-rich compounds for special applications is related to the method of preparation. Besides of melting and large scale reaction methods applied in the case of boron carbide meanwhile the formation of ceramics by hot pressing has become important. This procedure seems not to change the electronic properties considerably, at any rate not irreversibly. Therefore it can be expected that this commercially favorable production method can be used to electronic equipments. This would be an essential advantage compared with classical semiconductors, which are often needed in the form of expensive mono-crystals.

Known technical application of boron-rich materials: Till now only scarce advantage has been taken from the favorable prerequisites for the technical application of boron-rich materials mentioned. They are largely limited on boron carbide, and even in this case on the chemical composition B_4C at the carbon-rich limit of the homogeneity range. Such applications are: Use for abrasive material (grinding, lapping and polishing) - much cheaper than diamond; Tools for metalworking; Lightweight armor for persons and helicopters; Surface hardening by coating of tools; Effective fiber reinforcement of polymers; Shielding of neutrons; Control rods in nuclear reactors; Industrial ceramics (nozzles for sand-blaster, turbines for turbojet engines, mortars and pestles); Boron carbide / graphite thermocouples. Expected applications of electronic properties: Applications of boron-rich solids with respect to their electronic properties have been missing besides of the mentioned thermocouple, though the properties are very favorable, because they allow use under extreme conditions (high temperatures, high pressures, strong abrasive loading, chemically aggressive surrounding), which are not accessible for the most other materials. In this connection fundamental investigations on boron carbide have shown that it has very favorable prerequisites for the application in the thermoelectric energy conversion, at any rate more favorable than any other semiconductor known. The Seebeck coefficient of boron carbide is rather high, similar to those usually found in semiconductors. But contrary to all the other semiconductors hitherto known, in boron carbide it increases monotonously up to very high temperatures (> 2300 K). Hence in connection with the normal electrical and the low thermal conductivity very favorable prerequisites for a highly efficient direct thermoelectric energy conversion are available, e.g. to recycle waste heat or to transform solar thermal energy immediately into electrical energy. One essential problem in this respect hitherto unsolved is the n-type doping of boron carbide; but qualitative investigations have already led to the conclusion, that this is possible in principle, and moreover the Seebeck coefficient in ternary compounds of the same structure as boron carbide or of related structures can be increased essentially by suitable doping. Because of the similarity of properties caused by closely related structures, boron-rich refractory compounds in general are very promising candidate materials for the improvement of the thermoelectric properties. The boron-rich compounds include mainly binary and ternary boron-rich borides [e.g. MeB_{12}, MeB_{66}, (Na, Mg, Ln)MeB_{14}, the boron modifications and solid solutions of transition elements in β-rhombohedral boron, boron carbides, and structurally related phases].

After opening by the school of Japanese scientist Akimitsu high-temperature conductivity in MgB_2 at 39 K [4] and ferromagnetism in CaB_2C_2 up to 770 K [5], inexhaustible interest to connections of boron and carbon as to sources of new materials, even more 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 mechano-chemical 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.). Mechano-chemical 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 ($-\Delta H$, in kcal / mole, see [12]) synthesis of such borides from elements makes, for example, for: MgB_2 ($-\Delta H = 22.0$), 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 modeling 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.

II. 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 iso-static 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-micrometer 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 glove box, 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 iso-static 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 mechano-chemical 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-centrifugal (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 samples of 4 possible orientations of an axis drove mill: vertical, horizontal and ±15° to last.

For comparison and for exception of possibility of the iron rubbing we also used SPEX 8000 Mixer/Mill [18-20] with tungsten carbide vial set (V = 160 cm^3) and one tungsten carbide ball (N = 1, R = 0.55 cm or $^7/_{16}$" in diameter). The relative rate of colliding milling bodies attainable in SPEX8000 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 aluminum ~ 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 monochromator (D8 Discover with GADDS, Bruker), intensity data were collected with CuK_α radiation over a 2θ range from 8° to 80° at a step width of 0.04°.

III. Results and Discussion

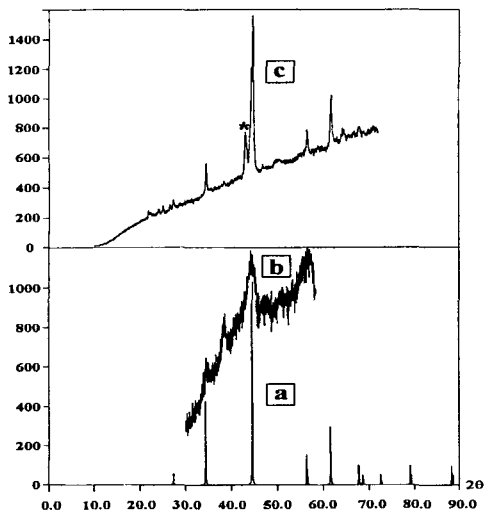

Fig. 1. X-ray data on the systems 2B-Al: a) standard AlB_2 (see Pdf No. 39-1483, 10-232, 9-154 and 8-126); b) a product of mechanical activation within 90 minutes in the mill AGO-2; c) the same product after the thermal analysis in an atmosphere of argon up to 900 °C; the mark (*)

answers the most intensive reflex of compounds Al_xFe_y, where the attitude x/y ≥2.5.

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 mono-disperse 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 B-C-Mg and B-C-Ca with atomic composition 2:2:1 within 21 hours of activation are formed completely amorphous fine powders; 3) DTA in argon (see Fig. 2) results in crystallization only aluminum 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).

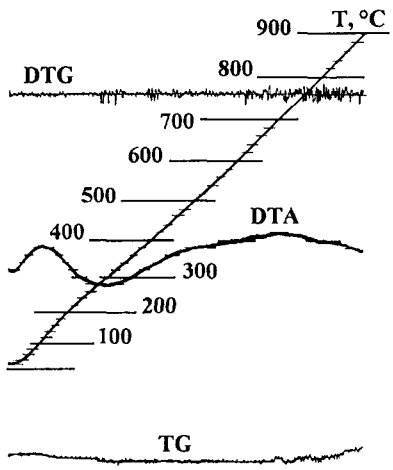

Fig. 2. Thermal analysis of mechanically activated system 2B-Al, processed during 90 min in mill AGO-2.

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, 2B-0.5Mg-0.5Al, 2B-2C-0.5Mg-0.5Al, 2B-2C-Mg, 2B-2C-Ca, and 2B-2C-0.5Mg-0.5Ca) , 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.

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 magnesium can be carried out only under a high pressure of argon [4]. Transition of magnesium in a gas phase at annealing of the samples of system 2B-0.5Mg-0.5Al explains presence of reflexes of the phases containing only not a few magnesium, such as MgB_{12} and $MgAlB_{14}$ (fig. 3b).

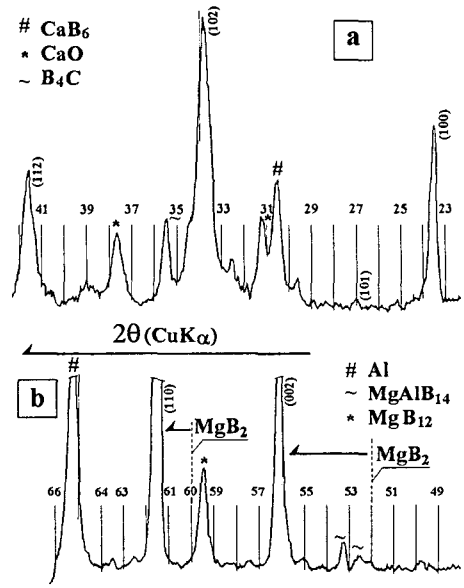

Fig. 3. X-ray data: a) system 2B-2C-Ca processed during 21 hours in mill АГО-2 after its annealing within 2 hours in a current atmosphere of argon at ~ 1000 °C (at annealing initial black color of the powder varies on reddish-brown); b) processing 2 hours, SPEX 8000 mill, the system 2B-0.5Mg-0.5Al, annealing time 2 hours, an atmosphere of argon, ~ 1000 °C.

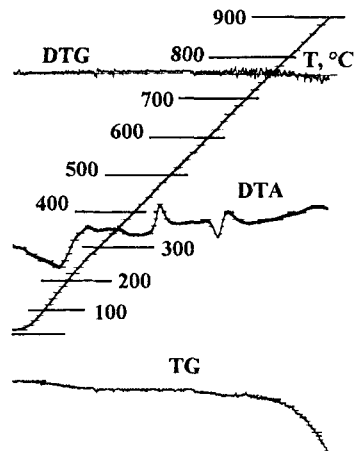

Fig. 4. Thermal analysis of mechanically activated system 2B-Mg, processed during 90 min in mill AGO-2.

The most important result consists in an opportunity direct mechano-chemical 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) 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.

IV. Conclusion

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

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