Mechanochemical synthesis of activated Me–BN (Me=Al, Mg, Ti) nanocomposites

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ABSTRACT

Mechanochemical synthesis in mixtures of light metals (Al, Mg, Ti) with hexagonal boron nitride under ball milling was studied. Well-pronounced stage behavior of the synthesis process was established and described in terms of dose of mechanical energy supplied to the material under milling (energy approach). At the initial stage the porous composite with nanometer-sized metal crystallites and high specific surface forms. The composite exhibits high reactivity with respect to external reactants, such as atmosphere and water. Mechanical activation also strongly facilitates the solid-state reaction between components, decreasing the temperature required for its initiation down to 450 °C. Solid-state reaction under milling takes place only after prolonged milling and results in formation of poorly crystallized metal borides and nitrides.

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1. Introduction

Joint mechanical activation of metals with lamellar materials in ball mills is a known way for production of composites with high reactivity. Mechanochemical synthesis provides a possibility for obtaining composites where metal nanoparticles are separated by porous interlayers of a lamellar material permeable to gases and liquids. The metal nanoparticles originating under milling have non-oxidated surface with large concentration of defects and, being surrounded by such interlayers, should and indeed reveal high reactivity with respect to external reactants (hydrogen uptake [1,2], oxidation by water [3] and atmosphere gases [4] etc.). Internal solid-state reactions also proceed much easier after mechanical activation [5,6].

Graphite is among the well-known materials with lamellar structure. In the previous research [7,8] mechanochemical synthesis of Al–C nanocomposites was studied in detail, and formation of composites with high reactivity was established. However, graphite is unsuitable for some applications, e.g. hydrogen production in reaction between mechanoactivated Al/C mixtures and water, where undesirable impurities of CO and CO_2 arise. Therefore, the possibility of using other lamellar materials (such as hexagonal boron nitride, h-BN) instead of graphite is worth being considered.

Besides, metal nitrides and borides are often used as strengthening phases due to their high hardness, and their formation in solid-state reactions in activated metal-BN composites is also a point of interest [9,10].

The present paper studies the process of mechanochemical synthesis of light metals (Al, Mg and Ti) with hexagonal BN. Aluminum and magnesium were chosen because of their high energy capacity in oxidation reactions; titanium is often used for hydrogen storage and for production of hard borides and nitrides. BN content was 15–50 wt.% for Al–BN mixtures and 15 wt.% for the others. X-ray diffraction, BET surface measurements, laser diffraction and differential scanning calorimetry were used to obtain information about composition, structure and thermal behavior of the activated mixtures. Reactivity of ball-milled composites with respect to atmosphere gases and water was traced.

2. Experimental techniques

Al, Mg (purity > 99.5 wt.%, particle sizes 30–100 μm) and Ti (purity > 99.5 wt.%, particle size about 250 μm) powders and hexagonal BN powder (purity > 99%, particle size 3–4 μm) were used as starting materials. Mechanochemical synthesis was carried out in a Fritsch Pulverizette-7 planetary ball mill with vials and balls made of hardened bearing steel under protective Ar atmosphere, the ball-to-powder weight ratio was 14:1. Forced air cooling was used in order to prevent excessive heating of the vials; the temperature rise of vial walls was less than 50 °C. The depth of mechanical activation was characterized by the dose D of energy supplied to the material under milling instead of widely used milling time [11]. The dose (J/g) is defined as $D = Jt$, where J is specific power intensity of the mill and t is milling time. The value of J determined by test-object technique was 3.3 W/g. The contamination of the powder by the materials of the milling tools did not exceed 0.5 at.%, as followed from

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weighting of grinding bodies before and after milling, except samples at large doses about 200 kJ/g that will be specially discussed.

Structural characterization of milled samples was performed by X-ray diffraction (XRD) with monochromatic CuK$_\alpha$ radiation. Specific surface area of the powders was determined using low-temperature (77 K) BET adsorption technique. Particle size distribution was measured using laser particle size analyzer. Thermal stability of the composites was investigated by means of differential scanning calorimetry (DSC) at a heating rate of 10 K/min under purified He atmosphere.

3. Results and discussion

According to the performed experiments, the processes of mechanochemical synthesis in studied Me–BN systems proceed in a similar way. Therefore the synthesis in Al–BN will be described in detail, then the peculiarities of Mg–BN and Ti–BN systems will de discussed.

3.1. Mechanochemical synthesis in Al–BN

The specific surface area S of the mechanically activated Al–BN mixtures rises quickly at small doses, then reaches its maximum and gradually drops (Fig. 1). The maximum value of S is proportional to the BN content that points to the possibility of independent breaking of components at the initial stage. This assumption is also confirmed taking into account the growth rate of pure BN surface under milling (taken from [12]). Its dependence on dose is presented in Fig. 1 where the right axis corresponding to pure BN has a threefold scale with respect to the left axis. The initial portions of curves of pure BN and Al–30 wt.% BN are similar under these conditions, indicating the proportionality between boron nitride content and the growth rate of the specific surface. Therefore, the growth of S takes place mainly due to BN surface which points to the independent breaking of Al and BN without formation of dense composites.

Despite the large values of specific surface accessible to gases (measured by BET technique), the external surface of particles is much lower. Fig. 2 shows the particle size distribution functions, which represent the relative contribution of different size particles into external surface of the system (so-called "surface distribution"). The main contribution is provided by the particles of a micrometer size, and the external surface calculated from distribution function is less than 1 m^2/g for all doses and compositions. Therefore, the full surface accessible to gases is mainly the surface of pores and cracks, i.e. the powder consists of micrometer particles where aluminum grains are surrounded by porous layers of
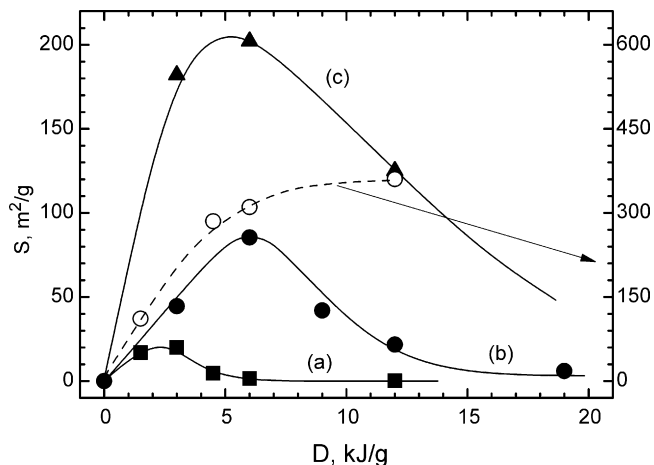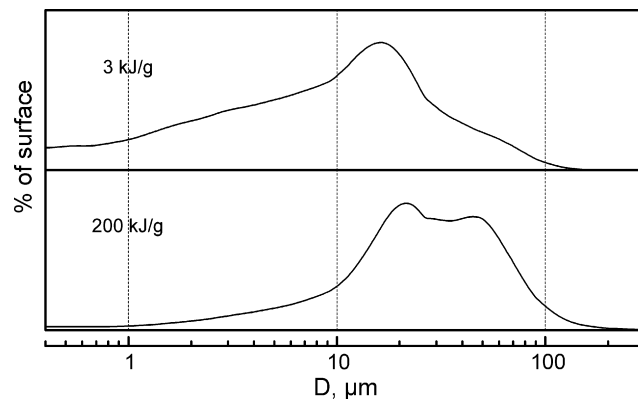

Fig. 2. Particle size distribution functions of Al-15 wt.% BN mixtures.

boron nitride. Further milling results in considerable drop of the full surface (up to two orders of magnitude) while particle size distribution changes slightly which points to formation of dense Al/BN composites.

XRD patterns of mechanically activated samples of various compositions are presented in Fig. 3. Both Al and BN peaks are visible at small doses of 1.5–6 kJ/g. The peaks broaden under milling, indicating transition of components into nanocrystalline state; the Al grain size reaches 25 nm after milling for 12 kJ/g and then decreases slowly to the final value of 10 nm. Crystalline BN peaks quickly lose their intensity upon milling and almost vanish at 12 kJ/g. As no shift of Al peaks is observed, indicating the absence of dissolution of boron or nitrogen atoms in Al lattice, the disappearance of BN peaks can be only linked to formation of grain boundary BN layers. Indeed, the Al grain size of about 20 nm corresponds to intergrain boundary area of 50 m^2/g, and boron nitride being separated over that area gives layer thickness of 2 nm (for Al-15 wt.% BN mixture) which is undetectable by means of XRD. As BN concentration increases, the layer thickness should rise, and broad halo around the position of the first BN peak is observed. The formation of grain boundary segregations is a common effect and, for example, has been observed in a set of binary Fe-based systems [13] as well as in Al–C [7]. Moreover, the conclusion about the formation of BN layers separating Al crystallites is in line with the results of surface mea-
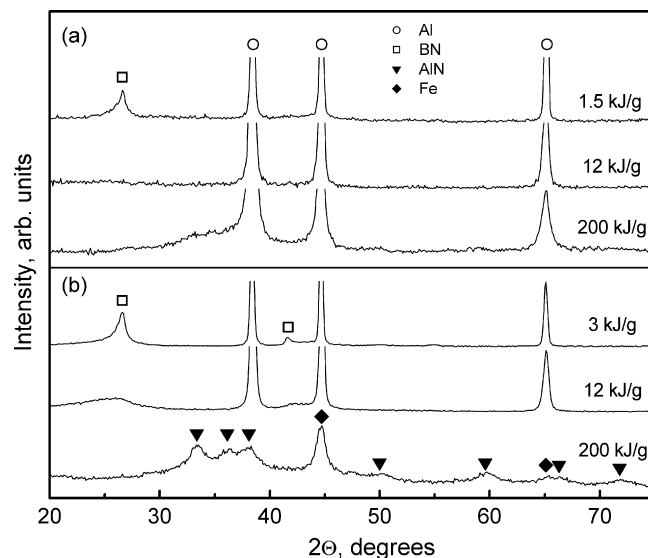

Fig. 1. Specific surface area of activated mixtures: Al-15 wt.% BN (a), Al-30 wt.% BN (b), Al-50 wt.% BN (c) and pure BN (dashed line).

Fig. 3. X-ray diffraction patterns of Al–BN mixtures after mechanical activation: Al-15 wt.% BN (a) and Al-50 wt.% BN (b).

surements. Prolonged mechanical treatment results in the broad halo in XRD patterns at 35°–60° (see Fig. 3) that corresponds to Al + BN reaction products. The increase in BN concentration provides slower disappearance of pure BN peaks and faster emergence of halo. The 200 kJ/g patterns for compositions with 30 and 50 wt.% BN show broadened peaks of AlN which obviously crystallizes from the amorphous phase. The last spectrum also shows peaks of α-Fe stemming from contamination of the powder with the materials of milling tools due to high hardness of boride and nitride phases.

Typical DSC curves reflecting the thermal behavior of activated composites are presented in Fig. 4. The Al-15 wt.% BN sample with the dose of 3 kJ/g exhibits the exothermic effect starting at 600 °C. Its shape is complicated due to superimposed sharp endothermic peak at about 650 °C, which corresponds to the temperature of the melting point of aluminum. The DSC curve of samples with higher doses (e.g. 12 kJ/g presented in Fig. 4) has well separated exo- and endothermic effects because of shift of the exothermic peak toward lower temperatures down to 450 °C. The exothermic peak is presumably assigned to the solid-state Al + BN reaction. Measurements of DSC curves during subsequent cooling of the samples, as well as during repeated heating and cooling of the same sample, shows the only sharp peak near 650° proving its identification with melting and reverse crystallization of Al. DSC curves corresponding to the systems with 30 and 50 wt.% BN show two exothermic effects (see Fig. 4, upper curve); the former starts at 450–600 °C and is identical to the previously discussed peak, while the latter is broad and lies near 700 °C. There are also no traces of Al melting peak for these compositions.

XRD patterns of the heated samples after DSC analysis are presented in Fig. 5. Peaks corresponding to AlB$_2$ and AlN phases can be clearly seen on the patterns. Their intensity grows with the rise in dose or in BN concentration. The residual Al peaks are also observed for Al-15 wt.% BN composition but vanish for mixtures with higher BN content. XRD patterns of the samples heated to 600 °C (after first exothermic peak) show anomalous intensity and width ratio for both AlB$_2$ and AlN peaks: the AlB$_2$ (1 0 0) and AlN (1 0 2) peaks are extremely intensive and narrow in comparison to the others. It indicates that crystallites have a texture oriented in the given directions, and possibly form nanowires at the initial crystallization stage. When heated up to 900 °C, the composites give XRD patterns with normal peaks intensities, indicating formation of "common" non-textured AlB$_2$ and AlN phases. Some unidentified peaks (marked with crosses) are also present for the samples heated to 600 °C which may be ascribed to some intermediate phase as they disappear after extra heating. The second exothermic peak in
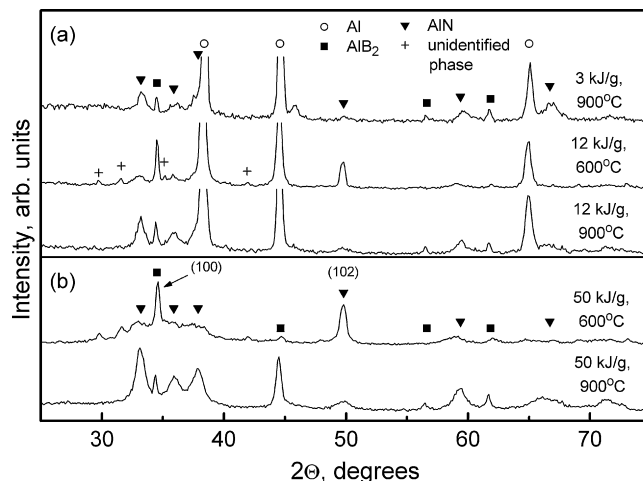

Fig. 5. X-ray diffraction patterns of mixtures after mechanical activation and subsequent heat treatment for various temperatures: Al-15 wt.% BN (a) and Al-30 wt.% BN (b).

DSC curves may be attributed either to some reaction involving this phase or to relaxation of the texture of boride and nitride phases.

Summarizing the experimental data about mechanochemical synthesis of Al–BN composites, some conclusions are to be made. First of all, the synthesis proceeds in several stages: (1) independent activation and breaking of components, formation of composites with large specific surface; (2) formation of dense composites with Al nanograins separated by thin BN layers; (3) solid-state Al + BN reaction with formation of amorphous phase with its further crystallization into AlB$_2$ and AlN. The similar staged behavior was previously observed in the course of mechanochemical synthesis in Al–C mixtures [7]. Mechanical treatment strongly facilitates solid-state Al + BN reaction occurring under heating, reducing its starting temperature down to 450 °C. The products of the thermally-induced reaction are textured and presumably form as nanowires oriented in (1 0 0) and (1 0 2) directions for AlB$_2$ and AlN correspondingly, however heating to 900 °C removes the texture effects.

3.2. Mechanochemical synthesis in Mg–BN and Ti–BN

The ball milling process in Mg-15 wt.% BN and Ti-wt.% BN proceeds similarly to that in Al–BN. The specific surface area grows quickly and reaches several tens of m^2/g at the dose of 3 kJ/g, while the external surface of the particles remains lower by two order of magnitude, indicating formation of porous composites. The surface collapses and dense composites form when the dose reaches 12 kJ/g, but no synthesis products are observed at this stage. Prolonged milling of Ti–BN mixture results in formation of TiB$_2$ and TiN phases along with residual Ti, and strong contamination of the mixture with Fe from milling tools occurs, presumably due to high hardness of milling products. For Mg–BN mixture, no traces of a solid-state reaction was observed under milling, i.e. layered Mg/BN composites keep up to the dose of 200 kJ/g. Nevertheless, DSC measurements have shown that solid-state Mg + BN reaction can be induced by heating of the activated mixture.

3.3. Reactivity of activated Me–BN composites

Previously described DSC measurements have demonstrated the increased reactivity of composites with respect to internal solid-state transformations. The temperature required for the start of the solid-state reaction is much lower than the melting point
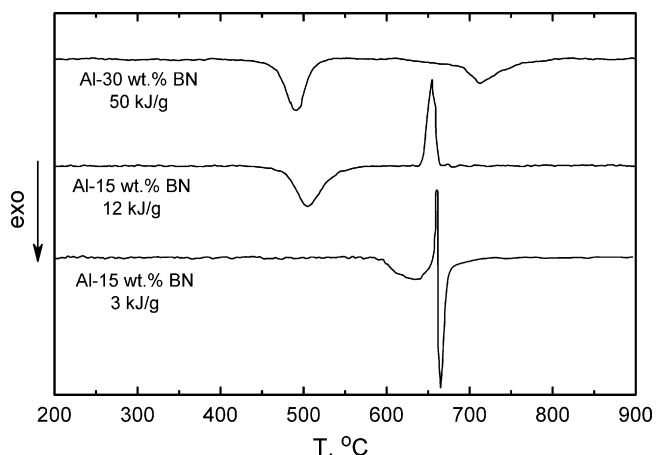

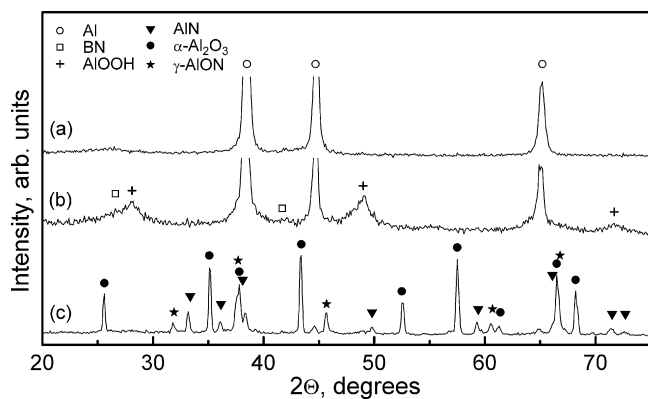Fig. 4. DSC curves of Al–BN mixtures after mechanical activation.

Fig. 6. X-ray diffraction patterns of activated Al-20 wt.% BN mixture after oxidation in water: as-milled (a), after slow oxidation (b) and coarse fraction after explosive oxidation (c).

of pure aluminum, making the synthesis of aluminum boride and nitride quite easy.

Mechanically activated composites react easily with external reactants like atmosphere and water as well. The samples milled for 3–12 kJ/g are subjected to oxidation when placing onto open air and even pyrophoric in some cases (e.g. the Al-30 wt.% BN sample with 3 kJ/g dose). It is interesting that XRD pattern of the burned powder is similar to that after DSC (presented in Fig. 5) showing AlB_2 and AlN products with small additions of Al_2O_3 phase. Therefore, oxidation in air that inevitably heats the sample serves as a fuse for initiation of solid-state Al + BN reaction. In other words, the well-known self-propagation high-temperature synthesis occurs as a consequence of Al–BN oxidation in air. The same phenomenon was also observed for mechanically activated Ti–BN mixture, despite less reactivity of titanium in comparison with aluminum.

Reactivity with respect to water was studied for the sample of Al-20 wt.% BN composition milled at 8 kJ/g with specific surface area of 24 m^2/g. The slow oxidation of Al/BN composites proceeds in water at 95 °C. The reaction depth measured by hydrogen release quickly reaches 30% after 10 min and then grows much slower up to 44%. The XRD patterns of final reaction products are presented in Fig. 6, indicating the presence of Al, BN and AlOOH phases. Therefore, boron nitride is not engaged into reaction, and full oxidation of Al does not occur under given conditions.

Explosive oxidation of the reaction mixture by water takes place at 105 °C. The reaction product consists of two fractions: fine powder with the structure similar to that obtained under slow oxidation and coarse particles with sizes up to 1 mm. XRD pattern of the latter fraction shows residual Al, α-Al_2O_3 (corundum), AlN and γ-AlON (spinel-type) phases without any traces of residual BN (see Fig. 6(c)). The qualitative analysis of the water after the reaction reveals the presence of H_3BO_3. Therefore, two processes take place simultaneously under explosive process: oxidation of aluminum and solid-state interaction between Al and BN.

4. Conclusions

Mechanochemical synthesis in Me–BN (Me=Al, Mg, Ti) proceeds in several stages: (1) independent activation and breaking of components, formation of composites with large specific surface; (2) formation of dense composites with Al nanograins separated by thin BN layers; (3) solid-state Me + BN reaction (except Mg–BN system) with formation of an amorphous phase with further crystallization into metal boride and nitride. Mechanical activation strongly facilitates solid-state Me + BN reaction occurring under heating, reducing its starting temperature down to 450 °C. Borides and nitrides formed during this thermally-induced reaction initially show a pronounced crystallographic texture that is removed after heating up to 900 °C. Mechanically activated composites reveal high reactivity to atmosphere (burning accompanied by Me + BN solid-state reaction) and to water (slow oxidation of Al without engaging boron nitride into the reaction and explosive oxidation which involves BN).

Acknowledgements

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