Synthesis of $AlMgB_{14}$: Effect of modes of mechanical activation of the raw powders on the properties of obtained materials

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Abstract. In work studies of phase composition, hardness and density of materials based on $AlMgB_{14}$ synthesized by hot pressing method at temperatures of 1300 and 1400 ℃ under pressure 50 MPa from aluminum, magnesium and boron powders (E1 mixture), as well as from original powder of aluminum-magnesium alloy (E2 mixture) were conducted. $AlMgB_{14}$ phase content of obtained bulk samples is ~ 95 wt. %. The maximum hardness of 14GPa and density of 2.1 g/cm^3, respectively, has a sample, marked as E1, synthesized at a temperature of 1400 ℃.

1. Introduction

Materials based on Ultra-hard materials are of great practical importance in various industries. Such materials can be used as parts of complex mechanisms, additional coatings, depending on their properties. A wide class of superhard materials is occupied by borides. They have high heat resistance, hardness and are able to withstand constant loads. The most promising material in this class is AlMgB14. $AlMgB_{14}$ (so-called, BAM) are promising wear-resistant materials in the field of engineering, engine building, space and aviation industries. BAM is of great interest due to the high hardness reaching 28-32 GPa, with a low friction coefficient, reaching values of 0.06-0.02 [1-3]. Materials based on $AlMgB_{14}$ can be used as thin wear-resistant coatings for contact surfaces of components. Today studies have been conducted on the structure of BAM, physical and mechanical properties in various compounds[4-6]. The possibility of deposition coatings based on $AlMgB_{14}$ on steel surfaces [7-8] and glass surfaces [9] is being actively studied.

Matkovich and Economy [16] first reported orthorhombic single-crystalline $AlMgB_{14}$ compound in1970. Cook et al. have developed approaches to the obtaining of polycrystalline materials based on $AlMgB_{14}$ by methods of mechanical alloying (MA) of raw powder mixtures Al-Mg-B and subsequent hot pressing in different modes. The powders of aluminum, magnesium and boron were mixed in an atomic ratio of 1:1:14, milled and sintered using hot pressing in the temperature range from 1300 to 1500 °C.On the basis of the conducted studies, it was found that during hot pressing the phases $AlMgB_{14}$ and $MgAl_2O_4$ are formed.The obtained material had a density of 2.54 g/cm^3 and a hardness of 32-35 GPa.Studies on the variation of the raw powder mixtures showed that the addition of 30 wt. % TiB_2 allows to increase the hardness of materials based on $AlMgB_{14}$ up to 46 GPa [4].

In work [10] studies have been conducted on the synthesis of $AlMgB_{14}$ from various powder mixtures by vacuum sintering and subsequent hot pressing with TiB_2 system. The material containing the $AlMgB_{14}$ phase content of 88 wt. % was obtained at a sintering temperature of 1400 °C for 2 hours from aluminum, boron and Mg-precursor powders.

In work [11], $AlMgB_{14}$ was obtained by the two-stage sintering method. In the first step, aluminum, magnesium, and boron were mixed in Al:Mg:B atomic ratio of 1:6:14 and pressed. The obtained disks were sintered at a temperature of 850 °C in argon atmosphere. In the second step, $AlMg_6B_{14}$ disks were sintered in a vacuum. During sintering, the magnesium evaporated from $AlMg_6B_{14}$ to $AlMgB_{14}$. $AlMgB_{14}$, $MgAl_2O_4$, and MgB_2 phases were detected. The hardness of the obtained material was 11 GPa. The disadvantage of this method is the complexity of the process in which it is necessary to use high-purity powders and special conditions.

To intensify the process of obtaining $AlMgB_{14}$, hot pressing or spark plasma sintering methods are used. The principle of hot pressing is based on the simultaneous sintering and consolidation of powder mixtures. The heating of the powder mixture in the graphite matrix occurs due to the transfer of electric current into Joule heat. Sintering temperatures typically range from 1273 to 1973K, depending on the powder mixture. At the same time, to obtain materials with a density close to theoretical, it is sufficient to apply a small pressure (about 30-60 MPa) compared with cold pressing and

subsequent sintering in a high-temperature furnace. Moreover, the sintering time is significantly reduced and amounts to about 10-15 minutes. To avoid oxidation of the powder mixture in the sintering process, the process is carried out under high vacuum or inert gas. In [12], the methods of mechanical alloying and hot pressing (sintering temperature is 1500 °C, pressure is 60 MPa, holding time is 8 minutes) were used to obtain bulk samples $AlMgB_{14}$. The average hardness of the samples was 26.1 GPa. The average density of the samples was 2.62 g/cm^3.

The main problem in the synthesis of materials based on $AlMgB_{14}$from raw powder mixtures of aluminum, magnesium and boron is contamination of the products obtained by various impurities ($AlMgB_{22}$, α-AlB_{12}, AlB_2 and $MgAl_2O_4$). Contamination of spinel phase $MgAl_2O_4$ leads to a significant deterioration in the mechanical properties of the synthesized materials. This is especially evident in the production of thin wear-resistant coatings from bulk materials based on $AlMgB_{14}$ [13]. The low hardness of 8-16 GPa films obtained in [13] against the hardness of 28-32 GPa of bulk materials is due to their amorphous structure, in which B-B bonds are practically absent and weaker B-O oxide bonds are manifested.

In work [14], pulsed electric current sintering (PECS) method was used to obtain $AlMgB_{14}$. To reduce the content of the $MgAl_2O_4$ phase, the boron powder was annealed in a high-temperature vacuum furnace before mixing and then mixed with aluminum and magnesium powders. As a result, a material was obtained with an $AlMgB_{14}$ content of ~ 93 wt. %, hardness of 26.1 GPa and fracture toughness of 3.1 MPa m$^{1/2}$. A comparison was made between the modes of mixing and sintering the raw materials. The mechanism of the formation of $AlMgB_{14}$ and $MgAl_2O_4$was presented in the temperature range from 600 to 1400 °C. It was found that the formation of $AlMgB_{14}$ occurs in several stages. At the first stage, in the temperature range from 600 to 1000 °C, tetraboride $AlMgB_4$ is formed. Then, at temperatures above 1000 °C, $AlMgB_4$ decomposes into $AlMgB_{14}$ and Al, Mg. Spinel $MgAl_2O_4$ is formed at a temperature of 800 °C and prevents the formation of $AlMgB_{14}$.

The question of reducing the spinel phase remains unresolved to this day.Thus, the purpose of this work is to study effect of modes of mechanical activation of the raw powder mixtures on the phase composition, impurity content and properties of the materials synthesized from them.

2. Methods and materials

In the first set of experiments, as the raw powders were used aluminum powders with a particle size of 12μm, magnesium with a particle size of 80 μm and amorphous black boron with a particle size of 2.3μm, respectively. The powders were mixed in the ratio Al:Mg:B – 1:1:14, and mechanically activated in a planetary mill. To avoid contamination of powder mixtures with oxide impurities, mechanical activation was carried out in argon atmosphere. The time of mechanical activation varied from 1 to 5 hours. Steel balls with a diameter of 8.7 mm were used as grinding bodies. A charge ratio (grinding balls to powder mass ratio) of 2 was used.The obtained mixture was marke dasE1.

In the second set of experiments, the raw materials used were amorphous black boron powder, as in the first experiments, and powder of aluminum-magnesium alloy with an aluminum and magnesium content of 51% by 49%, respectively. Powder of aluminum-magnesium alloy was mechanically activated in a planetary mill for 9 hours. Then boron was added to the mechanically activated aluminum-magnesium powder in a stoichiometric ratio. The obtained mixture was marked as E2.

Powder mixtures obtained in the first and second experiments were synthesized by hot pressing. The maximum temperature was 1300 °C and 1400 °C under pressure of 50 MPa with an exposure time of 8 minutes. In order to avoid oxidation of materials, sintering was carried out in argon with the preliminary evacuation.

The average particle size of the Al-Mg-B mixtures was measured with the ANALYSETTE 22 Micro Tec Plus Analyzer. The density of the synthesized bulk materials was measured by the Archimedes method. The XRD analysis of synthesized products was perfomed using a Shimadzu XRD 6000 diffractometer with Cu-Kα radiation. Vickers hardness of the synthesized bulk materials was measured using a Duramin 5 hardness meter with a load of 98N and a dwell time of 10 s.

3. Resultsand discussions

3.1. Particle size

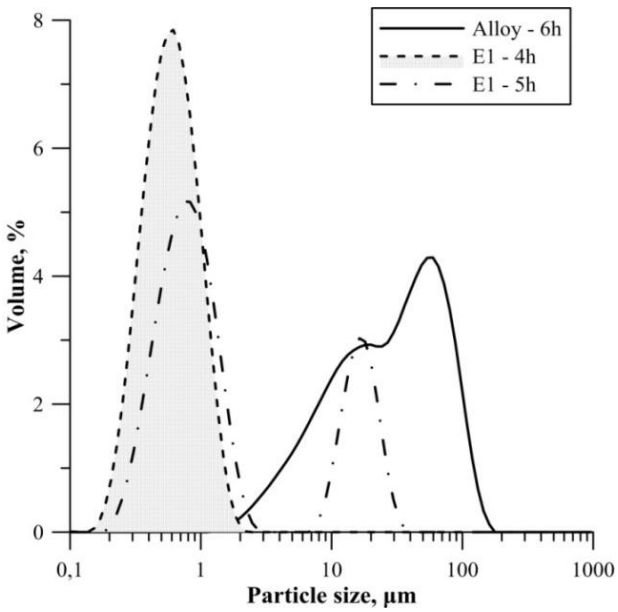

Figure 1. The particle distribution histogram.

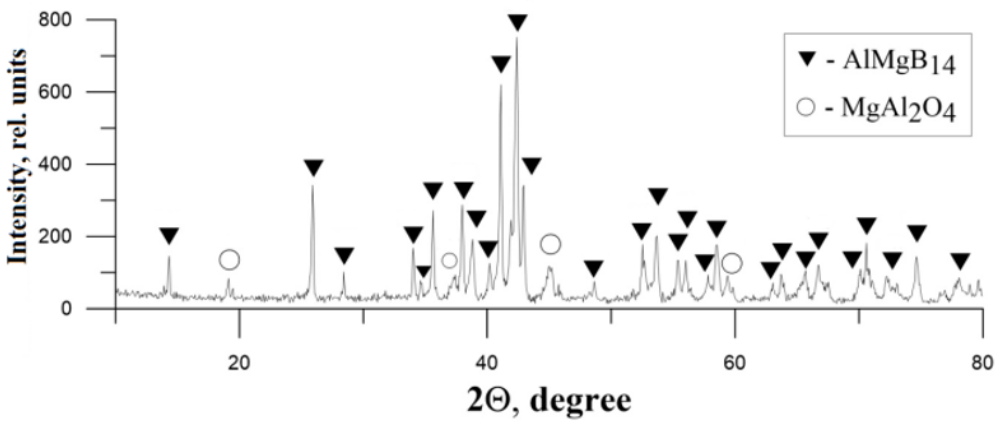

Figure 2.XRD of bulk sample synthesized at a temperature of 1300 ℃ by hot pressing method from E2 powder mixture

In the first set of experiments, after an hour of mechanical activation the average particle size of Al-Mg-B powder mixture decreases from 10 μm to 2 μm. The minimum particle size is observed after 4 hours of mechanical activation. Subsequent processing leads to a sharp increase of particle size from 0.8 μm to 10 μm. The histogram of the particle distribution shows that after 4 hours of MA the particle distribution is unimodal. As the processing time of the mixture is increased in a planetary mill, the particle distribution becomes bimodal (Fig. 1). In the second set of experiments, after 6 hours of mechanical activation of the aluminum-magnesium alloy powder, the average particle size decreases from 180 μm to 35 μm (Fig. 1).

The sharp increase in the average particle size for the E1 mixture and the aluminum-magnesium alloy powder, as well as the formation of the second mode in the particle distribution histogram for the E1 mixture, is probably due to the agglomeration of particles from the submicron range [15].

3.2. XRD results

XRD-pattern of sample obtained by hot pressing at a synthesis temperature of 1300 °C from the powder mixture E2 is shown in Figure 2. Using the "Powder Diffraction File" database and the POWDER CELL 2.4 analysis program, the approximate phase content was calculated from the XRD-pattern (Table 1).

In Table 1, phase composition of synthesized materials from E1 and E2 powder mixtures is presented. Phase composition is represented by phases of $AlMgB_{14}$ and $MgAl_2O_4$. All bulk materials after hot pressing contain more than 90% of the $AlMgB_{14}$ phase. The maximum phase concentration of $AlMgB_{14}$ is found in the sample from the powder mixture E2. $MgAl_2O_4$ was also detected in all samples. The formation of $MgAl_2O_4$ due to contamination of raw powders.

Table 1. Concentration of $AlMgB_{14}$ and $MgAl_2O_4$ in products obtained by hot pressing method from E1 and E2 powder mixtures.

Sample	Temperature (°C)	Time of MA, (h)	$AlMgB_{14}/MgAl_2O_4$ (wt. %)
E1.	1300	5	94/6
E1.	1400	5	96/4
E2.	1400	-	97/3

The smaller content of the spinel phase of $MgAl_2O_4$ in the bulk material E2 compared to bulk material E1 is due to the fact that in the E2 mixture, mechanical activation was carried out without the boron powder, which strongly accumulates oxygen. To reduce the content of $MgAl_2O_4$, it is necessary to optimize the methods of mixing powder mixtures, and pre-anneal boron powder in a high-temperature vacuum furnace to reduce the oxygen concentration.

3.3. Density and Hardness

The hardness of the samples was determined by the Vickers method under constant loads. For each sample, 10 measurements were performed. The density was measured by the Archimedes method. Theresultsofthedensityandhardnessofthesynthesizedproductsfromthepowdermixtures E1 and E2 are presented in Table 2.

All samples sintered at temperatures below 1400 °C have low hardness. This is due to the fact that at lower temperatures it is necessary to use a higher pressing pressure for powder mixtures. To obtain materials with high hardness and density, it is necessary to optimize the sintering regimes of powder mixtures by hot pressing.

Table 2. Density and hardness of products obtained by hot pressing method from E1 and E2 powder mixtures.

Sample	Temperature (°C)	Time of MA, (h)	Density, g/cm^3/Hardness, GPa
E1.	1300	5	1,82 / 5
E1.	1400	5	2,1 / 14
E2.	1400	-	1,7 / 2

The bulk sample from the E1 powder mixture after 5 hours of mechanical activation synthesized at a temperature of 1400 °C has a maximum density and hardness of 2.1 g/cm^3 and 14GPa, respectively. This material has a dense structure with a pore content of not more than 10 %.Due to the fact that the E2 mixture was not mechanically activated, the synthesized bulk sample has a high porosity. This is confirmed by the results obtained in the measurement of hardness.

4. Conclusion

$AlMgB_{14}$ was successfully fabricated by hot pressing under various mixing conditions, mechanical activation and synthesis temperature. The raw powders were industrial powders of aluminum, magnesium and boron, as well as an original powder, obtained from the aluminum-magnesium alloy. All bulk samples obtained by hot pressing at temperatures of 1300 °C and 1400 °C are represented by a high content of the $AlMgB_{14}$ phase (more than 90%).

Spinel formation is associated with contamination of the initial powders, especially boron powder, as well as with the conditions of mixing and sintering the obtained powder mixtures. It was found that phase composition of the products from the E2 powder mixture is represented by a smaller number of impurities. However, bulk samples from the E2 powder mixture have a high porosity and, as a consequence, a low density. This is due to the fact that the mixing of boron powder and Al-Mg alloy powder was carried out without the use of a planetary mill. On the one hand, a material was obtained without a significant number of impurities. On the other hand, the homogeneity of the powder mixture was not achieved, which resulted in low density materials. The maximum hardness of 14 GPa has a sample synthesized at a temperature of 1400 °C from the powder mixture E1. In order to obtain a material with a higher hardness, it is necessary to optimize the regimes for obtaining powder mixtures and their sintering by hot pressing

In order to increase the density of samples from the E2 powder mixture, it is necessary to increase the homogeneity of the powder mixture by the method of mechanical activation. At the same time, to reduce the concentration of the spinel phase $MgAl_2O_4$, it is necessary to use high-purity powders; the steps of obtaining and processing the powder mixture should be carried out under high vacuum or under inert gas conditions. To reduce the oxygen concentration in the powder of amorphous boron, it is necessary to carry out its preliminary annealing in a high-temperature furnace.

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