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Article

High-Temperature Synthesis of Superconducting MgB_2 Materials in a Centrifuge

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Abstract: There is a wide variety of superconducting materials, but only a few of them are suitable for practical industrial use, and one of the most promising superconductors is MgB_2. Its main advantages are a critical temperature close to 40 K, which allows for operation in a cryogenic environment, low cost of precursors, and the ease of manufacture. In this paper, we attempted to obtain superconducting materials based on magnesium diboride in a new way by using a high-temperature centrifuge and then investigated how centrifugal acceleration could affect the superconducting characteristics of the materials in a greater way during combustion synthesis. As a brief result of this research, it was found that the value of centrifugal acceleration affected the critical current density (J_c = 1.4 A/cm^2) of the MgB_2 composites, although it did not considerably impact the critical transition temperature of the MgB_2 materials (remained at around 37.5–38 K).

Keywords: magnesium diboride; solid-state synthesis; high-temperature centrifuge

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1. Introduction

The superconductivity of magnesium diboride was first discovered by Japanese scientists in 2001 [1]. There has been high interest in magnesium diboride (MgB_2)-based superconductors because of their potential practical use in cryoelectronic devices at the temperature of liquid hydrogen. The various applications of superconducting materials were discussed almost immediately after the discovery of its superconductivity. The greatest application of superconductors is currently found in the field of creating strong magnetic fields. Modern industry has been trying to produce different types of wires and cables used for the manufacture of windings for these superconducting magnets, which can produce significantly stronger fields (more than 20 T) than those of iron magnets. The use of superconductivity can also lead to the creation of ultra-fast electronic machines [2,3]. Moreover, MgB_2-based superconducting materials have a huge potential for use in different commercial and non-commercial directions over the world, including medical devices, radiation detection, generators, magnetic separation, magnetic levitation, superconducting magnetic energy storage, and high-energy physics applications [4].

At present, there are several well-known methods for synthesizing MgB_2 superconducting materials, such as thermal explosive synthesis [5], the in-tube method [6], HPCVD [7], sol-gel technology [8], etc. Additional modifications to these methods of magnesium diboride synthesis have also been introduced, such as switching from a stoichiometric to a non-stoichiometric composition of the green mixture of boron and magnesium under the following different environments: in a vacuum [9], the air atmosphere [10] and the inert gas [11]. And one of the most promising ways to synthesize magnesium diboride composites would be solid-state synthesis (or solid-state combustion), coupled with one of the modifications (under external high pressure of inert gas [12] and air [13], level of doping [14,15], etc.). The main technological problem is to keep all the green components in a reaction zone during the solid-state process without losing any of the magnesium atoms to evaporation (boiling point of Mg: 1091 °C) under high temperature, as the process' temperature usually reaches up to 1100 °C. Because of the use of external pressure, it is possible to significantly suppress the undesirable process—the evaporation of magnesium during the synthesis of MgB_2 composites—and obtain a material with excellent functional characteristics, including a density of 98% of the theoretical value, and high values of superconducting characteristics and mechanical properties [16]. In this paper, a similar effect of external pressure was created by conducting synthesis in a high-temperature centrifuge [17]. The laboratory version of this device (Figure 1) was developed for the study of combustion processes under the conditions of rotation [18], allowing us to reach an angular speed of up to 2500 rpm. In this way, the combustion of the oxide systems could go into a superadiabatic mode and create a flow of metal clusters, the thermal and kinetic energy of which would cause the start and irreversibility of chemical reactions with a high Arrhenius barrier [19].

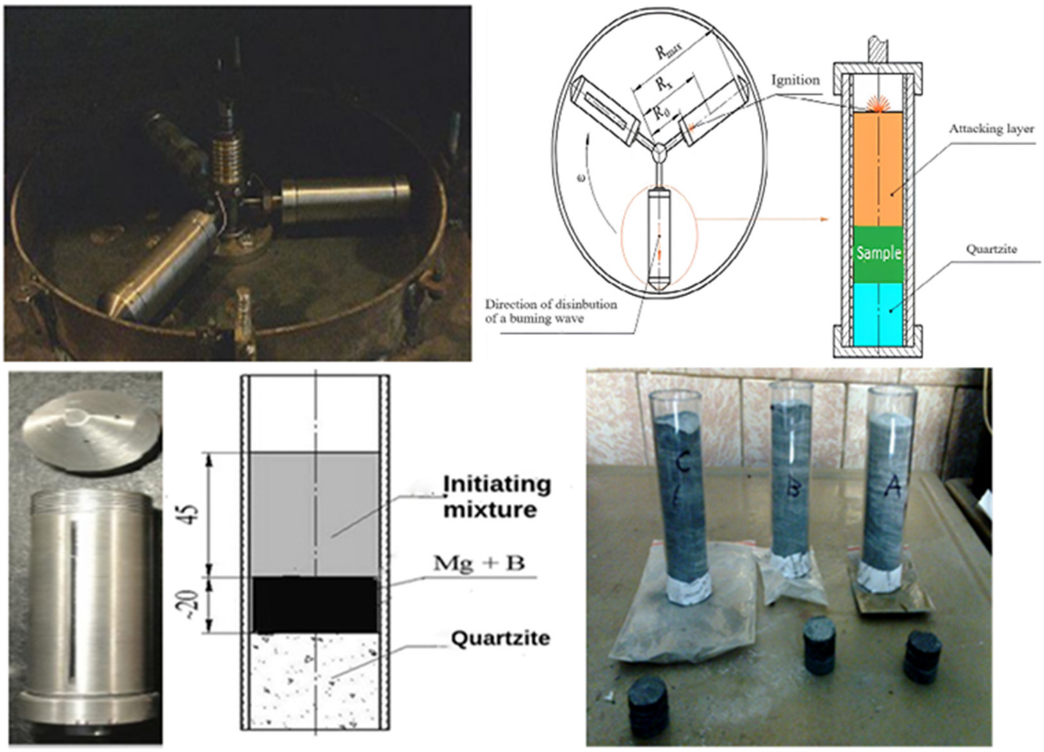

Figure 1. Schematic of loading the components into the reactor of a high-temperature centrifuge.

The centrifugal acceleration affected the flow rate of the clusters, the process' temperature, and the viscosity of the liquid phase. The attacking potential of the reduced metal clusters also affected the formation of intermediate and final synthesis products, providing a high degree of conversion. The high rate of temperature increases in the combustion wave led to the formation of a non-equilibrium metastable structure, changes in the solubility of impurities and, due to the action of these factors, distortion of the crystal lattice. It was possible to create the following conditions in this device: A temperature of up to 3000 K for solid-state synthesis, and a centrifugal acceleration of up to 2500 rotations per minute [20].

In this work, we investigated a new method for producing superconducting materials based on magnesium diboride using a high-temperature centrifuge during combustion synthesis and determined the effect of centrifugal acceleration on the superconducting characteristics of the obtained material. This method has the potential for the fast synthesis of different types of superconducting materials, from LTS to HTS, with a high-density value (which might be very close the theoretical one) in one step.

2. Materials and Methods

2.1. Materials

In synthesizing the superconducting magnesium diboride materials, amorphous boron powders (B94 grade A, 20 microns) and magnesium powders (MPF-1 grade, 250 microns) were used.

2.2. Methods

A thoroughly mixed and ground mixture (in a proportion of Mg 55.3 wt.% and B 44.7 wt.%) of the initial magnesium and amorphous boron powders was pressed into a pellet form using the hydraulic press with a force of 0.4 GPa. Quartzite was used to fill the remaining empty spaces in the crucible.

As the magnesium and boron system was weakly exothermic, we needed to provide an additional external source of energy to initiate the process of solid-state synthesis. The following composition was used as the additional initiating mixture: 55 wt.% of CuO + 12 wt.% of Al + 33 wt.% of Al_2O_3. Thus, the overall weights of the components were given in Table 1. The high-temperature centrifuge (Figure 1) comprised the following: A shaft installed engine, crosspiece with three metal sleeves fixed on it and balanced at a 1200-degree angle, crucibles installed inside these sleeves and covered from both sides, current collectors contacting with a brush assembly, and an ignition spiral. The crucibles were 35 mm diameter and 130 mm long quartz tube glasses.

Table 1. Input data of the prepared mixture for conducting a solid-state combustion process in a high-temperature centrifuge.

The Layer's Composition (Sandwich Location)	The Layer Mass, gr	The Layer Height, mm
An initiating mixture (55%CuO + 12%Al + 33% Al_2O_3)	10	~45
Studied Sample (Mg + B powders)	15	~10
Quartzite grains	11	~30

We used three values of rotation speed as follows: 1000 rpm, 2000 rpm, and 2500 rpm. The relative centrifugal forces (g forces) were calculated to be 145, 581, and 908, respectively.

The combustion process in the crucible was initiated by inserting the ignition spiral into the crucible through the cover and connecting it with the current collector. The number of centrifuge revolutions was regulated by changing the electric engine value. The unit was rotated in the horizontal plane. Simultaneous combustion processes in all the reactors were provided with precise balancing of the crucibles on the shaft. There were holes for the output of gas formed in the combustion process, and for the ignition of the initial composition in the quartz tube. When the desired rotation speed was reached, we switched the electric impulse on and ignited the additional initiating mixture (which transferred its chemical energy to our studied sample). Later, the sample started to burn up, showing that the combustion process had taken place. It took just several milliseconds to conduct solid-state synthesis (combustion) in this condition to obtain the desired material. Table 1 shows the optimal selected parameters for the preparation of all components necessary for conducting a solid-state combustion process in the high-temperature centrifuge.

The schematic [19] for loading the all-chemical components into the quartz tube of the steel crucible in the high-temperature centrifuge is shown in Figure 1.

The phase composition of the synthesized samples was studied by X-ray diffraction analysis using a DRON-4M diffractometer (JSC "IC "Burevestnik", Saint-Petersburg, Russia). A magnetometric analysis method was employed (in ZFC and FC modes) using the Quantum Design PPMS EverCool-II cryogenic equipment (World Headquarters, San Diego, CA, USA)to determine the superconducting characteristics of samples. The surface microstructure of the sample was performed using a JSM-6510LA scanning electron microscope (JEOL, Tokyo, Japan).

The HSC Chemistry 6.12 software facilitated simulations of potential products for both the Mg + B system and the Mg + B and CuO + Al + Al_2O_3 system interfaces. These simulations were conducted under adiabatic conditions with temperatures rising to 1500 °C. To determine the molar ratios of potential products, graphs were created using the “Equilibrium Compositions” module. Gibbs minimization method was employed for the calculations. Moreover, on the same software, a “Reaction Equations” module was used to calculate the ΔH°rxn value of the MgB_2 compound (Equation (1)) to be utilized in the calculation of Reaction Specific Heat Value (RSH) for MgB_2 formation. RSH, which was calculated through Equation (2), was required to be between 2250 and 4500 J/g in the combustion synthesis reactions to meet with the self-sustainable characteristics of the reactions. If RSH was between those values, once the reactions were initiated, it would go forward without any additional energy. If the RSH value was less than 2250 J/g, some energy must then have been provided to the system to make the reactions happen.

$$\mathrm{Mg} + 2\mathrm{B} \rightarrow \mathrm{MgB_2} \tag{1}$$

$$\mathrm{RSH} = \Delta H^{\circ}\mathrm{rxn}/\Sigma\ \text{Molar mass of products} \tag{2}$$

3. Results and Discussion

According to the results of the X-ray phase analysis of the synthesized samples (Table 2, Figure 2), the main goal of the experiment was achieved as follows: The magnesium diboride phase (about 61–70 wt.%) was obtained during the solid-state process under centrifugal acceleration. The whole process lasted for approximately 0.8 s. In addition to MgB_2 main phase, the following phases were formed: MgO (16–22 wt.%), Mg, and MgB_4. The intermetallic phases, $CuMg_2$ and AlB_2, were also identified in small amounts, where most of them were found on the surface of the sample. As can be seen from Table 2, when we increased the rotation speed up to 2500 rpm, the yield of the superconducting phase (MgB_2) in the sample reduced. It was predicted that as the speed of rotation of the centrifuge increased the temperature in the reaction zone would also increase. The initial powders (magnesium and boron) had interacted with the initiating mixture and formed an intermetallic phase ($CuMg_2$, AlB_2). In this case, it might also be that fewer magnesium and boron atoms were left for the chemical interaction to form the MgB_2 phase.

Table 2. XRD results of the synthesized powders.

Name	The Content, wt.%					
	MgB_2	MgO	$CuMg_2$	MgB_4	Mg	AlB_2
Sample A (1000 rpm)	63.7	23.1	2.1	6.9	-	4.2
Sample B (2000 rpm)	70.8	21.7	1.8	3.8	1.9	-
Sample C (2500 rpm)	63.2	15.4	3.7	10.4	-	7.3

Figure 3A shows a photo of the obtained sample after conducting solid-state synthesis in the high-temperature centrifuge. The sample retained its original shape. It can also be noted that a brown-red film layer of the intermetallic phases, $CuMg_2$ and AlB_2, was formed on the surface of the sample. Relying on this result, we can assume that the initiating mixture during synthesis not only transferred its thermal energy, but also partially interacted with the surface layer of the sample. According to the micrograph obtained (Figure 3B) by a scanning electron microscope, the average particle size of the sample was about 2.5–3.0 µm, well distributed, and did not contain large micropores. This means that we could obtain a dense material using external centrifugal acceleration during the solid-state process. The theoretical calculated density of MgB_2 was 2.57 g/cm^3. We did some measurements of our samples via the Archimedes principle. Our sample's density without the brown layer was approximately 2.39 g/cm^3 (about ~93% of the theoretical one). Our sample's density with the brown layer was approximately 2.35 g/cm^3 (about ~91.4% of the theoretical one). The small decrease in density for the sample with the brown layers might be due to the possible presence of micropores between the main body of the sample and the brown layers.

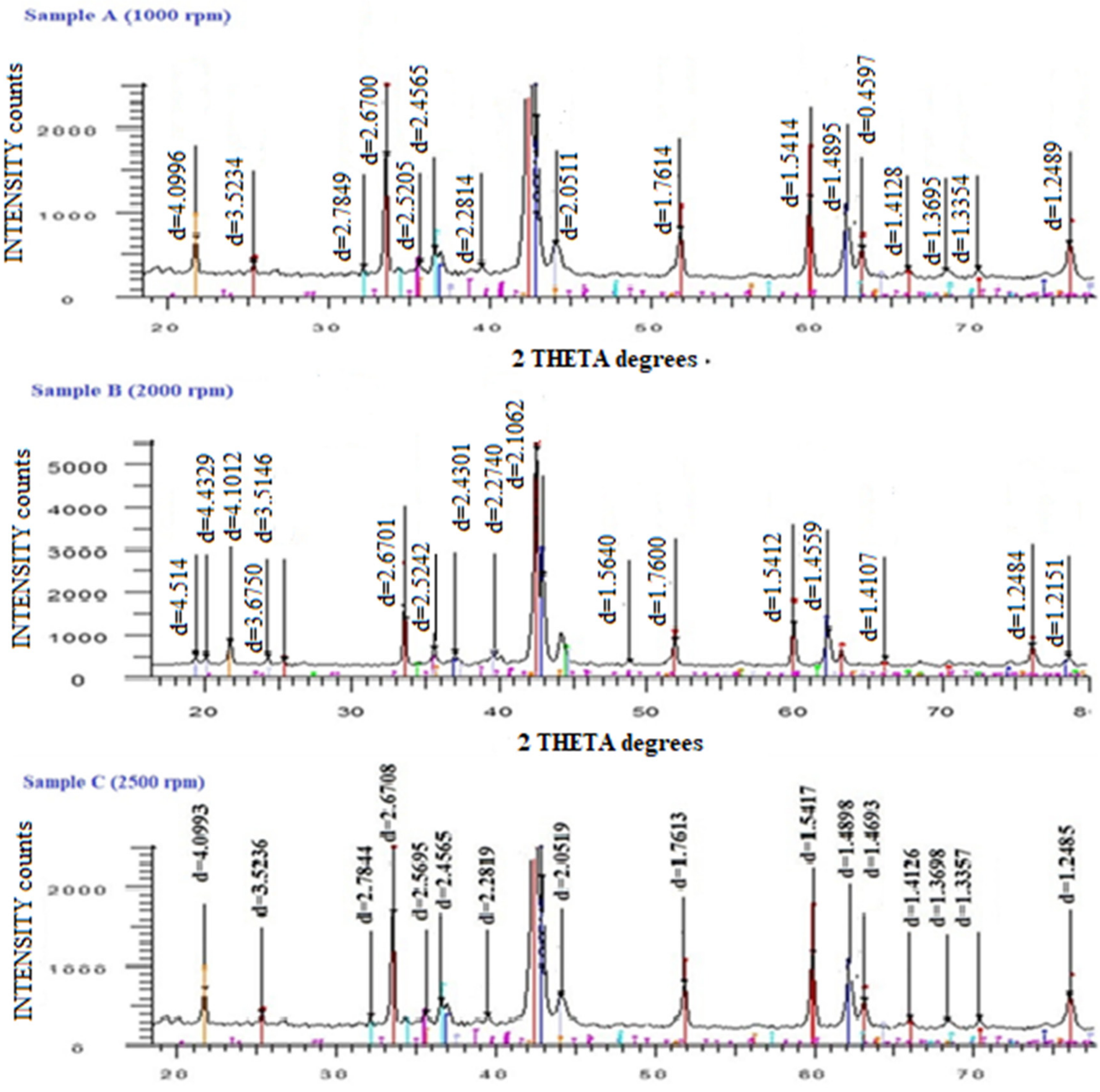

Figure 2. XRD pattern after synthesis for Sample A, B, and C.

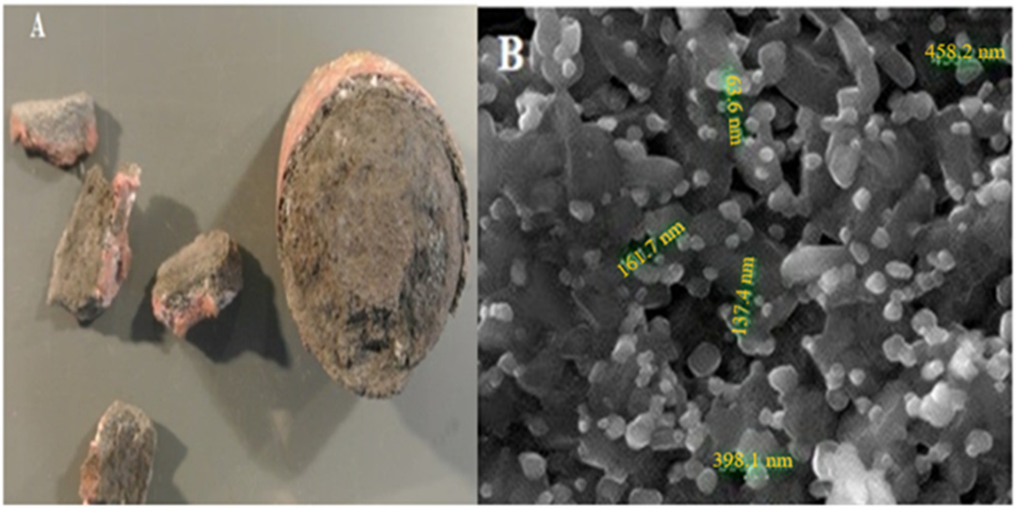

Figure 3. External appearance and microstructure of Sample B after synthesis in the high-temperature centrifuge. (**A**) General photo; (**B**) Microphotography.

We collected a high-speed video recording, at 400 frames per second, of the process being carried out (Figure 4). Based on the thermocouple measurements, the highest temperature during the solid-state combustion process was about 1100 °C.

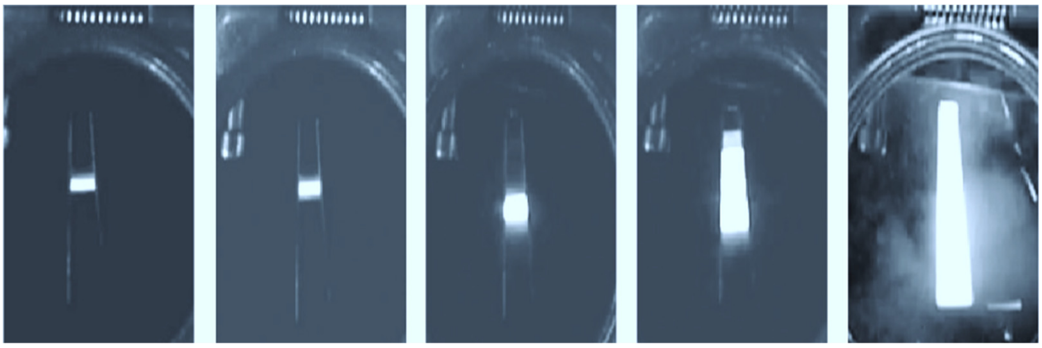

Figure 4. Video recording of the solid-state combustion process at 2000 rpm (Sample B).

The thermodynamic simulation results, which were plotted by means of the HSC Chemistry 6.12 software, are shown in Figures 5 and 6, respectively, for both the Mg + B and Mg + B and CuO + Al + Al_2O_3 interface systems. It is well known that the Mg + B system is exothermic. The amount of MgB_2 phase decreased with increasing temperature. At temperatures of greater than 1300 °C, because of the possible evaporation of the Mg, some B remained in the elemental state, in the forms of amorphous boron [B(A)], beta-rhombohedral boron [B(B)], and glassy structure [B(GL)]. Moreover, because of the boron phase-rich system, the formation of boron-rich magnesium (e.g., MgB_4) was promoted.

The ΔH°rxn value of MgB_2 was calculated to be –92.048 kJ. Through Equation (2), the RSH value of the reaction was calculated as 2004.31 J/g, and it was less than the 2250 J/g lower limit. It (the MgB_2 synthesis through Equation (1)) showed that magnesium diboride was slightly exothermic and some additional energy was needed to initiate the combustion process. That is why, in this study, the CuO + Al + Al_2O_3 mixture was located next to the Mg + B mixture in the reaction tube. But, in this case, the contamination of the sample surface from the initiating mixture was because of the interaction of the two interface systems. In Figure 6, it is possible to see the probable products, particularly in the interface. Although its formation amount decreases with increasing temperature, the MgB_2 was the main product to obtain. Some MgO was also obtained due to the reduction of CuO by the Mg. Thus, some MgO phases were formed. With increasing temperature, due to the Mg boiling and CuO reduction, elemental boron phases were obtained with slight amounts of Cu–Mg intermetallics and Al–B phases. Also, there was a reduced copper phase in the system.

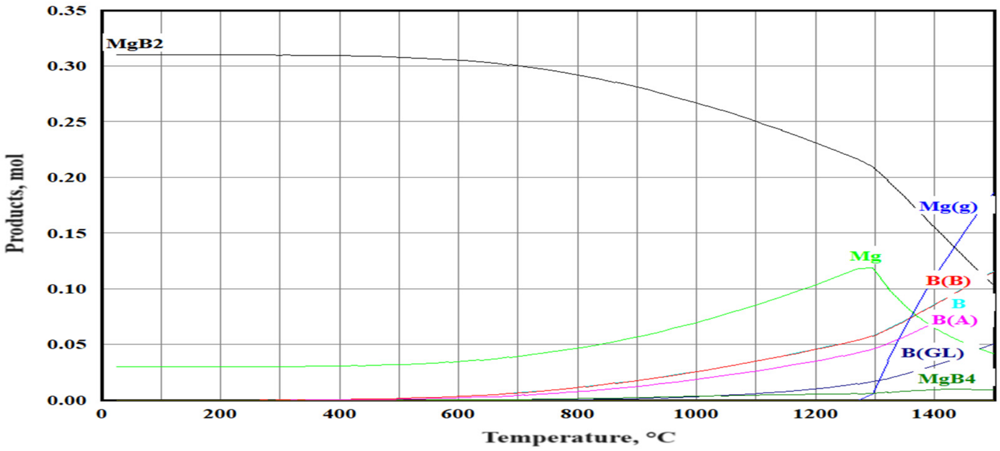

Figure 5. Possible reaction products for Mg + B system with increasing temperature.

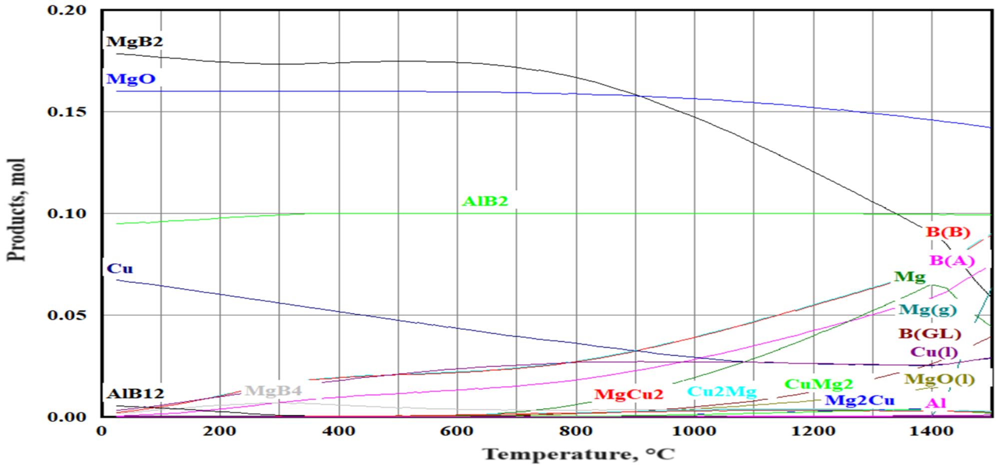

Figure 6. Possible reaction products for Mg + B and CuO + Al + Al_2O_3 interface with increasing temperature.

The superconducting characteristics of the samples in the ZFC and FC modes were magnetometrically measured (Quantum Design PPMS EverCool-II) in the temperature range of 4.2–100 K and magnetic fields of 10 Oe. The test sample was cooled in a zero external magnetic field from room temperature to 4.2 K, after which a small magnetic field (10 Oe) was applied. Then, the magnetic moment (ZFC) of the sample was measured in this constant field as the temperature increased. The sample was again cooled to 4.2 K in the same field (FC). When measuring the temperature dependence of the magnetization of the samples, a decrease in the magnetic moment of the samples at temperatures $37 < T < 38$ K was detected, preceding a sharp response of the magnetic moment when the material passes into the diamagnetic state at T ~37.5 K. This temperature characterizes the transition temperature from the normal state to the superconducting state, which indicates the origin of the superconducting phase in the samples at these cryogenic temperatures. The results obtained show that the rate of rotation of the centrifuge during synthesis enabled the attainment of critical transition temperature, which was close to the theoretically possible T_c parameter. The obtained sample's T_c value could be compared with that of the best samples from different techniques for obtaining MgB_2 superconducting materials.

We also estimated the M (H) dependence of our samples at 5 K. The value of the critical current density of samples was calculated using the Bean formula [21]:

$$J_c = 30 * \Delta M/d \quad (3)$$

where J_c is the critical current density of the samples, and d is the average particle size. ΔM is the difference in the decrease and increase of the magnetization curve, determined by the magnetic hysteresis (Figure 7). The values of the critical current density of magnesium diboride synthesized at different rotational speeds in the self-magnetic field were assessed using this formula.

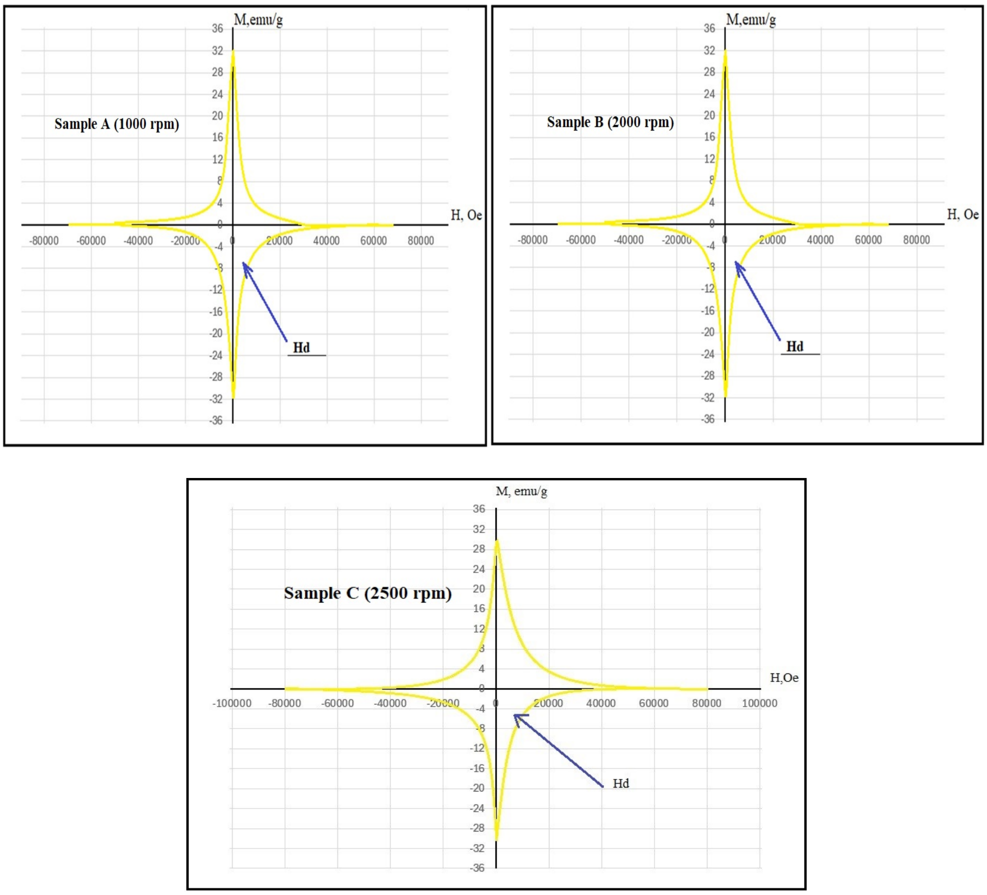

Figure 7. The hysteresis loop curve M (H) for MgB_2 composite.

It was found that the optimal rotation speed (2000 rpm) in the high-temperature centrifuge during the synthesis of magnesium diboride gradually increased the value of the $J_c(0)$ in the samples up to 1.4×10^6 A/cm^2. We considered that this rotation speed (2000 rpm) might have shown a better result because of the optimal interaction between the CuO + Al + Al_2O_3 mixture and the MgB_2 sample, given that the final sample obtained had less impurities and the deep injection of the mixture into the body of the MgB_2 sample. Table 3 shows the main superconducting characteristics of a composite based on magnesium diboride synthesized under centrifugal acceleration.

Table 3. Superconducting characteristics of the obtained samples.

Name	Critical Transition Temperature, K	The Critical Current Density, A/cm^2
Sample A (1000 rpm)	37.5	0.9×10^6
Sample B (2000 rpm)	38.0	1.4×10^6
Sample C (2500 rpm)	36.2	0.8×10^6

4. Conclusions

MgB_2-based superconducting materials were synthesized under the influence of centrifugal acceleration in a high-temperature centrifuge for the first time. It was established that centrifugal acceleration can contribute to process intensification thus shortening the period of formation of the superconductor structure to the point where it takes just several milliseconds. It was also found that an increase in the speed of rotation of the centrifuge up to 2000 rpm gradually increased the value of the critical current density $J_c(0)$ up to 1.4×10^6 A/cm^2 in the magnesium diboride samples. At the same time, we observed that the injection of impurities into the surface layers of the synthesized material does not significantly affect the critical transition temperature of the MgB_2 samples. In this regard, further research on the effect of centrifugal acceleration on the processes of solid-state synthesis of magnesium diboride, as well as the superconducting properties of the material based on it, is very promising.

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