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# EFFECT GRAPHITE ON MAGNESIUM DIBORIDE SUPERCONDUCTIVITY SYNTHESIZED BY COMBUSTION METHOD UNDER ARGON PRESSURE: PART I

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Preliminary Note – Prethodno priopćenje

Solid-state synthesis of a superconductor based on magnesium diboride doped by graphite microparticles ($MgB_2$@C) at argon atmosphere has been described. The offered method allows the possibility to increase the critical current density of the studied samples at relatively low temperature in the inert environment. The superconducting characteristics of samples critical current density (Jc) and critical transition temperature (Tc) have been measured. The impact of the doping additives on superconducting characteristics of magnesium diboride has been analyzed. The results showed that the best optimal characteristics are for $MgB_2$@3%C that reveals a good critical transition temperature 38,8 K and the higher critical current density 2,7 x $10^6$ A / $cm^2$ at 5 K.

*Keywords:* magnesium diboride, graphite microparticle, solid-state synthesis, superconductivity, temperature

## INTRODUCTION

More than 100 years have passed since the Dutch physicist Heike Kamerling-Onnes discovered the phenomenon of superconductivity in 1911, for which he was awarded the Nobel Prize. We are talking about the ability of certain substances and materials when they are cooled below a certain temperature (the so-called critical transition temperature) to completely lose electrical resistance and conduct an electric current without any losses. In early 2001, superconductivity was accidentally discovered in an intermetallic compound. Yoon Nagamatsu, a Professor at Aoyama Gakuin University in Tokyo, discovered that a long – known chemical – magnesium diboride ($MgB_2$) goes into a superconducting state at a much higher temperature than all other compounds of this type. The Japanese scientist's report caused a real sensation in the world [1]. First, the critical transition temperature of magnesium diboride is still almost twice as high as that of its closest competitor among two-element intermetallic compounds [2].

Scientists did not expect anything like this from this class of substances. Second, it turned out that the superconductivity of magnesium diboride is fairly accurately described by the Bardeen-Cooper-Schrieffer theory – the same theory that failed to explain the high-temperature superconductivity of metal oxide ceramics. This also surprised scientists, because they have long been based on the thesis that classical superconductivity in stable chemical compounds at temperatures above 25 degrees Kelvin is simply impossible [3]. This news has caused a boom in research and publications: currently, there are several new articles on this topic in the world every day. Magnesium diborides have relatively low anisotropy and simple chemical composition [4]. Today, very active work is being done to make this compound suitable for wide practical applications. This material has a small specific mass, cheap and easy to produce – which is not the case with metal oxide ceramics. And it has such strength characteristics that will allow it to be used in a number of technical solutions [5]. A level of achievement in superconducting properties of such materials let them be prospective for applying in cryogenic equipment working on the levitation principle: electrical motors, new generators, modern pumps for transferring liquid gas and magnetic bearings [6]. An undoped magnesium diboride is not so suitable for applying due to the weak flux pinning and low values of Jc and Tc. A considerable rise of critical current density (Jc) in magnesium diboride might be reached via chemical doping with different sorts of material. Chemical doping is a simple and easily scalable method [7]. An essencial increase of critical current density (Jc) in magnesium diboride can be reached via chemical doping with carbon (C) containing compounds or composites, like $B_4C$, SiC, C or carbon single-walled nanotubes, carbohydrates, hydrocarbon etc. A several research groups synthesed and characterized materials with such chemical formulas as $(Mg_{1-z}T_z)B_2$ or $Mg(B_{1-y}M_y)_2$. The agenda was multifaceted: to seek changes in $T_c$, to conduct tests of superconducting mechanisms in magnesium diboride, and to introduce additional pinning centers, which could lead to a higher critical cur-

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rent density. To replace the boron site, a number of attempts were made with various elements. In most of these attempts, elemental magnesium, boron, and carbon were used as starting materials, and the synthesis was carried out at various pressures and temperatures. One of the difficulties associated with doping magnesium diboride may be the fact that the $MgB_2$ structure is strong and requires a close atomic level; to achieve substitution, mixing of the dopant with the doped element is required before or during the synthesis. Synthesis of the optimization and physical properties of almost single-phase carbon-doped $MgB_2$ with a nominal stoichiometry of $Mg\ (B_{0.8}C_{0.2})_2$, synthesized from magnesium and boron carbide ($B_4C$) as starting materials. The superconducting transition temperature was about at 22 K (more than 17 K lower than in an undoped magnesium diboride). Chunks of magnesium (99,9 % purity) and $B_4C$ powder (99 % purity) were sealed in tantalum tubes, sealed in quartz, and placed in a heated box furnace (heating for 2 hours at 600 °C, and then another 2 hours at 700 °C) and then (after the desired synthesis time) was quenched to room temperature.

## EXPERIMENTAL PROCEDURE

Superconducting samples of magnesium diboride undoped and doped with graphite (C) microparticles were obtained by the solid state reaction method under argon conditions in a high-pressure chamber (see Figure 1).

Powders of amorphous boron (about 20 - 30 μm), magnesium (200 - 250 μm), and graphite (45 - 90 μm) were used to prepare for the experimental samples. The summary chemical equation which describes the reaction of $MgB_2$ formation and which has been used to quantify the composition of raw materials are as follows:

Undoped: $Mg+B \rightarrow MgB_2$;

Doped: $Mg+2B+C \rightarrow Mg\ (B_{y-1}C_y)_2$

In each batch, all ingredients weigh 20 g. After weighing (by an electronic scale) them with the accuracy of 0,000 1 g, the Mg, B and graphite powders were dry mixed in an agate mortar by manually for 15 min to get more homogenized mixer.

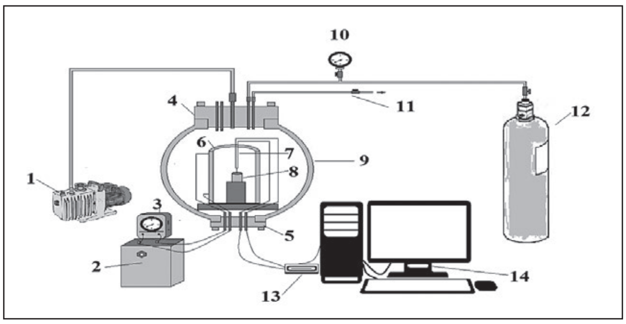

**Figure 1** High Pressure Chamber
1 a vacuum pump, 2 a transformer, 3 an ammeter, 4 an upper chamber cover, 5 a lower chamber cover, 6 a tube heating furnace, 7 a thermocouple, 8 a sample, 9 a chamber vessel, 10 a pressure gauge, 11 an inlet and outlet valves, 12 an argon baloon, 13 LTR-U-1 data acquisition system unit, 14 a computer

## RESULTS AND DISCUSSION

According to the x-ray diffraction (XRD) analysis, the following phases were formed in the Mg-B-C system: magnesium diboride (within 63 – 74 wt. %), magnesium oxide (within 17 – 23 wt. %), and small impurities of Mg and $MgB_4$ were identified (Table 1 and Figures 2-6). Graphite does not form a separate phase in the sample, probably carbon atoms partially chemically substitute of boron atoms in the lattice structure of magnesium diboride as $Mg(B_{1-y}C_y)_2$.

Table 1 **XRD results after combustion at solid state reaction mode**

| Name of the sample | The results of XRD / wt. % | | | |
|---|---|---|---|---|
| | $MgB_2$ | MgO | Mg | $MgB_4$ |
| Undoped $MgB_2$ | 85,0 | 12,6 | 2,4 | - |
| $MgB_2$@1 % C | 69,9 | 22,8 | 7,3 | - |
| $MgB_2$@3 % C | 74,2 | 17,6 | 6,4 | 1,9 |
| $MgB_2$@5 % C | 67,2 | 23,3 | 6,0 | 3,5 |
| $MgB_2$@7 % C | 66,3 | 22,7 | 5,0 | 6,0 |

As can be seen from Table 1, when magnesium diboride doped with carbon in the amount of 1 wt.% - 3 wt.%, the yield of the main phase of $MgB_2$ increases in the final product (from 67 wt. % to 74 wt.% respectively), and a further increase in the doping component leads to a smooth decrease in the main phase of $MgB_2$ in the final product up to 66,3 wt.%. One reason of this might be, when a concentration of graphite atoms increased, then probably some part of them could effect on forming of $MgB_4$ phase or otherwise $Mg(B_{1-y}C_y)_4$. As we know, $MgB_4$ phase is not useful one and has negative impact on superconducting characteristics.

Figures 2-7 shows the microphotographs of undoped and doped magnesium diboride. The undoped sample has spherical and squared particles with the average grain size about 0,2 – 0,5 μm. The doped sample has a small amount of microporous in a structure, consists of spherical and rounded irregularly shaped particles with

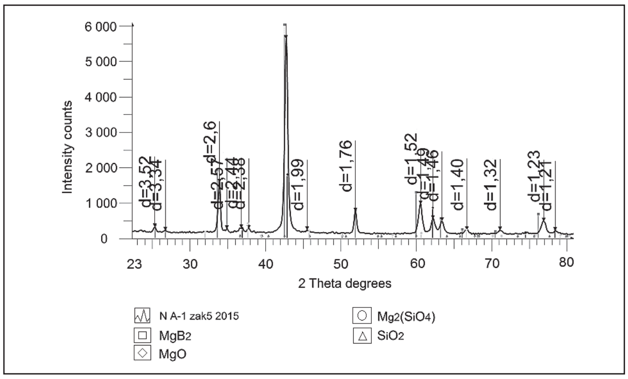


**Figure 2** XRD pattern of undoped $MgB_2$

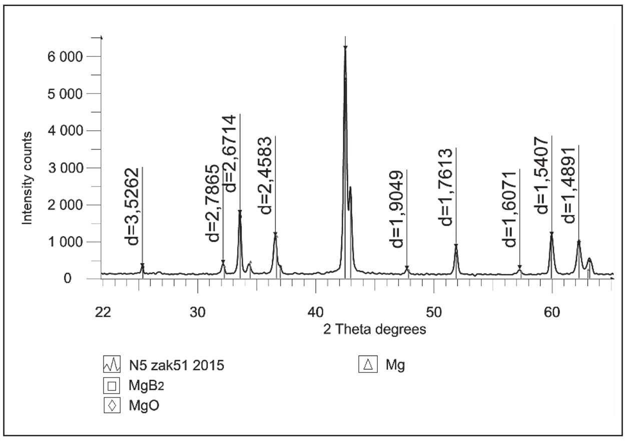


**Figure 3** XRD pattern of $MgB_2$@1 % C

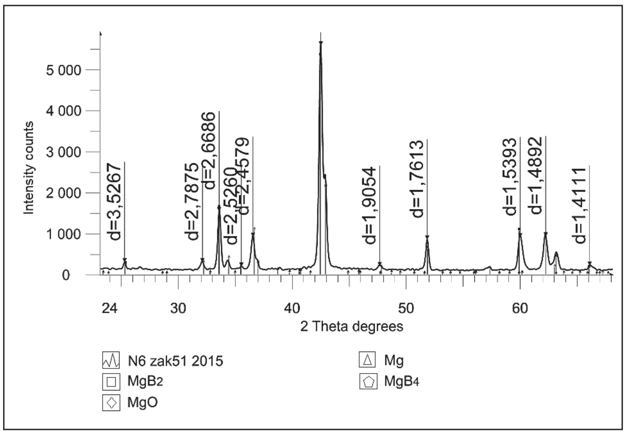


**Figure 4** XRD pattern of $MgB_2$@3 % C

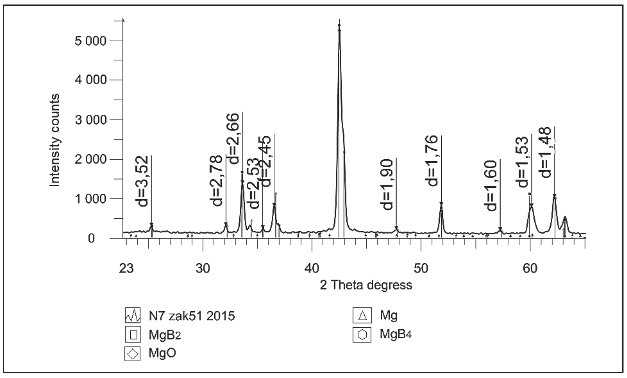


**Figure 5** XRD pattern of $MgB_2$@5 % C

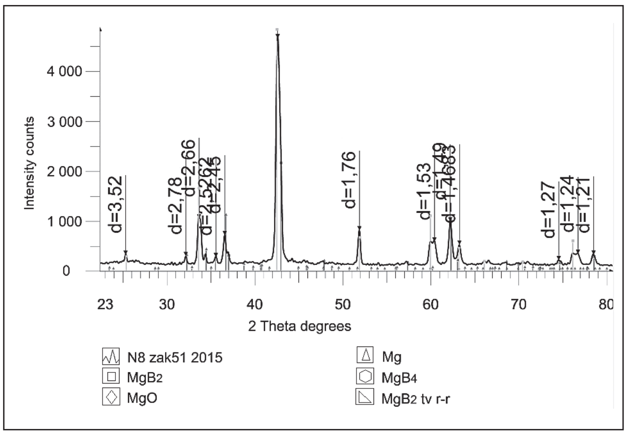


**Figure 6** XRD pattern of $MgB_2$@7 % C

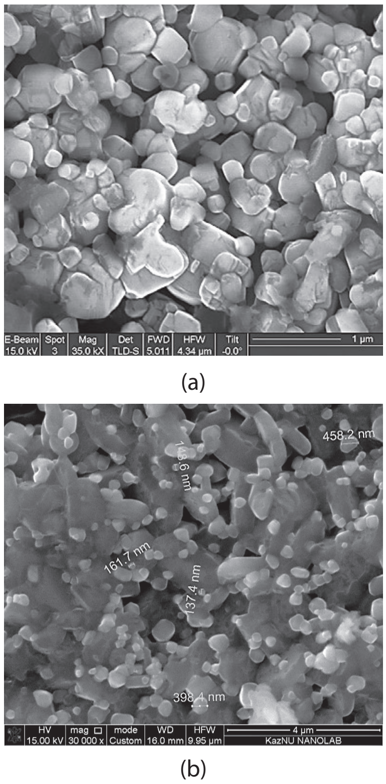


**Figure 7** Microphotography of undoped (a) and doped (b) with graphite of $MgB_2$

the average grain size about 0,25 – 0,4 μm. When measuring the temperature dependences on the magnetization of samples of the Mg–B–C system, a fall in the magnetic moment of samples at temperatures of 38 < T < 40 K was found, which precedes a straight response of the magnetic moment to the diamagnetic state at T = 38,5 K. This temperature characterizes the transition temperature from the normal state to the superconducting one. The obtained data indicate the origin of a superconducting phase in samples of the Mg–B and Mg-B-C systems, at temperatures of more than 38,5 K. The critical current density value of samples was computed by using the Bean's formula [7]:

$$J_c = 30 * \Delta M / d$$

$J_c$ is a parameter of the critical current density of the sample, and d is the average particle size. ΔM is the difference in decreasing and increasing the magnetization curve. The value of the $\Delta M$ value was taken from the hysteresis loop curves. Using this formula, we found the value of the critical current density of magnesium diboride containing graphite microparticles at various concentrations in their own magnetic field. It was found that an increase in the graphite content in magnesium diboride proportionally reduces the value of Jc of the samples. One reason might be that an increase in the content of graphite in the composition distorts the crystal structure of the superconducting phase $MgB_2$, because the carbon atom radius ($r_c$ = 0,772 À) is much less than the boron atom radius ($r_b$ = 0,822 À). It is determined that doping with 3 wt. % of micrographite is the optimal dose for obtaining higher critical current densities for $MgB_2$ samples with the critical current density was 2,9 x $10^6$. In comparison with work, where authors could get a nanographite doped (0,1 wt. %) magnesium diboride with the following superconducting parameters of the critical current density 1,1 x $10^6$ at 5K. This is interesting result, which shows micro particles have more effect on $J_c$ parameter of $MgB_2$ superconductor than nanoparticles one. Meanwhile, it obvious that doping of micrographites do not have any impact on the critical transition temperature of samples.

## CONCLUSION

A superconductor based magnesium diboride with a different content of graphite microparticles was obtained by combustion mode at an argon environment. The offered method allowed the possibility to considerably increase the critical current density of the studied samples at relatively low synthesis temperature in the inert environment. Obtained results revealed that the best optimal parameters are for MgB2@3 % C sample that shows the highest critical transition temperature 38,8 K and a critical current density 2,9 x $10^6$ A / cm².

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**Note:** The responsible for England language is L. D. Sergeeva, Almaty, Kazakhstan