Research Article | Submit Manuscript

Turkish Journal of Materials

Effect of the excess Mg on the microstructure and superconducting properties of in-situ MgB_2 bulks

B. Savaşkan [1,*] and S. B. Güner [2]

[1] Department of Energy Systems Engineering, Faculty of Technology, Karadeniz Technical University, Of, Trabzon, 61830, Türkiye

[2] Department of Physics, Faculty of Arts and Sciences, Recep Tayyip Erdoğan University, Rize, 53100, Türkiye

Published: 31.12.2024

Turk. J. Mater. Vol: 9 No: 1 Page: 9-14 (2024) ISSN: 2636-8668

*Corresponding author's e-mail: bsavaskan@ktu.edu.tr

ABSTRACT: In this study, we focused on the role of magnesium in the conventional sintering in-situ process and its effect on the superconducting and microstructure properties of the MgB_2+Mg bulks. Magnesium additions (10-35 wt.%) were mixed into in-situ (Mg+B) powder to obtain composite powders that were sintered at 675 °C by means of the conventional in-situ sintering. The structural and superconducting properties of the MgB_2 samples were studied by using X-ray diffraction (XRD), scanning electronic microscope (SEM), and electrical resistivity (R-T) measurements. MgB_2 was verified as the main phase in all the samples by X-ray diffraction. Superconducting properties were also enhanced with Mg additions, especially by the 10 and 15 % (in weight) MgB_2 -Mg samples compared to the unmodified MgB_2 sample. The optimum amount of magnesium additions was found to be around 10 % for the in-situ MgB_2 samples in this study.

Keywords: MgB_2 bulk, in-situ, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), critical temperature.

Cite this article: B. Savaskan, S. B. Guner. Effect of the excess Mg on the microstructure and superconducting properties of in-situ MgB_2 bulks. Turk. J. Mater. 9(1) (2024) 9-14.

1. INTRODUCTION

The superconductivity of magnesium diboride (MgB_2), an intermetallic compound, with a critical temperature (T_c) of about 39 K was discovered in 2001 [1]. The T_c of MgB_2 is higher than that of conventional low-temperature superconductors (LTS), Nb-Ti (9.7 K), Nb3Sn (18.3 K) which operate below 20 K, and they require extensive use of expensive liquid helium (LHe) [2-3]. MgB_2 materials can be used below 30 K, therefore liquid hydrogen (LH) around 20 K is ideally suited for cooling the MgB_2 superconductor. The combination of liquid hydrogen and MgB_2 superconducting bulks presents a unique opportunity for the applications of hydrogen energy such as high-performance submersible liquid hydrogen (LH) pumps which require superconducting magnetic bearings and magnetic levitation systems [4-5]. In addition, MgB_2 bulks can be manufactured at much easier, short notice and at a lower cost than high-temperature superconductors (HTS) such as RE-Ba-Cu-O (RE : Rare Earth element) cuprates. Furthermore, grain boundaries in MgB_2 act as flux pinning centers and also support the current flow in polycrystalline samples. This behavior, unlike the cuprate superconductors, has enabled the development of processing routes to fabricate MgB_2 in different shapes like wires, tapes, thin films and bulks [3, 6, 7].

Conventionally, MgB_2 bulks are synthesized by in-situ sintering route, where elemental Mg and B powders react to produce MgB_2 at moderate temperature (generally between 600 - 800 ºC). In a typical in-situ sintering process, Mg melts (the melting point of magnesium is around 650 °C) and diffuse into Boron grains thus the resulting MgB_2 phase can be obtained with relatively easily without applying any external pressure during the heating process [8]. Although the MgB_2 phase can be obtained relative easily in in-situ processing technique, the main problem of this process is porous structure in MgB_2 bulks and the resulting sample is typically around 50% dense [6-11]. This is mainly because of the evaporation of Mg during the heat treatment at high temperature and also one mole Mg and two moles B react to form one mole of MgB_2, a 25% reduction in volume occur. Based on this certain challenge, to improve the grain connectivity of MgB_2 several approaches carried out by the researchers are non-stoichiometric compositions, different precursor powders and sintering aids. From this point of view, several research groups have used excess Mg to obtain dense and well-connected MgB_2 bulks and wires [12-20]. Zeng et al. showed that the addition of excess Mg prevents the Mg loss, reduces the MgO content and the microcracks and also improves the grain connectivity, the critical current density (J_c) and upper critical field (H_{c2}) [14]. Ma et al. found that the residual Mg makes the microstructure more homogenous and dense at the low sintering temperatures [12].

Although several researchers have investigated the effect of excess Mg in the case of MgB_2 bulks produced by the in-situ process, in these studies the use of excess Mg is limited to the use of 10 %. The effect of Mg additions above 10 % in the case of the in-situ method has not been investigated so far. In this work, therefore, we focused on the role of magnesium in the conventional sintering process and its effect on the superconducting and microstructural properties of in-situ MgB_2 +Mg bulks.

2. MATERIAL AND METHOD

The MgB_2 bulk samples were prepared by an in-situ sintering method. Elemental Mg powder (purity: 99.8%, 325 mesh, Alfa Aesar, USA), and amorphous nano-B powder (purity: 99 %, d50 < 400 nm; supplied from Pavezyum, Türkiye) were used as precursor powder. The amount of excess Mg powder was 0, 10, 15 and 35 wt. % of the MgB_2 powder with 2 grams. Different contents of Mg powder were added in each sample and mixed in an agate mortar for 30 minutes in an air atmosphere. The powder mixture then was pressed into pellets of 20 mm in diameter and 3.5 mm in thickness using a uniaxial pressing machine. Following the pressing process, the pellets were wrapped in titanium foil and were placed in a chromium tube which is in the center of the cylindrical furnace. After that, the chromium tube was vacuumed and the pellets were sintered at 675 °C for 2 hours. During the heating process, high-purity Ar gas was supplied into the chromium tube. The heating and cooling rates were used 5 °C/min. The schematic demonstrates the conventional sintering procedure in Figure 1.

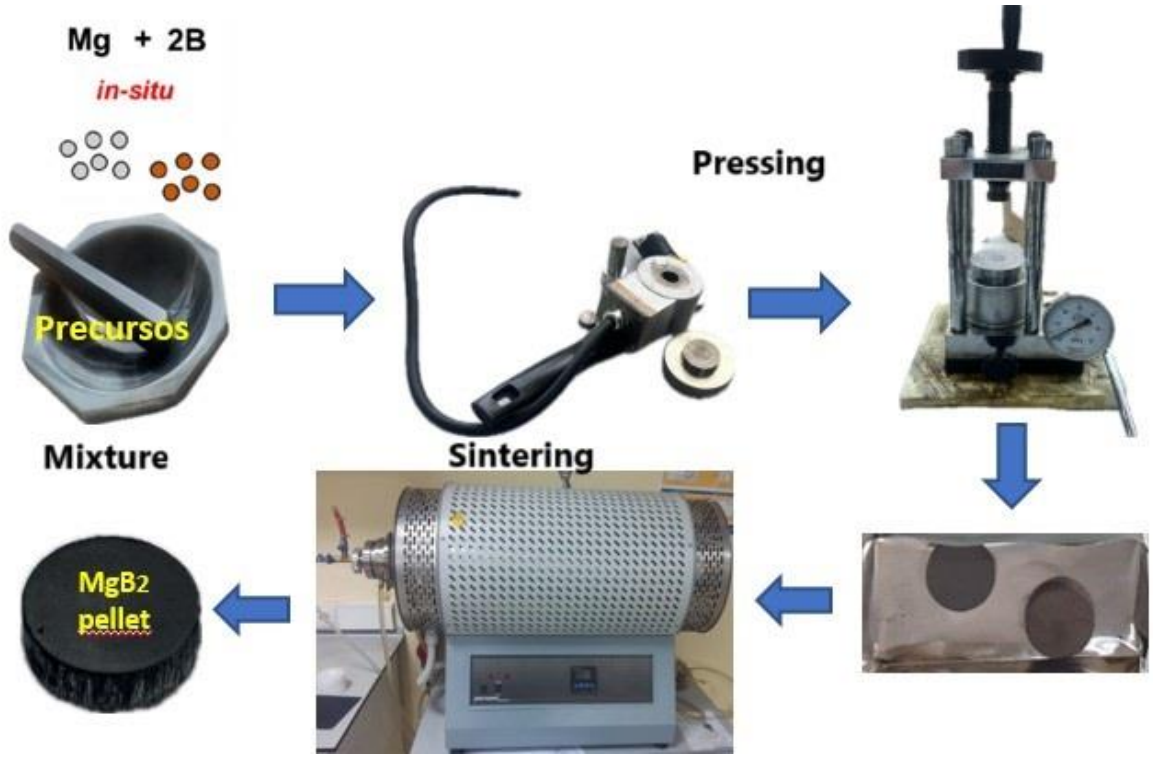

Figure 1. Workflow of MgB_2 bulk synthesis

To analyze the structural properties of MgB_2 samples, the X-ray diffraction (XRD) data were obtained using a Rigaku D/Max-III diffractometer with a step size of 0.02 in the range of 20-80° using CuKλ (λ= 1.5406 Å) target. The lattice parameters (a and c), crystallite size and strain detected in the MgB_2 +Mg bulk samples were calculated from the XRD data

by using Rietveld refinement. The microstructures of MgB_2 bulks were investigated by scanning electron microscope (SEM) JEOL JSM 6610 with an accelerating voltage of 20 kV in the secondary electron image mode on small specimens cut from the MgB_2 samples.

The electrical resistivity as a function of temperature in a range of 15-50 K was performed by a standard DC four-point transport measurements using a closed-cycle cryostat at low temperatures to obtain the effective cross- sectional area for macroscopic current transport in the MgB_2+Mg samples.

3. RESULTS AND DISCUSSION

Figure 2 (a) shows the XRD patterns for 10 %, 15 % and 35 % (all in weight) Mg- MgB_2 and unmodified MgB_2 sintered by the conventional in-situ route. From the analysis, the main phase was MgB_2 with peaks of (001), (100), (101), (002), (111), (200) and (201) and those correspond to hexagonal MgB_2 structure for all samples. The amount of residual Mg phase increased drastically with increasing Mg additions. On the other hand, no MgB_4 phase could be detected by XRD. As shown in Figure 2 (b), the (100) and the (101) peaks of the Mg-MgB_2 samples with larger Mg additions shifted towards higher angles which is consistent with a shrinkage of the a-axis lattice parameter. In other words, magnesium additions had a visible effect on the composition of the MgB_2+Mg samples, in particular on the fractions of residual Mg.

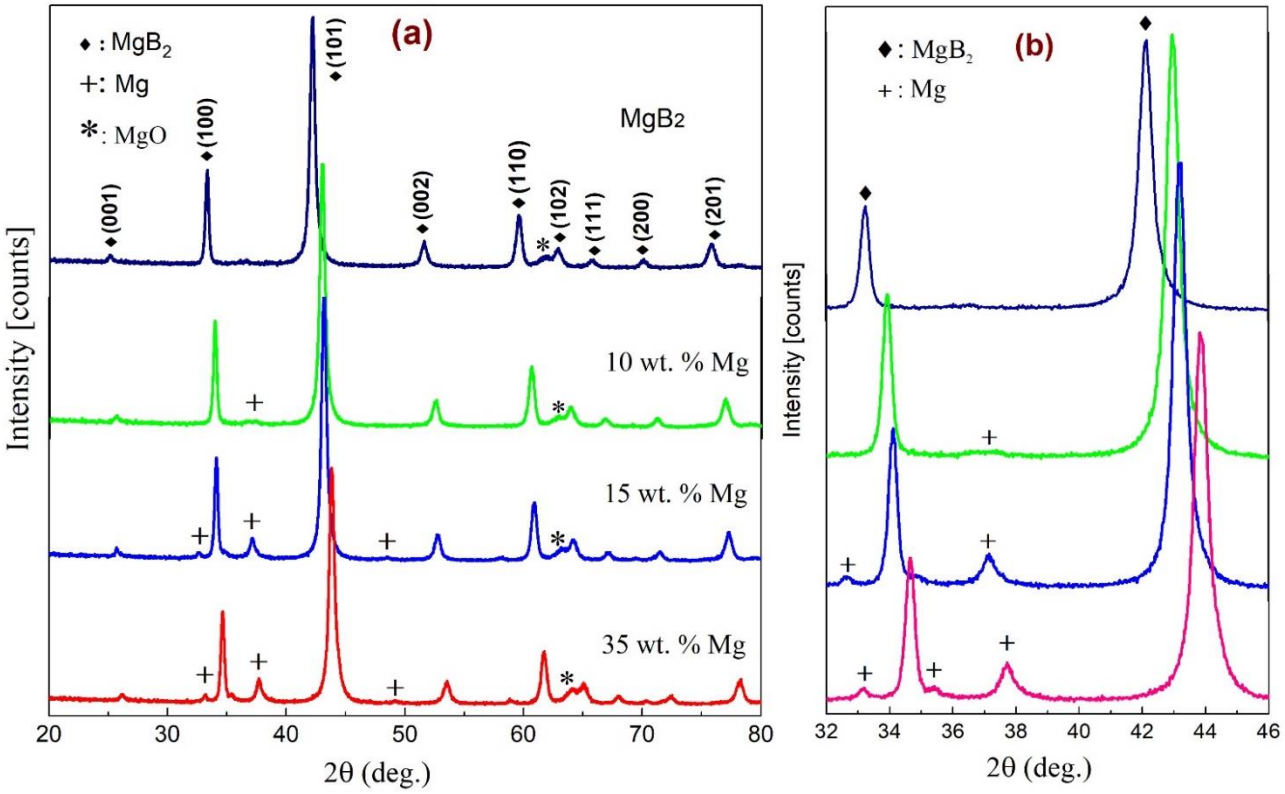

Figure 2. (a) The XRD patterns of MgB_2+Mg and unmodified MgB_2 samples, (b) Variation of the (100) and the (101) peaks

To quantify the phase compositions, XRD patterns of MgB_2+Mg samples were analyzed by Rietveld refinement and the results are summarized in Table 1. Table 1 shows the lattice parameters, c/a, and crystalline size values of the samples calculated from the XRD patterns. It was observed that the lattice parameters drop with increasing addition of Mg amount. The a-axis lattice parameter decreased from 3,1061 Å for the unmodified MgB_2 sample to 2,9874 Å for the 35 wt.% Mg sample. The variation of the c-axis lattice parameter is very similar to that of a-axis lattice parameter. In addition, the c/a values have shown opposite behaviour that of the lattice parameters, which indicates the presence of lattice strain in the MgB_2+Mg samples [16,17].

Figure 3 shows the scanning electron microscopy (SEM) images for MgB_2 bulk samples containing different fractions of Mg additions at 1000× in SE mode (a) 0 %, (b) 10 %, (c) 15 % and (d) 35 %. Unmodified MgB_2 sample has a very porous structure, which is the nature of in-situ MgB_2 processing. In contrast, the 10 w% and 15 % samples showed less porosity, dense microstructure and cleaner inter-particle interface. This observation is attributed primarily to the presence of excess Mg, which is known for improving grain connectivity, the elimination of micro-cracks and avoiding Boron-rich impurity phases. This is consistent with the works of Zhang [14] and Matthews [7] which reported similar findings and concluded that 10 % Mg excess played an important role in cleaning the grain boundary and healing the micro cracks as well. In contrast, MgO and Mg-rich areas were found in the 35 wt.% Mg sample as shown in Figure 3 (d). This is in good agreement with the XRD results.

Table 1. Lattice parameters, their ratio and critical temperatures of the unmodified MgB_2 sample, and the MgB_2–Mg samples containing 10, 15 and 35 % Mg (in weight)

Samples	a = b [Å]	c [Å]	c/a	Full Width at Half Maximum (FWHM) (110) (deg)	Crystalline size [Å]	$T_{c,onset}$ [K]
MgB_2	3.1061	3.5446	1.14117	0.62	0.0151	36.96
10 % Mg + MgB_2	3.0583	3.4906	1.14135	0.54	0.0171	37.53
15 % Mg + MgB_2	3.0332	3.4666	1.14289	0.54	0.0172	37.41
35 % Mg + MgB_2	2.9874	3.4192	1.14454	0.59	0.0158	37.11

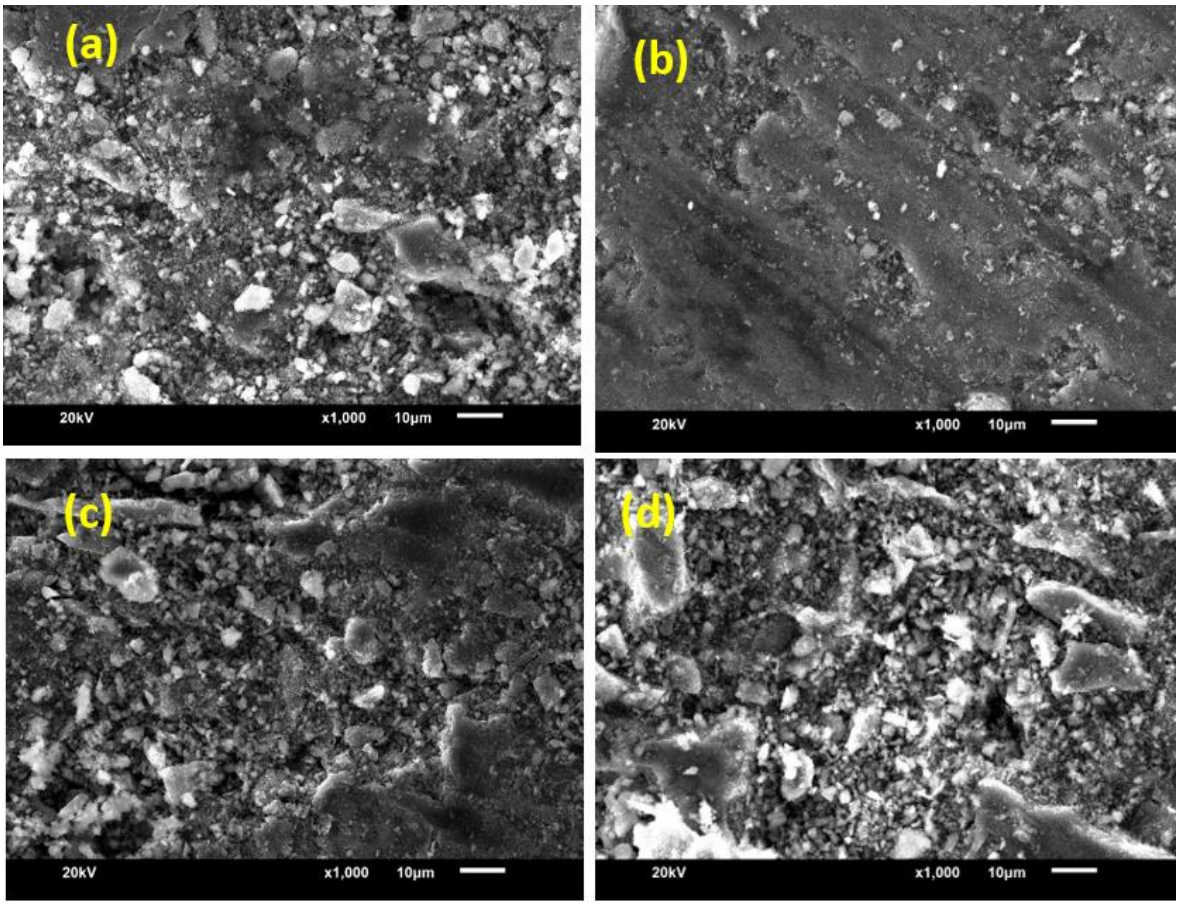

Figure 3. SEM images of the MgB_2+Mg bulk samples containing different fractions of Mg additions at 1000× in SE mode (a) 0 %, (b) 10 %, (c) 15 % and (d) 35 % (in weight)

Zero-field-cooled (ZFC) measurements in Figure 4 show that the superconducting transition temperature ($T_{c,\ onset}$) increases in 10 % Mg and 15 % Mg specimens. This is consistent with the SEM analysis (Figure 3) showing that the microstructure of the 10 % Mg sample sintered to a much greater extent than unmodified MgB_2. The enhancement of the Tc values indicates the improvement of the material crystallinity. The unmodified $MgB_2$and 35 % Mg samples have a large superconducting transition width (ΔT_c) and lower T_c, which can be attributed to their poor density. Matthews et al. [7] reported a similar reduction in ΔT_c in the 10 % Mg sample is an effect of the Mg additions. The decrease of the $T_{c,onset}$ of the 35 % Mg sample could be related to the residual Mg accumulation on the grain boundaries and high macrostrain. This means that the 35 wt.% Mg sample contains a significant fraction of residual Mg remained after the sintering process. In addition, such degradation of the superconducting properties of 35 % Mg sample can be explained by high Mg content in the microstructure and the presence of considerable MgO, as seen from XRD patterns in Figure 2. Therefore, this result is in good agreement with the XRD and the SEM results of the MgB_2+Mg samples.

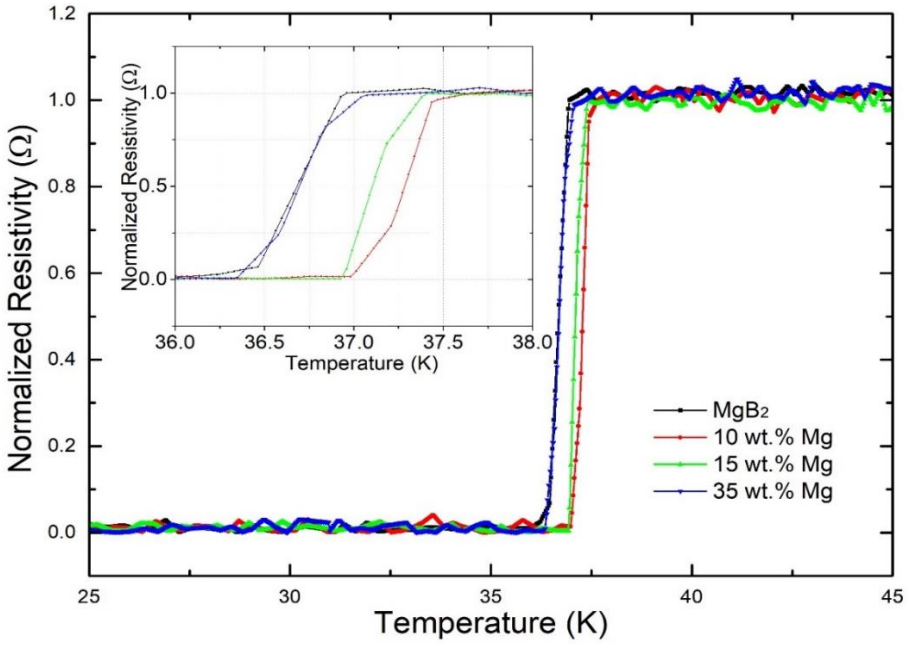

Figure 4. Superconducting properties of the unmodified MgB_2 ,and the MgB_2+Mg samples containing 10, 15 and 35 % Mg

Figure 5 shows the electrical resistivity as a function of temperature for the unmodified $MgB_2$and the MgB_2+Mg bulk samples containing 10, 15 and 35 % Mg. The unmodified MgB_2 sample has a large resistivity and does start dropping at 37.5 K and reaches zero resistance its superconducting transition width is ΔT_c = 1K. The high resistivity in the unmodified sample suggests that intergrain coupling is weak.

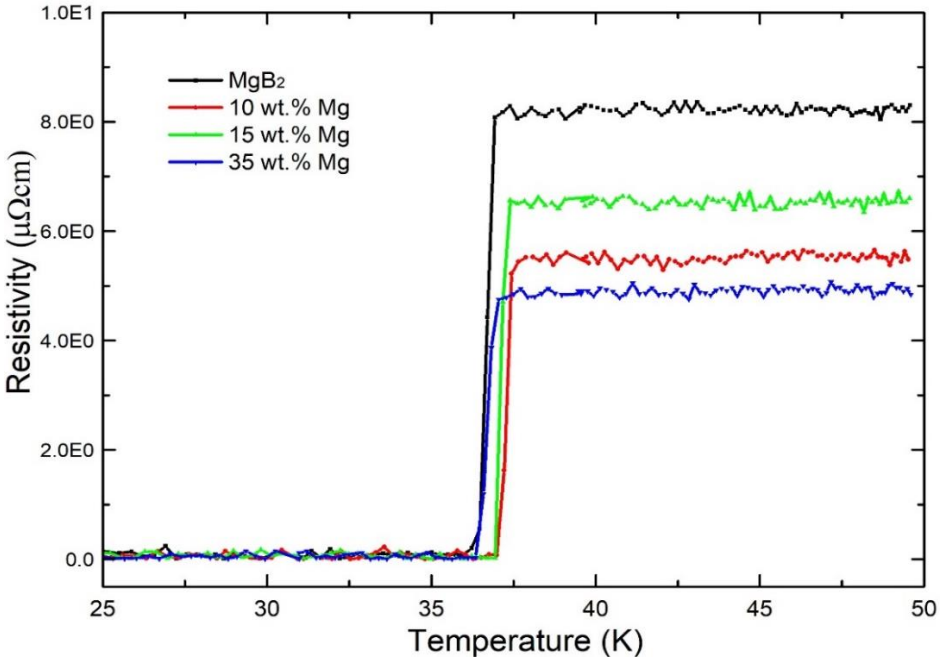

Figure 5. Temperature dependence of resistivity for the unmodified MgB_2 and the MgB_2+Mg bulk samples containing 10, 15 and 35 % Mg

4. CONCLUSION

In summary, we have investigated the role of Magnesium in the conventional in-situ sintering process and its effect on the microstructure and superconducting properties of the MgB_2+Mg bulks. Mg has a very substantial effect on the density of the MgB_2 bulks and their composition. Addition of the 10 wt.% Mg and 15 wt.% Mg resulted in a Mg liquid phase and led to significant density improvements and thus enhanced the critical temperature. The results showed that Mg addition to in-situ powders develops the superior connectivity potential of MgB_2bulk superconductor.

ACKNOWLEDGMENT

This work was supported by the Scientific Research Projects Coordination Unit of Karadeniz Technical University with the project FYL-2024-15871.

REFERENCES

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Superconductivity at 39 K in magnesium diboride, Nature. 410 (2001) 63–64.

[2] G. A. B. Matthews, T. Mousavi, S. Santra, C. R. M. Grovenor, P. S. Grant, S. Speller, Improving the connectivity of MgB_2 bulk superconductors by a novel liquid phase sintering process, Supercond. Sci. Technol., 35 (2022) 6.

[3] Y. Xing, G. Russo, P. L. Ribani, A. Morandi, P. Bernstein, J. Rossit, S. Lemonnier, F. Delorme and J. Noudem, Very strong levitation force and stability achieved with a large MgB_2 superconductor disc, Supercond. Sci. Technol. 37 (2024) 02LT01.

[4] B. Savaskan, U.K. Ozturk, S.B. Guner, M. Abdioglu, M.V. Bahadır, S. Acar, M. Somer, A.M. Ionescu, C. Locovei, M. Enculescu, P. Badica, Bulk MgB_2 superconductor for levitation applications fabricated with boron processed by different routes, Journal of Alloy and Compounds. 961 (2023) 170893.

[5] T. Prikhna, M. Eisterer, B. Büchner, R. Kluge, V. Sokolovsky, V. E.Moshchil, A. Bodenseher, J. Filzmoser, D. Lindackers, S. S. Ponomaryov, M. V. Karpets, F. N. Werfel, U. Flögel–Delor, A. Vakaliuk, and V. B. Sverdun, Trapped Fields of Hot-Pressed MgB_2 for Applications in Liquid Hydrogen, IEEE Transactions on Applied Superconductivity. 33 (2023) 5.

[6] A. Bhagurkar, Processing of MgB_2 Bulk Superconductor by Infiltration and Growth, Ph. D. dissertation, Brunel University, London, England, (2017).

[7] G. A. B Matthews, S. Santra, R. Ma, C. R. M Grovenor, P. S. Grant and S. C. Speller, Effect of the sintering temperature on the microstructure and superconducting properties of MgB_2 bulks manufactured by the field assisted sintering technique, Supercond. Sci. Technol. 33 (2020) 054003.

[8] A. Yamamoto, H. Tanaka, J. Shimoyama, H. Ogino, K. Kishio, and T. Matsushita, Towards the Realization of Higher Connectivity in MgB_2 Conductors: In-situ or Sintered Ex-situ, Japanese Journal of Applied Physics. 51 (2012) 010105.

[9] B. Savaşkan, Strong Influence of Pressure on the Magnetic Properties of MgB_2 Bulk Superconductors, Sakarya University Journal of Science. 27 (2023) 48-54.

[10] B. Savaşkan, Effect of the Sintering Temperature on Electromagnetic Behaviour of MgB_2 Bulks Using Experimental and Numerical Methods, Journal of Superconductivity and Novel Magnetism, 35 (2022) 2737–2748.

[11] Y. Xieng, Densification of MgB_2 superconducting cryomagnets: Synthesis and physical properties studies, Ph.D. dissertation, Normandie University, France (2022).

[12] Z. Ma, Y. Liu, Q. C., Liming Yu, Significant improvement in the critical current density of MgB_2 bulks in situ sintered at low temperature by excess Mg addition, Physica C. 496 (2014) 49-52.

[13] R. Zeng, L. Lu, J. L. Wang, J. Horvat, W. X. Li, D. Q. Shi, S. X. Dou, M. Tomsic and M Rindfleisch, Significant improvement in the critical current density of in situ MgB_2 by excess Mg addition, Supercond. Sci. Technol. 20 (2007) L43–L47.

[14] R. Zeng, L. Lu, W. X. Li, J. L. Wang, D. Q. Shi, J. Horvat, S. X. Dou, M. Bhatia, M. Sumption, E. W. Collings, J. M. Yoo, M. Tomsic, and M. Rindfleisch, Excess Mg addition MgB_2 /Fe wires with enhanced critical current density, Journal of Applied Physics. 103 (2008) 083911.

[15] S. B. Güner, B. Savaşkan, K. Öztürk, Ş. Çelik, C. Aksoy, F. Karaboğa, E.T. Koparan, E. Yanmaz, Investigation on superconducting and magnetic levitation force behaviour of excess Mg doped-bulk MgB_2 superconductors, Cryogenics. 101 (2019) 131–136.

[16] B. Savaskan, E. T. Koparan, S. B. Güner, K. Öztürk, Ş. Çelik, Enhanced Magnetic Levitation and Guidance Force in MgB_2 Bulks by Synthetic Engine Oil Immersion Journal of Superconductivity and Novel Magnetism. 32 (2019) 827–837.

[17] B. Savaskan, E. T. Koparan, S. Celik, K. Ozturk, E. Yanmaz, Investigation on the levitation force behaviour of malic acid added bulk MgB_2 superconductors, Physica C. 502 (2014) 63–69.