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Improvement of superconducting properties of MgB_2 by changing the argon ambient pressure and sintering conditions

Burcu Savaskan[1], Kemal Ozturk[1], Sukru Celik[2] and Ekrem Yanmaz[1]
[1] Department of Physics, Faculty of Arts and Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey
[2] Department of Physics, Faculty of Arts and Sciences, Rize University, 53100 Rize, Turkey.

E-mail: **savaskanb@hotmail.com, turkke@hotmail.com**

Abstract. We have investigated various characteristic properties depending on sintering conditions of MgB_2 samples prepared by the standard solid state reaction method. It is inferred from experimental results that the crystallinity of samples were improved when the pressure of the Ar ambient increased. Also, it was found that the sintering temperature above 850 ºC caused extremely high amount of decomposition of the superconductor phase. Finally, it was considered that the sintering process of MgB_2 must be carried out under the pressure of Ar ambient higher than 8 bar to impede the volatility of Mg in the structure of MgB_2. The J_c values of samples systematically enhanced with the increase of sintering time and in particular, the sample sintered for 180 min. exhibited the highest J_c (0) of 4.9×10^3 A cm^{-2} at 30 K. The obtained results demonstrate that the sintering conditions of MgB_2 have a significant influence on $T_{c\ (onset)}$ and J_c, which are directly related to practical applications of MgB_2 based superconductor components.

1. Introduction

The discovery of superconductivity at ~39 K in the magnesium diboride (MgB_2) compound stimulates scientific interest because of it's high critical temperature (T_c) value among the metallic superconductors. It has simple electronic structure, simple binary chemical composition and relatively low fabrication cost [1-4].

Due to the volatility of magnesium and the high melting point of boron, MgB_2 material usually grown in closed systems. In the various studies it is reported that high pressure techniques could be useful to prevent the evaporation of Mg from the compound and to suppress the decomposition of MgB_2 [5]. Any losses of Mg for forming the MgB_2 phase cause a generation of impurities resulting in poor microstructure as well as the superconducting properties such as critical current density [6]. Hence, fabrication of the MgB_2 bulk superconductor sample is generally performed under the inert gas ambient such as Argon, Hydrogen or Nitrogen. Technological applications of superconductors depend primarily on their critical current density property. The various experimental results have demonstrated that the sample of bulk MgB_2 has rather high values of critical current density (J_c) at zero field, but exhibits a rapid decrease of J_c in an applied magnetic field. These problems inflict strong limitations on use of MgB_2 e.g. for energy storage system and superconducting magnets. It is known that the field dependence of J_c are related to the presence of structural defects that can act pinning center and a lack of natural defects in MgB_2 may be responsible for the rapid decline of J_c with increasing field [7]. Many attempts, such as element addition or doping (Cu, Co, Li, Mo, C) [8, 9], nanoparticles (SiC) addition, the introduction of defects by irradiation [10, 11] etc., have been made to improve pinning properties and J_c of the MgB_2 sample. Although the addition or doping of several impurity compounds or elements have been found to be effective in improving the pinning and the critical current properties. Additionally, most likely the actual composition of MgB_2 and the different fabrication and processing conditions are responsible for the different pinning properties.

[1] Corresponding author: Phone: +90 462 325 31 97, Fax: +90 462 325 31 95

Consequently, clarifying the mechanism influencing intrinsic pinning properties of the undoped MgB_2 is very important for practical applications and future investigations.

In the present study, we have investigated the effect of the sintering temperature, sintering time and Ar ambient pressure on the structural and superconducting properties in the MgB_2 samples prepared by a solid state reaction method. We have measured the temperature and field dependence of the magnetization at the different sintering conditions considering the shifting intrinsic pinning behavior of the samples. The experimental result shows that the structural and superconducting properties such as critical current density and flux pinning can be improved with varying of the sintering conditions of the MgB_2 sample.

2. Experimental details

Commercial powder of MgB_2 (Alfa Aesar) with nominal 99% purity was apportioned to 0.6 g, each of which was pressed into a pellet of 13mm in diameter under the pressure of 10 ton. Each pellet was transferred into a stainless steel tube and vacuumed to 10^{-3} bar using a rotary pump at room temperature. Then, vacuum valve was closed and Ar gas valve opened to set Ar gas pressure. After these processes the samples named as the pressure, temperature and time series were performed experimental procedure as below.

For pressure series; after vacuum to 10^{-3} bar using a rotary pump at room temperature the stainless steel tube was put into preheated tube furnace at 1050 ºC. In order to investigate the effect of Ar gas pressure, the samples were sintered at 4, 6, 8 and 10 bar in Ar ambient at 1050 ºC for 3 h. For temperature series; in order to investigate the effect of sintering temperature, some samples were sintered at 800, 850, 900, 950 and 1000 ºC with a 3 h constant sintering time and with 8 bar constant Ar ambient pressure.

For time series; in order to investigate the effect of sintering time, the samples were sintered at 800 ºC for 20, 40, 60, 120 and 180 min under constant 8 bar Ar ambient pressure.

The sintering and oxygenation temperatures of the samples were determined from the differential thermal analysis measurement (DTA) with model NETZSCH. The powders and bulk XRD data were collected over a 2θ range from 3º-70º, at a step of 0.02º at room temperature, using a Rigaku D/Max-IIIC X-ray diffractometer with CuK_α radiation. The magnetization properties were measured using a Quantum Design PPMS and VSM system. The M(H*)* properties of MgB_2 samples dependent on sintering time and temperature were measured up to 0.5 T for the constant temperature with 15 and 30 K while the M(T) properties were measured at 0.1; 0.2; 0.3; 0.4 and 0.5 T under the zero field-cooling regime (ZFC). The measurements were performed by the sweep rate of 5 mT s^{-1}. All the magnetization measurements were made afterwards by the first cooling the sample in zero field and then applying a field to begin the measurement. All samples were rectangular and typical dimensions were approximately 1.3x2.4x4.1 mm^3 respectively for magnetization studies.

3. Results and discussion

Figure 1 shows a DTA curve taken in the temperature ranges 30 ºC to 1000 ºC on MgB_2 powders in air atmosphere. A wide peak observed at around 250°C with small intensity which is compatible with the beginning of the forming temperature of the MgO phase with joining together magnesium and oxygen in MgB_2 compound. A high endothermic peak occurred at 710 ºC because of the oxidation MgB_2 grains in air atmosphere is shown in Fig 1. Finally, the peak seen over the 900 ºC is considered as the peritectic temperature of the Mg decomposing in a liquid state [12].

Figure 2 shows the room temperature XRD patterns of the pressure series at 1050 ºC for 3 h under 4, 6, 8 and 10 bar Ar gas pressure. The main phase of the all pressure series samples are orthorhombic MgB_4. In the sample sintered at 1050 ºC for 4 bar Ar gas only low intensity MgB_4 phase peaks were seen. Figure 2 clearly indicates that portion of the superconductor MgB_2 phase increases when the Ar ambient pressure increases. Due to volatility of Mg at high temperature sintering MgB_2 material decomposed easily and so the increment of the MgB_4 phases as shown in Fig 2 (a) [13].

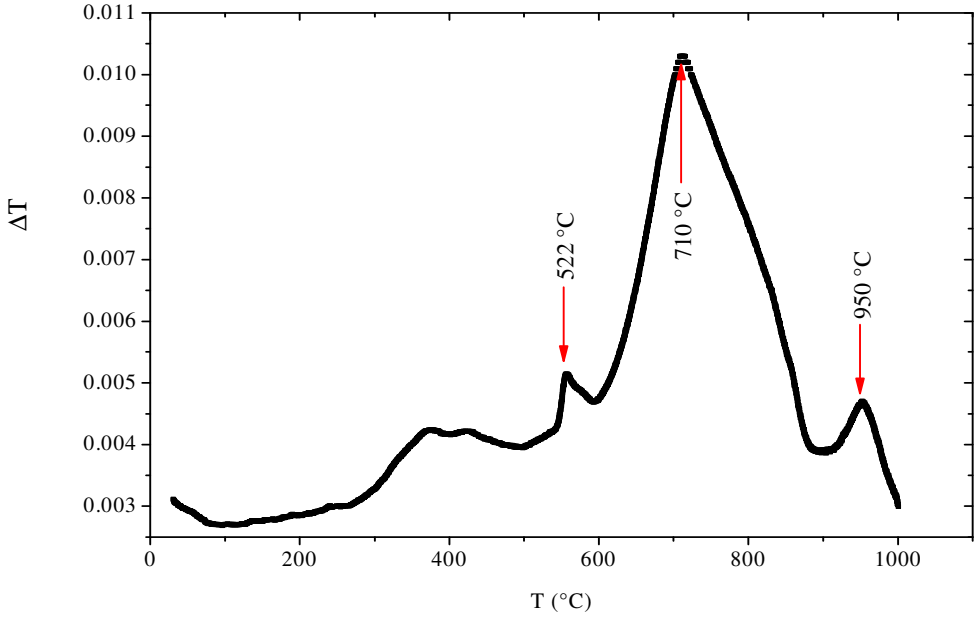

Figure 1. DTA result on MgB_2 powder in air atmosphere from 30ºC to 1000 ºC.

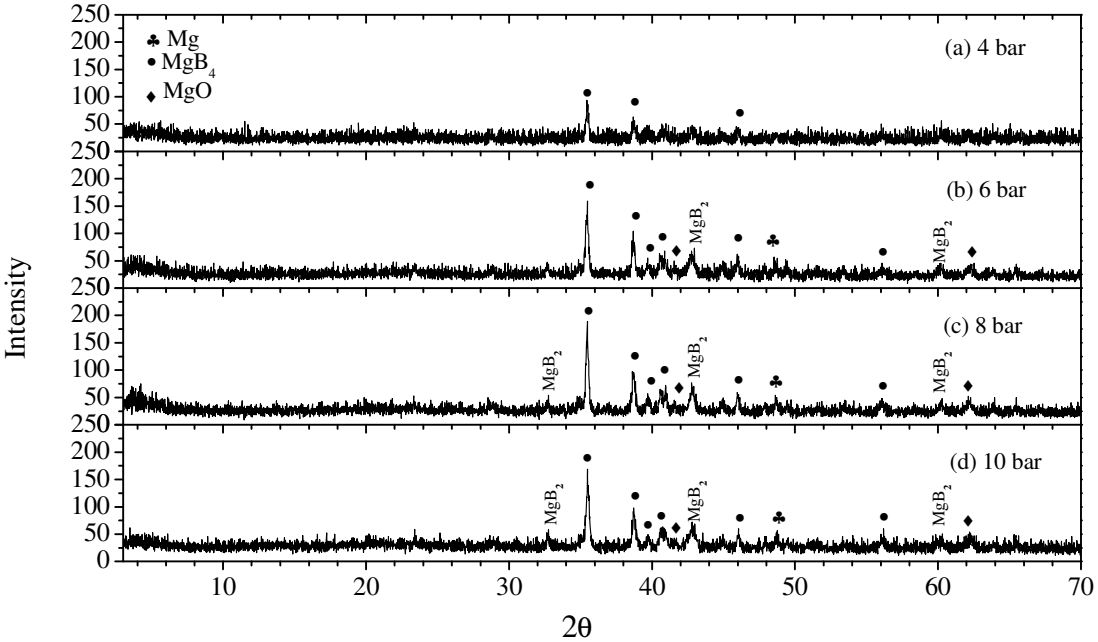

Figure. 2. The X-ray diffaction patterns of bulk MgB_2 sintered at 1050 ºC for 3 h under (a) 4 bar , (b) 6 bar, (c) 8 bar and (d) 10 bar Ar gas pressure.

This clarifies that sintering the MgB_2 material at 1050 ºC is too high to improve properties. In addition, it was found that during the sintering process the pressure of 4 bar Ar atmosphere is inadequate to prevent skip out of the Mg from sample surface. A little increase of the peak intensities and portion belong to MgB_2 phase with increasing of Ar gas pressure indicate that the skip out of Mg from sample surface can be hindered partially.

Figure 3 shows the typical XRD patterns of MgB_2 bulk samples sintered under 8 bar Ar gas pressure at (a) 800 ºC, (b) 900 ºC and (c) 1000 ºC for 180 min. It is clearly observed that the samples sintered at 800 and 900 ºC, show single phase except a small amount of MgO phase. Also, it is revealed that the sample sintered at 1000 ºC has MgB_4 and MgO impurity phases in addition to MgB_2 phase. It can be seen from XRD patterns that the MgB_4 and MgO impurity peaks intensity increase as the sintering temperature increases. This case is consistent with the fact that the amount of the MgB_4 phase increases with the Mg-deficiency [13]. So, in this work the increasing amount of MgB_4 induced the Mg-deficient. It was also reported that the obtained MgB_2 sample sintered at 600 ºC, revealed poor crystallinity from XRD and unreacted Mg peaks originating from low temperature processing [14, 15]. It is seen in Figure 3 that the peak intensities of MgB_2 decreases when the sintering temperature increased. The reason to that can be attributed to the decomposition of MgB_2 due to volatility of Mg and so the enlargement of the MgB_4 phases. Consequently, the optimum sintering temperature is found to be around 800 ºC for forming the bulk MgB_2. In addition, it was seen from the XRD that the sample sintered at 800 ºC for (a) 20, (b) 60 and (c) 120 min. sintering times, the dominant peaks were MgB_2 phase and a minor amount of MgO phase found in all the sintering times. Although the sample crystallinity almost the same for all the sintering times.

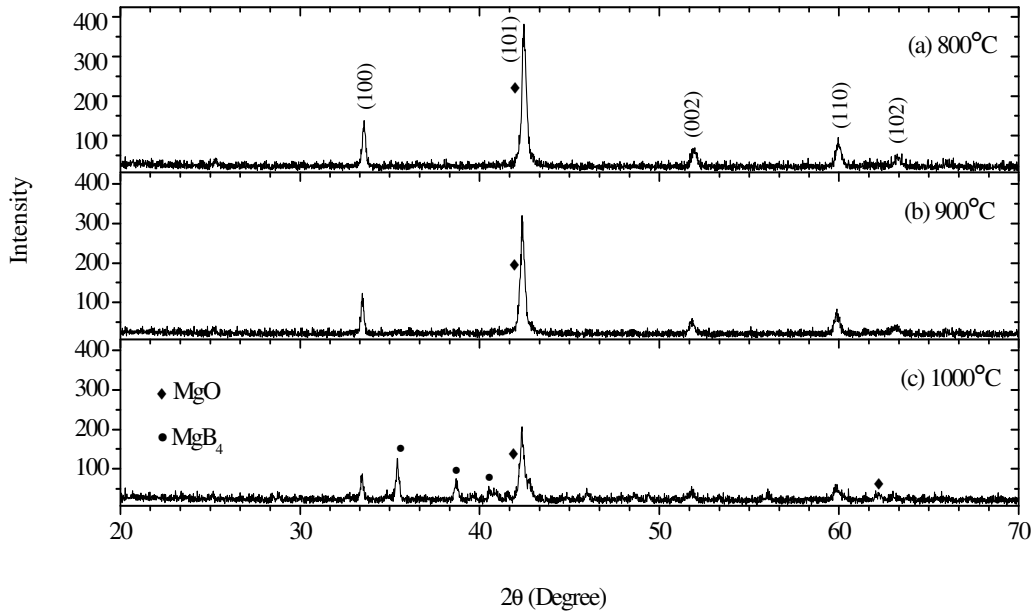

Figure 3. The XRD patterns of MgB_2 samples prepared at (a) 800 ºC, (b) 900 ºC and (c) 1000 ºC for 180 min. under 8 bar Ar gas pressure.

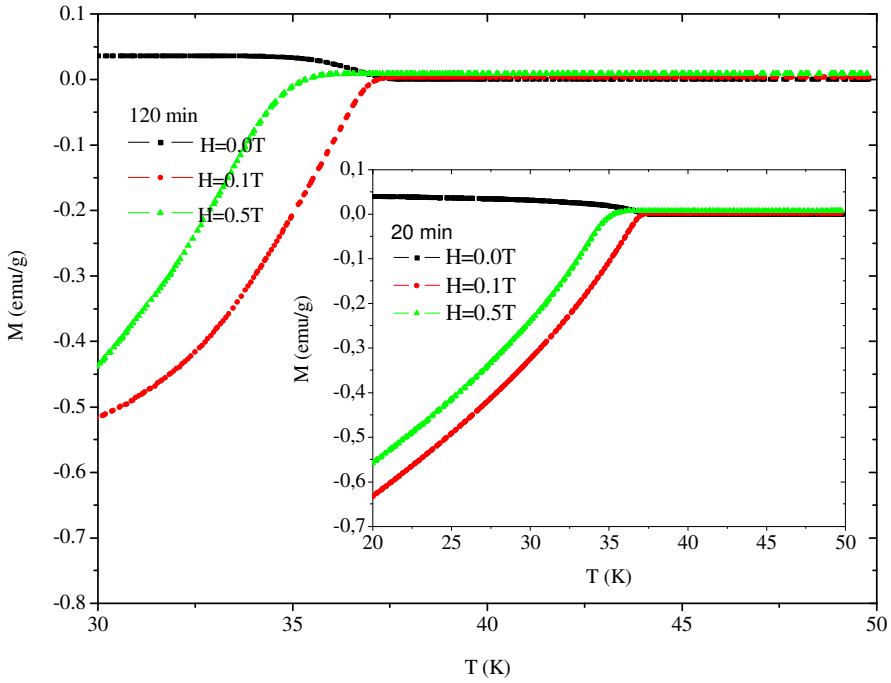

Figure 4. Temperature dependence of magnetization for MgB_2 samples sintered at 800 ºC for 20 and 120 min.(see inset figure) under the zero field cooling regime (ZFC)

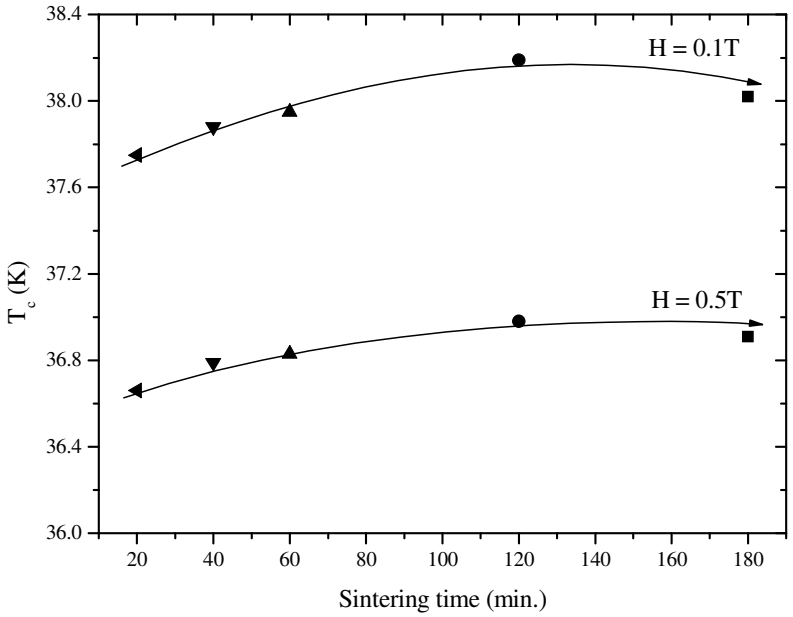

Figure 5. Relationship between superconducting transition temperature $T_{c\ (onset)}$ and sintering time for the sample sintered at 800 ºC and Tc measured in the field of 0.1 and 0.5 T under the ZFC regime.

The temperature dependence of magnetization was measured in the field ranged from 0.1 T to 0.5 T in ZFC mode in order to determine the superconducting transition temperature T_c. The superconducting transition temperature $T_{c(onset)}$ for the samples sintered at different temperatures as 800, 850, 900, 950 and 1000 ºC were determined using M-T curves to be 38.02, 37.90, 37.87, 37,86

and 37.84 respectively (under 8 bar Ar gas pressure for 3h). It was indicated above that the sintering temperature above 850 ºC cause the high amount of decomposition of MgB_2 superconductor phase. Consequently, it is consider that sintering process requires for pressure of Ar atmosphere higher than 8 bar to impede the volatility of Mg for sintering temperatures over 800 ºC. Figure 4 shows the temperature dependence of magnetization for MgB_2 samples sintered at 800 ºC for 20 and 120 min. (see inset figure) under the ZFC regime. The relationship between superconducting transition temperature $T_{c\ (onset)}$ and sintering time for sample sintered at 800 ºC and measured in the field ranged from in 0.1 and 0.5 T was presented in Figure 5. The value of $T_{c\ (onset)}$ ascended with increasing the sintering time between 20-120 min. and descended slightly for 180 min. The lowered $T_{c\ (onset)}$ as 37.75 K at 0.1 T observed for MgB_2 bulks sintered at 800 ºC for 20 min. can be explained by poor crystallinity. Because the improvement in superconducting transitions with sintering time coincide well with the improvement of crystallinity as shown Figure 5. It was reported in various studies [13, 16] that the amount of the MgB_4 impurity phase increases because of Mg-deficient due to volatility of the Mg when the sintering time and temperature increases. The decrease in the $T_{c\ (onset)}$ for 180 min. signifies the presence of weak links among grains of the MgB_2.

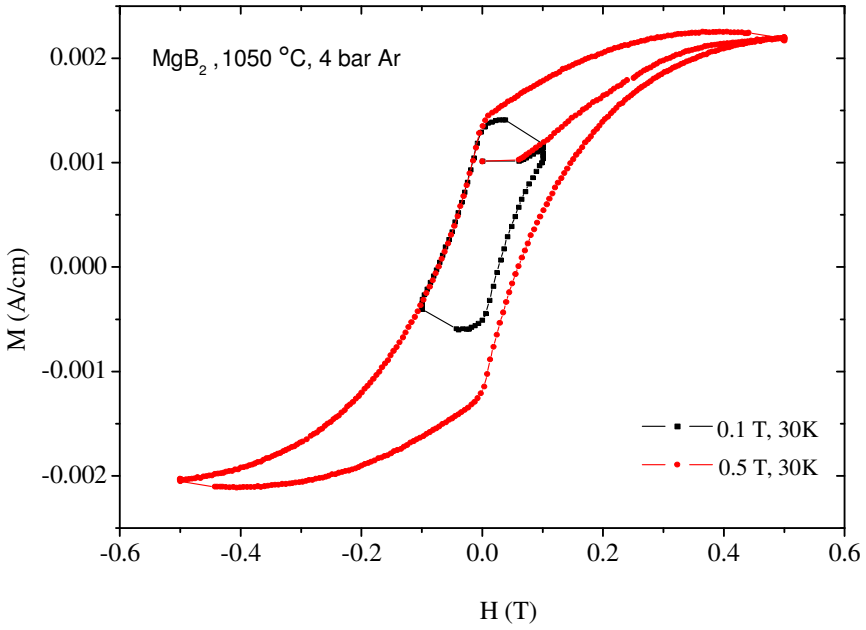

Figure 6. The magnetization hysteresis loop M(H) measured at 30 K of MgB_2 sample sintered at 1050 ºC for 3 h under 4 bar Ar gas pressure.

Figure 6 shows the magnetization hysteresis loop M(H) measured at 30 K for the sample sintered at 1050 ºC for 3 h under 4 bar Ar gas pressure. As shown in Fig 6 the sample exhibits a typical ferromagnetic behavior. M(H) curves in Figure 6 indicate that during the sintering process the pressure of 4 bar Ar gas is insufficient to prevent skip out of Mg from sample surface and so deterioration of stoichiometry. In addition, it was found that sintering temperature of 1050 ºC was too high for MgB_2 superconductor compound. In order to study sintering time effects on the superconducting magnetic properties, we examine the effects of sintering time on the superconducting magnetic hysteresis and critical current density. Figure 7 shows the magnetization hysteresis loops M(H) measured at 30 K for MgB_2 samples sintered at (a) 800, 900 and 1000 ºC and (b) sintered at 800 ºC for 20, 40, 60, 120 and 180 min. sintering times. It is clearly seen in Figure 7 (a) that the value of magnetization decreased with increasing of sintering temperature and the best condition found to be 800 ºC. The curves of Figure 7 (b) clearly indicate that the magnetization values systematically increase with increase of sintering time. Relation between magnetization loops width and the number of flux pinning center in

the material were reported in many times [17, 18]. In Figure 7 increasing of magnetization loops width as sintering time increase implies that the amount of the pinning centers improved. The critical current densities J_c values were calculated from the magnetization hysteresis data using the Bean critical state model [19] using the relation: $J_c = 20(M^+ - M^-)/L_1(1-L_1/3L_2)$, where M^+ and M^- are magnetic moment when increasing and decreasing the field, respectively. L_1 and L_2 are sample dimensions perpendicular to the field in cm with $L_1 < L_2$. The magnetic field dependence of critical current densities $J_c(H)$ at 30 K for time series samples were presented in Figure 8. The J_c values are systematically enhanced with an increase of sintering time.

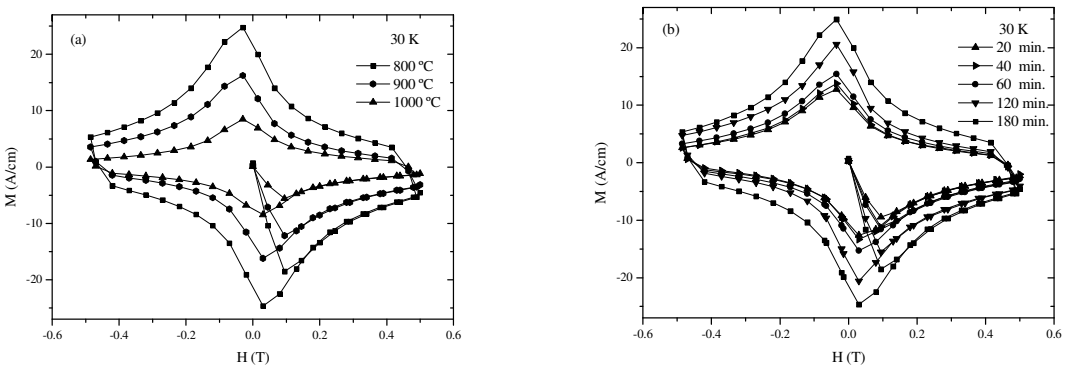

Figure 7. The magnetization hysteresis loops M(H) measured at 30 K for MgB_2 samples (a) sintered at 800, 900 and 1000 ºC and (b) sintered at 800 ºC for 20, 40, 60, 120 and 180 min. sintering times.

In particular, the sample sintered for 180 min. exhibited the highest J_c value of 4.9×10^3 A cm^{-2} at 30 K. Enhancement of J_c by increasing of sintering time can be explained by the improvement of grain connectivity because of MgB_4 nanoinclusions. As known the small grain size of MgB_4 leads to an increment of effective surface area between MgB_2 and MgB_4 grains that may be increase the quality of grain connection of the MgB_2 polycrystals. Also, the small grain size of MgB_4 sintered 800 ºC matches well with the coherence length of MgB_2 (about 12 nm). Consequently, these impurities can act as pinning centres in sample. For all these reasons, we consider that the MgB_4 nanoinclusions are responsible for the increase in $J_c(H)$ for the Mg-deficient samples induced by the convenient sintering time and temperature. This result is consistent with a previous report [20]. In addition, it was found that value of the J_c decreased when the sintering temperature was increased.

In conclusion, we have investigated various characteristic properties depending on sintering conditions of MgB_2 samples synthesis by the solid state reaction method. It was deduced from experimental results that the crystallinity improved when the pressure of the Ar ambient increases. Additionally, it was found that the sintering temperature above 850 ºC causes high amount of decomposition of MgB_2 phase. It was thought that the sintering process to make bulk structure have need for pressure of Ar atmosphere higher than 8 bar to impede the volatility of Mg. In general it was found that, the critical transition temperature increases with sintering time and it shows a maximum value as 38.19 K for 120 minutes. The J_c values systematically enhance with decreasing of sintering temperatures and increasing sintering times. Specially, the sample sintered at 800 ºC for 180 min. (under 8 bar Ar ambient pressure) exhibited the highest J_c of 1.5×10^4 and 4.9×10^3 A cm^{-2} respectively for 15 and 30 K measuring temperatures. The acquired results demonstrate that the sintering conditions of MgB_2 have a significant influence on $T_{c\ (onset)}$ and J_c, which are directly related to practical applications of MgB_2-based superconductor components. The suitable sintering temperature, sintering time and Ar ambient pressure were determined to be 800 ºC, 2–3 h and over 8 bar respectively.

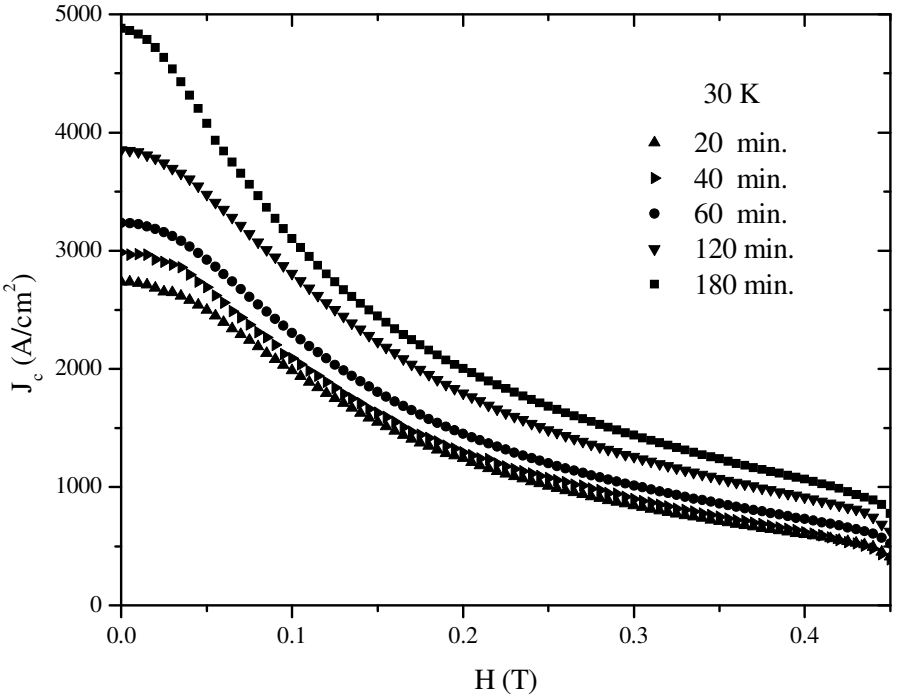

Figure 8. Magnetic field dependence of critical current densities $J_c(H)$ at 30 K for MgB_2 samples sintered at 800 ℃ for 20, 40, 60, 120 and 180 min.

References

[1] Nagamatsu J, Nakagava N, Muranaka T, Zenitani Y and Akimitsu J 2001 *Nature* **410** 63
[2] Huang X, Mickelson W, Christopher Regan B and Zettl A 2005 *Solid State Commun.* **136**, 278
[3] Du W, Xu H, Zhang H, Xu D, Wang X, Hou X, Wu Y, Jianga F and Qin L 2006 *J. Crystal Growth* **289** 626
[4] Wang S, Zhu Y, Liu Z, Zhou Y, Zhang Q, Chen Z, Lu H and Yang G 2003 *Chin. Phys. Lett.* **20** 1356
[5] Angst M, Puzniak R, Wisniewski A, Jun J, Kazakov S M, Karpinski J, Roos J and Keller H 2002 *Phys. Rev. Lett.* **88** 167004
[6] Yamamoto A, Shimoyama J, Ueda S, Katsura Y, Horii S and Kishio K 2004 *Supercond. Sci. Technol.* **17** 921
[7] Bugoslavsky Y, Perkins G K, Qi X, Colen L F and Caplin A D 2001 *Nature* **410** 563
[8] Hishinuma Y, Kikuchi A, Iijima Y, Yoshida Y, Takeuchi T and Nishimura A 2006 *Supercond. Sci. Technol.* **19** 1269
[9] Yakinci ME, Balci Y, Aksan MA, Adıguzel H I and Gencer A 2002 *J. Superconductivity* **15** 607
[10] Dou S X, Braccini V, Soltanian S, Klie R, Zhu Y, Li S, Wang X L and Larbalestier D 2004 *J. Appl. Phys.* 96 7549
[11] Bugoslavsky Y, Cohen L F, Perkins G K, Polichetti M, Tate T J, Gwilliam R and Caplin A D *Nature* **411** 561
[12] Shen J, Fang M, Zheng Y, Wang H, Lu Y and Xu Z 2003 *Physica C* **386** 663
[13] Bayazit E, Yakinci ME, Balci Y, Aksan M A and Balci Y 2007 *Physica C* **460 610**
[14] Chen S K and Glowacki B A 2006 *Supercond. Sci. Technol* **19** 116
[15] Bayazit E, Altin S, Yakinci ME, Aksan M A and Balci Y 2008 *J. Alloys Compd.* 457 42-46
[16] Zhao Y G, Zhang X P, Qiao P T, Zhang H T, Lia S L, Cao B S, Zhu M H, Han Z H, Wang X L and Gu B L 2001 *Physica C* **366** 1
[17] Feng Y, Zhou L, Wen J G, Koshizuka N, Sulpice A, Tholence J L, Vallier J C and Monceau P 1998 *Physica C* **297** 75

[18] Öztürk K, Çelik Ş, Çevik U and Yanmaz E 2007 *J. Alloys Compd.* **433** 46
[19] Bean C P 1962 *Phys. Rev. Lett.* **8** 250
[20] Xu G J, Pinholt R, Bilde-Sørensen J, Grivel J C, Abrahamsen A B and Andersen N H 2006 *Physica C* **434** 67