Synthesis and characterization of SiC and CNT doped MgB₂ superconducting wire

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Abstract. Silica nanoparticles and carbon nanotubes-doped magnesium diboride (MgB₂) superconducting wires have been successfully prepared via powder-in-tube (PIT) method. In this work, pure MgB₂ was doped using various dopants concentrations at 1 and 2 wt.% of each silica nanoparticles (SiC) and carbon nanotubes (CNT). The mix was sintered at 800°C for 3 hours before putting it in a 6 mm diameter stainless steel tube wire and drawn to get 3 mm diameter of stainless-steel wire. The materials were characterized using X-ray diffraction (XRD) for phase and structural analysis and scanning electron microscope (SEM) for surface morphology. Further, superconductivity characteristic of the wires was examined through a transition temperature using a cryogenic magnet. Structural characterization examined using X-ray diffraction showed that no other impurities of other phases were detected. Microstructural investigation using electron microscope showed even distribution of the particles with inherent porosities. Measurement at cryogenic temperature showed that pure MgB₂ and 2 wt.% CNT doped MgB₂ showed superconductivity characteristic after being sintered whereas others showed unique resistivity behaviors. After deformation by drawing process to form wires, all of the samples showed a superconducting behavior, however, the presence of SiC and CNT decreased the critical temperature, Tc, of MgB₂. Although the samples doped with CNT decrease the Tc, CNT doped samples showed higher Tc than that of MgB₂/SiC wires.

1. Introduction
Superconductor is defined as a material that has zero resistivity below a certain temperature. In this condition, the superconductor flows current without any obstacle. The temperature when the resistivity vanished is called as critical temperature (Tc) [1]. Magnesium diboride (MgB₂) is a superconductor with relatively high critical temperature (39 K). It has a simple structure by which it consists of magnesium and boron, and superconductivity in this MgB₂ was discovered by Nagamatsu and his coworkers in 2001 [2].

Superconductivity can be enhanced by determining the optimum microstructure of MgB₂ which includes the grain size, grain orientation, voids, cell structure and impurities [2]. Later on, researchers found that carbon addition in MgB₂ superconductor increases the current density significantly due to the substitution of carbon to boron lattices [4]. Therefore, SiC and Carbon Nano Tube (CNT) is given to synthesize MgB₂ superconductor with addition of carbon that make possible for MgB₂ as an HTS
application [4]. Unfortunately, carbon addition has a side effect to the critical temperature. The higher the carbon content lowers the critical temperature of MgB$_2$. As a result, addition below 20% are done by researcher [5]. Although below addition below 2% has not be proceeded due to the insignificant amount of addition. A journal of Vajpayee et al uses the lowest addition of SiC of 2% in powder in tube (PIT) method [6]. The current density enhances significantly and the critical temperature decreases insignificantly compared to their other sample conducted with higher amount of SiC. As well as the result of Vajpayee et al that uses 3% CNT addition to MgB$_2$ bulk, resulting highest critical temperature among other samples and higher current density than samples added by 15% and 20% CNT [7].

MgB$_2$ is an intermetallic compound, which means it has simpler crystal structure compared to the typical copper oxide superconductors that are often used in electronics, energy, transportation and medical industries [4]. Compared to Nb-based superconductor material, the MgB$_2$ superconductor has the advantages in terms of ease of manufacturing process, lightweight, cheap, but with good mechanical properties.

Doping were found helpful in some aspect and lowers the initial properties of pure MgB$_2$ superconductor [4].

The common and useful doping is SiC and CNT. These substances effects on homogeneity of the compound [4]. In any case impurity will achieved during the process but it would not agglomerate in one particular area by the presence of C and too much SiC/CNT will decrease the critical temperature since it will agglomerate with itself [5]. The journals of Varghese et al confirm that the highest effective percentage of SiC is on 2% and from Arpita et al is on 3% addition of CNT. Therefore, in this research we will implementing low-doped SiC/CNT to achieve deep knowledge how SiC and CNT affect this superconductor material.

2. Experimental Setup

2.1. Stainless Steel Tube Preparation

Superconductor wire was prepared by firstly preparing the stainless tube with outer diameter of 6 mm and inner diameter of 3 mm as cover tubes in order to enhance its formability during fabrication. The stainless-steel tube was cut with a length of 100 mm for each sample. The tube was annealed in a muffle furnace at 850 °C with a heating rate of 10 °C/min and was held for 3 hours. After the annealing, the tube was slowly cooled in the furnace to reduce the residual stress and to achieve good formability during the drawing process. Finally, the tube was cleaned using an abrasive paper, alcohol and compressed air to eliminate any oxide that might form during the annealing. To achieve a closed condition of the tube as a requirement for PIST (powder-in-sealed-tubes) fabrication method, one end of the tube was sealed through an electrical resistance welding (ERW) using E308-16 electrode. After the welding, the tubes were checked for any leaking and ready for the next treatment.

2.2. Superconducting Wire Preparation

In this work, five MgB$_2$ samples were prepared, i.e. pure MgB$_2$ sample, MgB$_2$ with the addition of 1 wt.% and 2 wt.% SiC, and MgB$_2$ with the addition of 1 wt.% and 2 wt.% CNT. Firstly, MgB$_2$ powder (Aldrich, ~100 mesh, > 99%) and the dopants (SiC, Iolitech Nanomaterials, 50 – 60 nm, 99% and carbon nanotubes, CNT, Cheap Tubes Inc., ~ 20-40 nm) were prepared by weighing stoichiometric amounts of MgB$_2$ at 1 wt. % and 2 wt. % dopants. After the weighing, the materials were mixed using an agate mortar for 30 minutes before being loaded at an ambient condition into the stainless-steel tube and sintered in a muffle furnace at 800 °C for 3 hours. After the sintering, the stainless-steel tube was rolled and drawn at room temperature to reduce the diameter of the tube to wire dimension. The final diameter of the wire after the drawing was 2 mm. This diameter reduction increased the length of the wire whereas the structure of the MgB$_2$ will be more compact.
3. Results and Discussion

The magnesium diboride was shown to be a dominant phase in the XRD result. Based on the source of JCPDS PDF-4 No. 04-018-7387 2014 edition system, peaks of MgB$_2$ are at 34°, 42°, 51°, 60°, 63°, 76° and 83°. As we can see at figure 4.3, that there are 7 peaks indicating the MgB$_2$ phase. The same case stated by Varghese et al. SiC phase is found 0.9% in the result on addition of 2% SiC. The low amount of SiC is resulting low coverage to the MgB$_2$ matrix. In this case, inhomogeneous mixing of SiC and amorphous crystallinity behavior also is resulting less intensity of the phase in the XRD result.

Although SiC phase is not detected, the addition of SiC is affecting the peak of MgB$_2$. The higher amount of SiC addition decreases the intensity of the MgB$_2$ particularly at 42° and acts as an impurity. Besides the MgB$_2$ phase, we can also see Fe-Cr-Ni phase at the 43° and 74° peaks. The sample were tested in wire condition with the width of MgB$_2$ matrix less than 1 mm that cause the phase of stainless steel 304 detected during the XRD characterization.

Scanning Electron Microscopy (SEM) were done to 8 samples. Which were 3 samples before rolling, and 5 after the drawing process. By having SEM result before and after sintering we saw the difference of microstructure based on the metal deformation. Various magnification was taken to achieve better image since the surface was rough. Mapping was also ensuing to see substance distribution in the sample’s surface.

The SEM result of pure MgB2 can be seen in fig. 4.2(left). As can be seen, there is inhomogeneity of diffusion during sintering, resulting a deposition of rich magnesium area. This phenomenon may occur because of the presence of impurities or a corrosion product that decrease the diffusion ability of magnesium towards boron particles. Small voids and porosity can also be observed on the specimen. These voids are a common phenomenon for PIT product particularly that uses small inner diameter tubes as its media [10]. By using smaller tube, it would be harder to determine the compaction force as the pressing machine has bigger surface area. So, this voids and porosity are caused by poor compaction process resulting from air entrapment and high free volume.

The pure MgB2 sample after been rolled, shows better morphology for superconductor as seen in figure 2 (right). Crystal structure are more dominated at the MgB2 matrix. Void’s size is decreased but we can still find it with 10000x magnification. The rolling process found to be helpful to compacting the MgB2 structure due to dislocation movement the matrix is denser as the rolling process occur. As we can see that agglomeration of small particles are occurred at the magnification of 10000x and
5000x. The journal written by S. K Chen et al. expressed that precipitation and agglomeration are the advantages for superconducting properties since it has higher density. Although it also has lower mechanical properties for wire application [6].

As we can see in figure 3(top left), that irregularity of grain size is huge and the crystals are attached with small particles. This is caused by different initial particle size of magnesium and boron with Nano-SiC. Hand milling process resulting irregularity of particle size after process affects the crystal morphology of the MgB2. The voids are also detected on 10000x magnification reveals that compaction process is not optimum.

**Figure 2.** Secondary electron images of pure MgB$_2$ after sintering only (left) and after rolling (right).

**Figure 3.** Secondary electron images of MgB$_2$ + 1% SiC (top left), MgB$_2$+2%SiC (top right), MgB$_2$ + 1% CNT (bottom left) and MgB$_2$ + CNT 2% (bottom right) after rolling.
In the Figure 4(a), the MgB$_2$ added with SiC formed a superconductor material after been rolled. The effect of SiC addition to MgB$_2$ superconductor is decreasment of critical temperature. Where the onset critical temperature of MgB$_2$ added with 1% SiC is at 36.1 K and 36.2 K for addition of 2% SiC. As we know that applied pressure on MgB$_2$ decreases the Tc, this result shows that this theory does not apply on the MgB$_2$ sample added with SiC [7]. Before the sample with addition of SiC has been rolled, the cryogenic result shows non-superconductor behavior. And after rolling, the sample shows a transition from non-superconductor to a superconductor material. This shows that rolling process will enhance the density of MgB$_2$ sample with SiC addition and able to transform the material to a superconductor wire.

As we can see at table 1 that the onset critical temperature is at 42.3 and it has a zero-critical temperature of 37.3. These values indicates that after the sample have been rolled the critical slope pattern is shifting to the lower temperature causing the rolled sample have a huge temperature value gap on the T$_c$ onset and T$_c$ zero. Proven a research by V. G. Tissen et al. that applied pressure on MgB$_2$ with a density of 2.23 g/cm$^3$ decreases its critical temperature [7]. A Related research “Superconductivity in Laser Ablated LaBa$_2$Cu$_3$O$_7$” conducted by M. Murgesan et al. proves that there is a minimum thickness for an optimal superconductor. When the thickness is less than the minimum value it will decrease the critical temperature and the superconductor properties [8]. Decreasing of electrical properties occurs when a powder metallurgy product is rolled after exceeding its true density of the material [9]. Internal crack occurs after rolling is proceeded after exceeding the true density of a powder metallurgy product [9]. Internal crack is initiated on the porosity or void.

![Figure 4(a)](image1.png)

![Figure 4(b)](image2.png)

**Figure 4.** R-T measurement result of MgB$_2$ + SiC (a) and MgB$_2$ + CNT (b).

**Table 1.** Critical temperature of MgB$_2$ at various doping concentration.

| Sample         | Tc onset (K) | Tc zero (K) |
|----------------|--------------|-------------|
| Pure MgB$_2$   | 42.3         | 37.3        |
| MgB$_2$ + 1% CNT| 36.1         | N/A         |
| MgB$_2$ + 2% CNT| 36.2         | N/A         |
| MgB$_2$ + 1% CNT| 42.1         | 28.2        |
| MgB$_2$ + 2% CNT| 34.6         | 19          |

Figure 4 shows us the normalized cryogenic result of MgB$_2$ with addition of CNT sample. As we can see that the presence of CNT in the MgB$_2$ decreases the critical temperature. The higher addition amount of CNT shifts the Tc to lower temperature. The MgB$_2$ with the addition of 1% CNT has an onset critical temperature of 42.1 and a zero critical temperature of 28.2 K. Although the onset critical
temperature is almost similar to the pure MgB$_2$ sample, the zero critical temperature is much lower than the onset. This is not favorable for a superconductor since the resistivity does not decreases rapidly.

The MgB$_2$ sample added with 2% CNT critical temperature is much lower than the sample added with 1% CNT. The added 2% CNT sample has an onset critical temperature of 34.6K and a zero critical temperature of 19K. This shows that the higher amount of CNT addition will decreases the critical temperature significantly. Decrease of critical temperature by addition of CNT is mainly due to the interaction of both MgB2 and CNT in which both of the materials acting as different conductors[29].

Where $I_{\text{max}}$ and $V_{\text{max}}$ are maximum photocurrent and voltage, respectively. Their values can be extracted from the maximum power of the I-V characteristics. Based on the data obtained from the photocurrent-voltage examination of the PSC device, the maximum power conversion efficiency (PCE) is found to be 3.4%. Compared to the existing efficiency [9], this value is still relatively low. This low value is expected because of inhomogeneous distribution of the perovskite layer that is yet to be improved, however, this current result is convincing and promising for the next development.

4. Conclusion

Finally, after finishing the data procurement and analysis of the acquired data of the research of synthesis and characterization of MgB2/SiC and MgB2/CNT superconductor wire, there are some points that could be concluded that synthesis of MgB2 using PIT method as a superconductor was achieved, rolling process increases brittleness and density of the samples. The addition of SiC/CNT in small amount may not be detected in XRD, rolled sample has less porosity compared to before rolled specimen, the rolled sample has higher critical temperature compared to unrolled sample, the addition of CNT samples has higher critical temperature than the addition of SiC samples, the presence of SiC or CNT in the MgB$_2$ superconductor decreases the critical temperature.

References
[1] Hummel R. E., Electronic Properties of Material 3th Edition, Berlin: Springer-Verlag, 2011.
[2] Adriana S and German S 2009 Nova Science 2 21163
[3] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu 2001 Nature 410 1-5
[4] Wei D 2009 MgB2 Superconductor Research (China: Yantai University)
[5] Varghese N, Vinod K, Syamaprasad U and Roy SB 2009 Journal of Alloy and Comp 484 734
[6] Vajpayee A, Awana V P S, Yu S, Bhalla G L and Kishan H 2009 Phys C 470 S653
[7] Murgesan M, Gnanasekar K I and Rao M S R 1997 Adv in Supercond Proc Sym 391 5-7
[8] Hausner H H, Roll K H and Johnson P K 1968 Perspective in Powder Metallurgy "Fundamentals, Methods, Applications, B.V: Springer-Science Business
[9] Zhang, Y Ma, Z Gao, D Wang, S Awaji 2007 IEEE Trans. Appl. Supercond, 17 2915

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