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Effects of surface-treated boron powder using chemical solvents on MgB_2 bulk superconductors

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Abstract

MgB_2 superconducting properties have been investigated with the surface-treated boron powders using the chemical solvents. Various solvents were used such as acetone, ethanol, methanol, and water to possibly modify the surface condition of raw boron powders as received. This treatment was done at an argon gas environment inside the glove box to reduce the further contamination during and after chemical treatments. It was found that T_c values were increased to 37.58-37.73 K from the pure sample of 37.50 K when they were treated in inert environment. High- fields J_c at both 5 & 20 K was all increased regardless of any kinds of chemical treatments mentioned above. It is also noted that the J_c at low-fields were increased in the order of solvents: ethanol > acetone > pure MgB_2 = methanol > water.

Keywords: MgB_2, superconductor, chemical treatment, surface reaction

1. INTRODUCTION

Since the discovery of superconductivity in MgB_2 many fundamental and industrial research have been carried out worldwide for the practical applications in future [1-4]. It has been the main issue and important topic to increase the superconducting critical currents under the external magnetic fields at the targeted temperature [1-3].

Significant enhancement of the magnetic vortex pinning properties of MgB_2 can be effectively and routinely obtained with the partial substitution of boron sites with carbon. It should be noted that the carbon provided by many carbon based compounds maybe the only candidate leading to the marked enhancement of critical current density (J_c) at higher fields [1-5]. On the contrary it is well known that J_c at lower fields are sacrificed when doped with carbon, which are more or less affected by the connectivity between the MgB_2 grains [6-8].

There are several factors to be considered when dealing with the starting powders of MgB_2 such as its size, purity, composition ratio, mixing process, etc for the good reaction and formation of MgB_2 phases and finally higher in-field J_c properties. It is recognized that as-purchased raw powders may have some drawbacks such as oxides of raw powders like MgO and B_2O_3, some organic pollutants from the dust, moisture when exposed to air or during the delivery and dealing of powders.

To reduce the oxides contained in Mg and B raw powders, simple reducing heat-treatment can be adopted and was conducted on boron powders using the inert gas with the mixed hydrogen at elevated temperature and the improvement of superconducting properties of MgB_2 are thus confirmed [9-11]. For the Mg powders the native oxide, MgO, is very easily formed on the surface of Mg and it is quite dense. So, it will be very difficult to reduce and hardly avoided even after any removal treatment.

Meanwhile, a kind of pollutants on the surface of raw powders like the various organic materials, moisture, etc are not paid much attention and even ignored so far in the research of MgB_2 superconductors, not only with short bulk samples but also long-length wires.

Therefore, in this work, we have investigated the surface treatment, “simple washing method” of boron powders, which is less sensitive than Mg powders, using the common chemical solvents like acetone, ethanol, methanol, even water to remove any pollutants on the surface. The effect of chemical washing on boron powders and successful enhancement of MgB_2 superconducting bulk samples will be discussed.

2. EXPERIMENTAL

For the surface treatment of boron powders (99%, <100 nm, Specialty Materials Inc, US), the common chemical solvents are used. Acetone (Extra pure, 99.5%, Samchun chemicals, Korea), ethyl alcohol (anhydrous, Special grade, 99.9%, Samchun chemicals, Korea), methanol (anhydrous, 99.8%, Sigma-Aldrich, US), and water (HPLC reagent, Samchun chemicals, Korea) were prepared and used as-purchased. To eliminate any possible re-contamination of the treated boron powders, chemical washing process was conducted inside the glove box, which was circulated

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with inert Ar gas. Oxygen and moisture level have been maintained less than 10 ppm during the experiment.

~1g of boron powders was put into the beaker and soaked for 1 h with the above solvents. Then solvents are poured away and boron powders are dried inside the beaker overnight. In case of boron powders treated with water, it was well dispersed and separation was not occurred between the boron powders and water. So, evaporation of water was done using the hotplate at ~100°C until the boron powders were left only.

Then, chemically-treated boron powders were mixed and milled properly with a stoichiometric amount of Mg powders (99%, ~5 µm, Tangshan Weihao, China). The mixed powders were pelletized under 10 ton pressure using uniaxial hydraulic press. Pure MgB_2 pellet was also prepared for reference. The MgB_2 pellets were heat treated at a temperature of 700℃ for 30 min under the flow of high-purity Ar gas and furnace-cooled down to room temperature in a continuous gas flow.

The phase analysis of pure and chemically-treated MgB_2 samples was performed by X-ray diffraction (Rigaku, D/Max 2500, Japan) using Cu Kα radiation. The microstructures of all the samples were observed by field-emission scanning electron microscopy (FE-SEM). The magnetization, magnetization vs. temperature (*M*-*T*) and magnetization hysteresis (*M*-*H*) properties were measured on all samples by using a quantum design vibrating sample magnetometer option (PPMS, Quantum Design). The J_c was calculated from *M*–*H* loops by Bean's critical state model of $J_c = 20\Delta M/a(1-a/3b)$, where ΔM is the height of the *M*–*H* loop, *a* and *b* are the thickness and width of the sample with the dimension (1x2x3 mm^3), respectively.

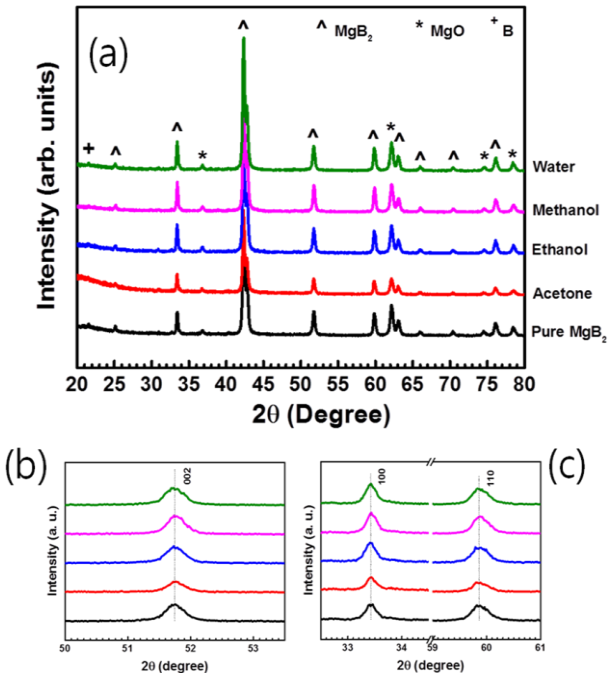

Fig. 1. (a) X-ray diffraction patterns of pure and chemically-treat MgB_2 samples with the solvents indicated, (b) the enlarged view of (002) plane and (c) (100) and (110) planes of MgB_2.

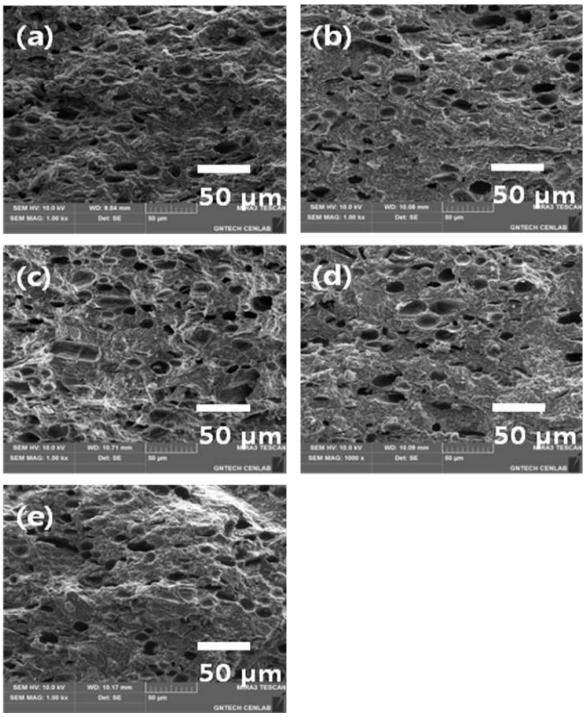

Fig. 2. FE-SEM images of MgB_2 bulk samples of (a) pure and (b)-(e) chemically treated with Acetone, Ethanol, Methanol, and Water, respectively.

3. RESULTS AND DISCUSSION

Chemically-treated and pure MgB_2 samples are analyzed first with the phase formation with XRD measurements and their diffraction patterns and indexing are shown in Fig. 1. Main MgB_2 phases are well formed at all the samples with the small impurity phases like MgO and B. It is found that there is not any noticeable change between the chemically-treated MgB_2 and pure one. As shown in Fig. 1(b) and 1(c) there is also no shift of angles with (002), (100), (110) planes of MgB_2 Bragg reflections, indicating that the lattice are not deformed and strained with the chemical treatment. Also, relative content of MgO, which is always found in MgB_2 samples, was not changed to main MgB_2 phases when it is compared between the MgO(220) and MgB_2(102) planes[1-5].

Actually, it is not expected that it is likely to have any carbon supply from all these chemical solvents used here. All the chemicals except water have a carbon as recognized from their formula. There are acetone of C_3H_6O, ethanol of C_2H_6O, and methanol of CH_4O. Since all the chemical treatments were performed almost at room temperature, chemical solvents are not likely to decompose to release the carbon behind for doping into the MgB_2. Also oxygen from the solvents does not seem to influence the MgO contents as discussed above.

Figure 2 shows the FE-SEM images of pure and chemically-treated MgB_2 samples at low magnification. It is seen that all the MgB_2 samples shows the typical microstructure and morphology of well known bulk-type. It is consisted of round type pores with the well-connected

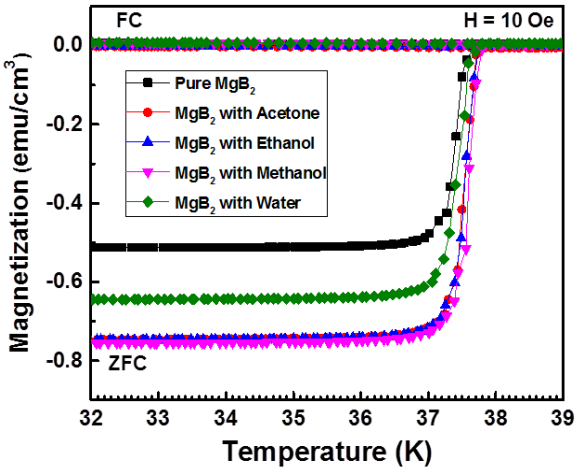

Fig. 3. Temperature dependence of magnetization easured in an applied field of 10 Oe for pure and chemically-treated MgB_2 bulk samples.

dense grains. The sizes of pores are more or less 5-30 µm ranges which are formed after the Mg are evaporated during the high temperature heat treatment process. Also there is no noticeable variance of morphologies among the MgB_2 samples measured at higher magnification (not shown here).

Since boron powders are covered by the oxide, which formed naturally on the outer shell, along with small amount of the existing B_2O_3 powders besides [9-11], both boron oxides can react with the chemical solvents like the water and methanol and it is reported that B_2O_3 is soluble in water and partially in methanol, thus these oxides may be reduced or removed after the chemical treatment in this work [12]. Hence, the connectivity between the MgB_2 grains can be improved with the better reactivity between the Mg and B [6-8] .

In this work, due to the re-contamination of boron powders after the chemical treatment all the process including mixing and grinding with Mg powders have been carried out inside the glove box with the inert atmosphere.

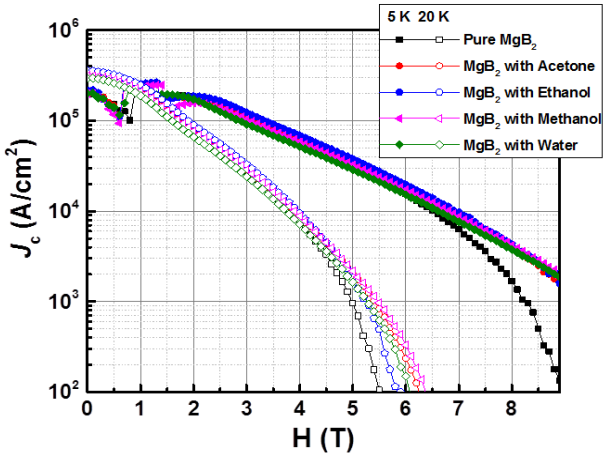

Fig. 4. Critical current density as a function of magnetic fields for pure and chemically-treated MgB_2 bulk samples at both 5 and 20 K.

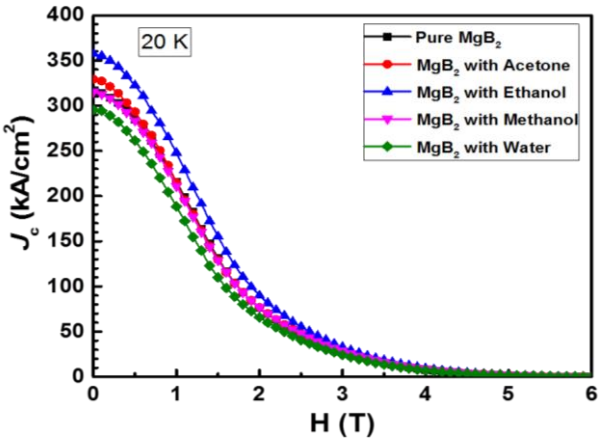

Fig. 5. Magnetic field dependence of critical current density of pure and chemically-treated MgB_2 bulk samples at 20 K with linear scale.

So, any reduced and removal of boron oxides are not proved and not confirmed. However, it is verified recently by the authors that B_2O_3 phases are almost removed from boron powders by chemical treatment through the X-ray diffraction measurement [13]. Further detailed effect of chemical treatment on microstructure and crystallinity of boron using TEM analysis is going on.

Superconducting properties of all the MgB_2 samples are checked with the magnetization versus temperature measurements as shown in Fig. 3. The superconducting transition temperature (T_c) of 37.50 K was obtained for the pure MgB_2. It is interesting to note that T_c was increased when boron powders are treated chemically with solvents. T_c of 37.69 K (acetone), 37.69 K (ethanol), 37.73 K (methanol), and 37.58 K (water) was measured.

The curves of ZFC measurement also shows the sharp transition of the chemically-treated MgB_2 compared to pure one owing to the better connectivity between the superconducting grains. Also, it is worth noting that the diamagnetic magnetization of the chemically-treated MgB_2 is larger than the pure one as evident from the Fig. 3. The nearly flat ZFC curve up to 36.5 K are of bulk superconductivity and improved inter-grain connectivity and magnetization values indicate the superconducting volume fractions increased.

In Fig. 4, the magnetic field dependence of critical current densities of MgB_2 samples are shown. Both at 5 and 20 K, J_c of the chemically-treated samples at higher fields are increased compared to the pure MgB_2. Since no doping was designed in this work and no sign of any carbon substitution into the B sites are detected as mentioned above from XRD analysis, it is surely not from the typically observed carbon doping phenomena. It is rather speculated that the strong inter-grain connectivity, removal of impurities like B_2O_3, and uniform grain size distribution from the clean surface of boron powders after the chemical treatment.

It is also found that J_c at lower fields are enhanced with chemical treatment of the ethanol solvents as shown in Fig. 5. This plot of J_c-B was transformed to the linear from the log scale of ordinate axis to show the change of J_c at lower

fields better. It is seen that the maximum J_c of ~350 kA/cm^2 at the self-field and 20 K are obtained with the ethanol treatment, which is much larger than the J_c of ~310 kA/cm^2 of pure MgB_2. It should be kept in mind that the absolute values of increase of 40 kA/cm^2 at self-field is much larger than the increased values of about 2 kA/cm^2 at higher field of 9 T.

In the case of acetone and methanol treatment, low-field J_c is quite similar to the pure MgB_2 sample. It should be noted that J_c is a little bit decreased with the water treatment, which is very likely to the case with the usual carbon doping. It is believed that evaporation of water at higher temperature to remove may influence the surface properties of boron powders left behind. Even if this trend at lower fields is not well understood at this moment, the grain connectivity, that is, density of MgB_2 is the key factor to be considered at this field range.

4. CONCLUSION

Surface-treated boron powders using the chemical solvents provided the simple and effective way to improve the superconductivity of MgB_2. Chemical treatment using the common solvents of acetone, ethanol, methanol, and water are used to possibly modify the surface condition of raw boron powders. T_c values of all the MgB_2 samples showed the increase to 37.58-37.73 K compared to the pure sample of 37.50 K and the superconducting volume fraction of MgB_2 increased as well. It was found that J_c at both temperatures of 5 & 20 K at higher fields was all increased about an order of magnitude regardless of the chemical solvents. In addition, it is worth mentioning that the J_c at low-fields can be enhanced when the boron powders are treated chemically with the solvents of ethanol and acetone than that of pure MgB_2.

ACKNOWLEDGMENT

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