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Comparison of in-situ MgB_2 Superconducting Properties Under Different Annealing Environment

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열처리조건 변화에 따른 in-situ MgB_2 초전도 특성 비교

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Abstract

Effect of mixed gas and additional Mg powder in an annealing process of the MgB_2 is investigated. Four different type of samples were prepared, each in different annealing environment of Ar, Ar+4%H_2, Ar with Mg powder and Ar+4%H_2 with Mg powder. Different annealing environment did not affect the electron-phonon interaction which is reflected from the same superconducting transition of 36.6 K for all samples. The reducing effect of hydrogen is clearly depicted from the presence of excess Mg in sample synthesized in Ar+4%H_2 gas implying the reduced rate of reaction between Mg and B. This has manifested itself in terms of slightly increased high-field critical current density of the sample. In contrast, the sample synthesized in Ar+4%H_2 with Mg powder, has shown overall enhancement in the superconducting properties as presented by higher diamagnetic saturation and critical current density.

Keywords : MgB_2, annealing, critical current density

I. Introduction

After more than a decade later from the discovery of superconductivity of MgB_2 superconductor [1], it is still in limelight due to its application-oriented and technologically favorable properties [2-4]. Recently, it is believed that prospect for MgB_2 superconducting wires is quite high in the liquid He free cryogenic regime of about 20 K [5]. The field of superconductivity has seen an era of high T_c superconductors, with sky rocketing technological expectations due to their higher operating temperatures in liquid nitrogen regime. But all such expectations remained unrealized due to problems in making it into longer wires or coils. They need to be highly textured to provide the required superconducting properties. This has not been a hurdle in case of MgB_2 superconductors, even though

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the operating temperature is lowered to 20 K.

Meanwhile, MgB_2 superconductors have been synthesized adopting the various processes to enhance its superconducting properties and some useful and cost-effective techniques were reported [6-10]. But we observe that there are widely varying properties of MgB_2 superconductor depending on the technique of synthesis, the used precursor, the annealing temperature, etc [11-12]. Improvement in critical current density for pure MgB_2 can be achieved by enhancing the phase formation and increase in sample density apart from grain boundary and other defects [13]. The main parameter behind the discrepancies between the different pristine MgB_2 samples is the higher vapor pressure of Mg and its affinity towards oxygen which results in the instability of Mg content. The chemical equilibrium during reaction between Mg and B can also be considered as a basic parameter that will influence the superconducting properties of the *in-situ* synthesized MgB_2 superconductor. In present investigation, the systematic study on the effect of varying annealing environment in terms of Ar, Ar+4 %H_2 gas, with and without presence of Mg powder is reported.

II. Experimental

In the present investigation magnesium diboride bulk samples were prepared from Tangsan Boron from China and $\geq$99 % pure Mg powder from Aldrich. Both the powders were taken together in the stoichiometric proportion for synthesis of MgB_2. The reaction between magnesium and boron for formation of MgB_2 includes; solid to solid, liquid to solid and gas to solid diffusion of magnesium into boron respectively depending upon the temperature range. Hence in other words, reaction between these two powders is driven by diffusion of Mg into boron. This requires the powders to be vigorously mixed and homogenized. Hence they were taken in an agate mortar and hand milled for about 2 hrs for enhanced particle to particle contact. Homogenized powder was then pelletized under the pressure of 10 ton/cm^2 by a uniaxial press and mold system. Amount of powder taken in the mold was sufficient to make a pellet of 150 mg in weight. The weight of pellet was kept constant for all the samples annealed under different annealing environment. The pellet so formed was then heat treated in the sealed tube furnace at the temperature of 650 ^oC for 2.5 hours.

Magnesium has a high vapor pressure and hydrogen forms a highly reducing environment. The presence of these elements in the annealing environment can significantly alter the superconducting properties of final sample. To understand the effect of different annealing environment, depending upon presence and absence of hydrogen and magnesium, samples were heat treated in different ambiance and were named accordingly. Thus the samples were annealed in Ar, Ar+4 %H_2, Ar+Mg and Ar+4 %H_2+Mg and were respectively named as IA, IAH, IAM and IAHM. The as-synthesized samples were then subjected to X-ray diffraction (XRD) analysis to confirm the formation of MgB_2 phase as well as to observe the presence of any unreacted constituent elements. Rigaku D/MAX 2200 diffractometer employing Cu Kα radiations was used to perform this analysis. Effect of different annealing environment on superconducting properties of as-synthesized samples was studied using a Quantum Design PPMS model 6000. Superconducting transition temperature was determined by zero-field cooled and field cooled magnetization measurement. Further the magnetic critical current density was determined by applying Bean's critical state formula [14]. on the field dependent magnetization measurement at 5 K and 20 K.

III. Results and Discussion

Preparation of MgB_2 phase involves direct reaction of Mg which has a high vapor pressure and B which has a high melting point. Both elements have a good affinity towards oxygen that further increases the

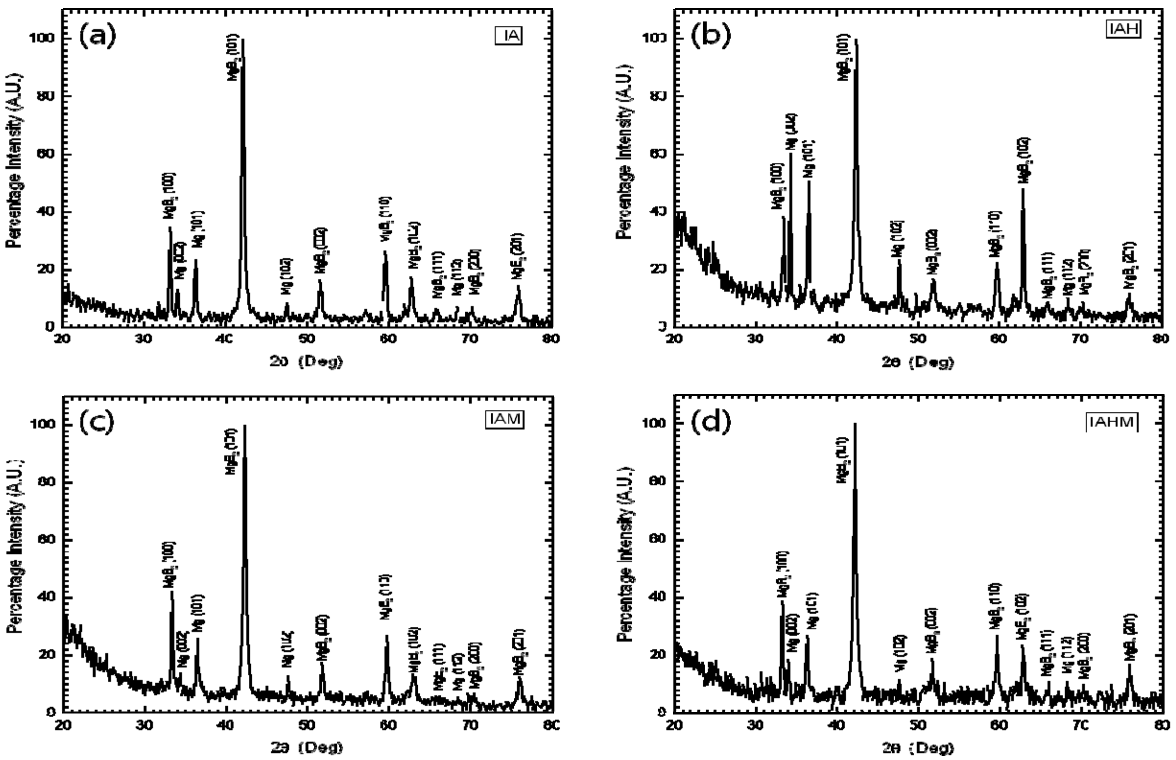

Fig. 1. X-ray diffraction pattern of samples (a) IA, (b) IAH, (c) IAM, and (d) IAHM in terms of percentage intensity. Here (101) peak of MgB_2 is considered as a 100 % intensity peak.

intricacy of the reaction. Under this situation, different annealing environment composed of Ar or Ar+4 %H_2, and with or without Mg powder, greatly influences the superconducting properties of MgB_2. This is clearly depicted from the XRD patterns as shown in Fig. 1 (a-d). All the conventional peaks belonging to MgB_2 are observed. This confirms that MgB_2 is the major phase in all samples. It must be understood that the annealing temperature is 650 ^oC which is also melting point of Mg. At this temperature, the rate of Mg sublimation is low but significant. The rate of reaction between Mg and B is also comparatively slow. Hence there is relatively incomplete reaction and residual Mg phase is observed. This is in accordance with the Mg peaks observed in the XRD pattern (Fig. 1(a)-(d)) for all the samples. Amount of unreacted Mg in sample is expected to depend on immediate environment used for annealing. It was considered that the Mg powder added in Fe tube during annealing will render more unreacted Mg as compared to those samples annealed without presence of Mg powder.

But in contrast to this assumption, it is observed that the sample IAH annealed in Ar+ 4 %H_2 has shown higher intensity of Mg peak indicating relatively large amount of Mg presence. The comparative picture of Mg content in terms of relative intensity of Mg peak is given in Fig. 2. Here the intensity of (101) MgB_2 peak is considered as a 100 % intense peak. Sample IAH shows higher intensities for Mg peaks (~40-50 %) as compared to all other samples (~15-25 %). Also the (002) peak of Mg is more intense than (101) peak which is in contrast to the XRD behavior for other samples. This indicates existence of some different kind of chemical reaction equilibrium to the one driving the reactions in other samples. It must be noted that the sample, IAHM, synthesized in presence of same

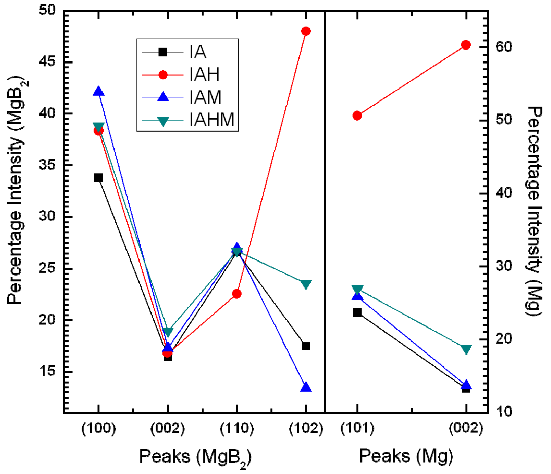

Fig. 2. Intensity profiling of main peaks for MgB_2 and Mg as observed in the XRD pattern.

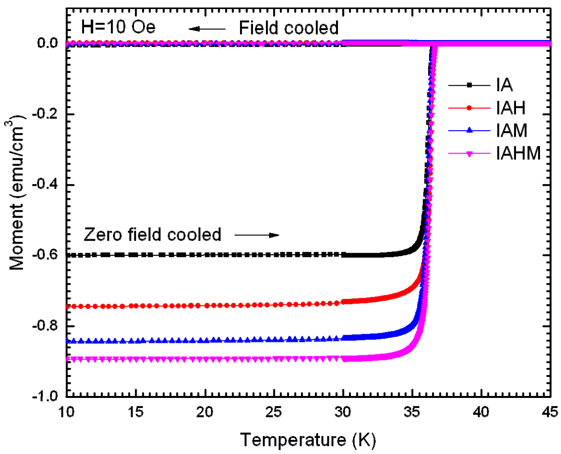

Fig. 3. Field cooled and zero field cooled magnetization plots for all samples.

environment as IAH except for presence of Mg in annealing environment, do not show presence of such high amount of unreacted Mg. This further strengthens our argument for some different kind of reaction equilibrium driving the reaction between Mg and B in sample IAH.

This may be due to the simultaneous reaction between Mg and hydrogen as well as reduction of Mg from MgB_2 by hydrogen. This will slow down the reaction between Mg and B which results in the increased Mg content in the sample. On the contrary, IAHM sample, which contains excess Mg powder during annealing, there is a continuous supply of Mg, which will counter the reducing effect of hydrogen. Further, the presence of Mg and hydrogen in conjunction with each other provides better annealing environment. Hydrogen plays a role of making fresh reaction sites by reducing MgB_2 and the excess Mg in the ambiance increases the chemical potential of Mg, which further supports the formation of MgB_2. This would provide a better MgB_2 phase formation and may improve the superconducting properties. The sample annealed in presence of Mg ambiance Fig. 1 (c) & (d) do not show as intense Mg peaks as sample IAH. This further indicates an altered chemical equilibrium between Mg and B reaction.

The plot in Fig. 3 shows the field cooled (FC) and zero field cooled (ZFC) plots for all the samples in the temperature range of 5 K to 45 K. The plot shows a clear diamagnetic signal at 36.6 K indicating same superconducting transition temperature for all the samples. It can be noted that the plot shows a sharp drop indicating diamagnetic signal which got saturated without any significant rounding for all samples. This shows that the annealing environment did not have any significant effect on the superconducting transition temperature. All the samples have shown reduced superconducting transition at 36.6 K as against 39 K, which may be due to the quality of boron precursor. Same superconducting transition temperature for all the samples is indicates same level of structural purity and electron phonon interaction is not affected from the change in annealing environment. Hence it can be claimed that extra Mg settles at the grain boundaries, instead of creating some structural defects.

A significant variation is observed in the extent of saturation magnetization with the change in annealing environment. The extent of diamagnetic saturation is least for sample IA which gradually increased for IAH, IAM and IAHM respectively. Enhanced density of the sample from only hydrogen and only magnesium in the annealing ambiance to combination of both is clearly evident.

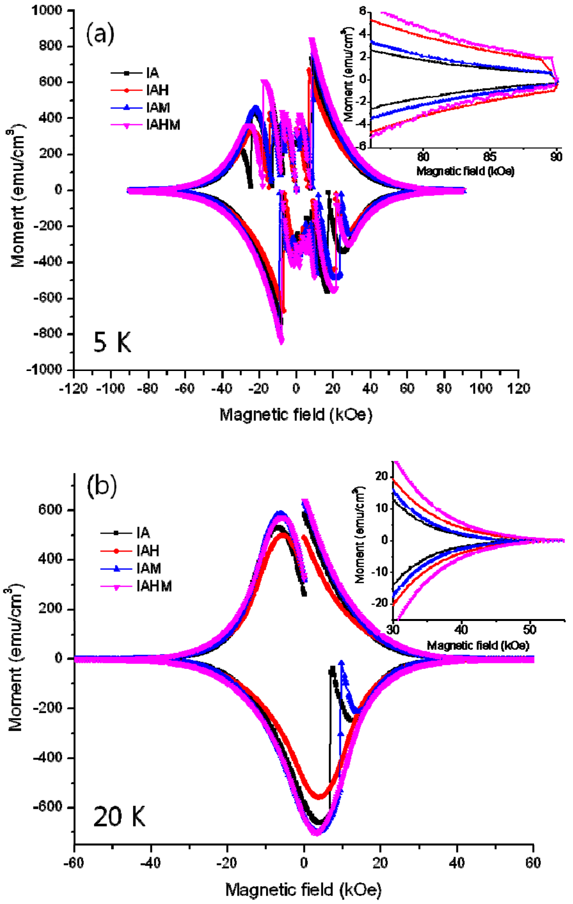

Fig. 4. Magnetization Vs. field plots at (a) 5 K and (b) 20 K. Inset in each case shows the MH behavior at higher field.

M-H response for all the samples is as shown in Fig. 4(a) & (b) wherein the field dependent magnetization is depicted at two different temperatures of 5 K and 20 K. All the samples have shown a high flux jump properties at the lower field indicating the sample having a high critical current density. There is very less dependence of annealing environment on *M-H* response. It is supportive to our argument that there is hardly any doping effect due to the different annealing environment used. The excess Mg as indicated by XRD is at grain boundaries instead of forming any impurity doping. The only significant difference between all the samples is gauged from the inset which shows open *M-H* loop for samples IAM and IAHM and nearly closed

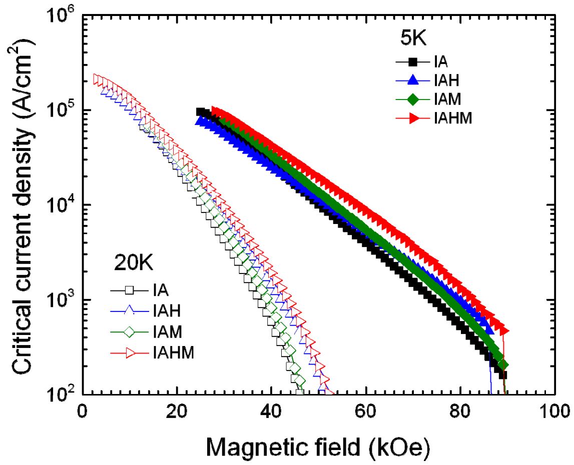

Fig. 5. Critical current density plots for all the samples at 5 K and 20 K.

M-H loop for IA and IAH samples at 90 kOe and 5 K. It is also evident from the increase in the value of field at which the respective loops closes at 20 K. This clearly shows that there is improvement in the irreversibility field of samples merely due to the presence of Mg in the annealing environment.

The critical current density was determined by using the Bean's critical state formula, $Jc=(20\Delta M)/\{a(1 - a/3b)\}$ Where, Jc is critical current density in A/cm^2, ΔM is the difference in the magnetization in emu/cm^3 for increasing and decreasing field, 'a' and 'b' is the thickness and width of sample with rectangular geometry. Fig. 5 shows the critical current density response at 5 K and 20 K. Samples have shown a superconducting critical current density of about 10^5 A/cm^2 at around 30 kOe for 5 K temperature. The same is at around 4×10^4 A/cm^2 at around 20 kOe and 20 K. Further, there is slight increase in the H_{irr} (irreversibility field) and critical current density at high field for samples (IAH and IAHM) synthesized in presence of hydrogen in the annealing environment. This might be due to the creation of certain pinning centers within the MgB_2 grains due to the reducing effect of hydrogen. There might be enhanced pinning in sample IAH due to the accumulation of Mg at grain boundary. In case of sample IAHM, the overall critical current density is high both at low field and high field value, at 5 K as well as at 20 K. This may be due to the combined effect of enhanced structural density with accumulation of Mg at grain boundary in the sample due to the presence of Mg during the annealing environment in conjunction with hydrogen.

IV. Summary

A systematic study on the effect of annealing environment on the superconducting property of as-synthesized MgB_2 is presented successfully. The presence of hydrogen along with argon during annealing induces a reducing effect which slows down the reaction between Mg and B giving large accumulation of Mg in the sample. Addition of Mg powder in the annealing tube along with Ar and H_2 gas has shown a positive effect. Enhanced overall density of the sample by virtue of increased Mg potential along with the reducing effect of H_2 is observed. This has manifested itself in terms of increase in the overall critical current density of the sample.

Acknowledgments

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