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Bulk Mg_xB_2 superconductor production by excess Mg and hot press methods and their properties

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ABSTRACT

Four different nominal compositions MgB_2, $Mg_{1.5}B_2$, Mg_2B_2 and $Mg_{2.5}B_2$ were produced by excess Mg method and hot press. These superconducting samples were compared in terms of structural, electric and magnetic properties. The superconducting phase was determined by XRD analysis, which indicated the formation of MgB_2 structure as a main matrix with some amount of non-superconducting phases, such as metallic Mg and minor amount of MgO. The electric properties of the samples were characterized by low temperature resistivity measurements under different magnetic fields 0.5, 1.0, 3.0 T. The results showed that the superconducting $T_{c,onset}$ and $T_{c,offset}$ transition temperatures moved to lower values. These results indicate that excess Mg method improves the superconducting and magnetic properties of MgB_2, as well as enhanced the rigidity and ductility of the samples. Experimental results showed the advantages of the proposed methods, established the most suitable transition temperature of the samples, as well as the decline from the superconducting to normal state.

1. Introduction

Since the discovery of superconductive properties MgB_2 with 39.0 K critical temperature (T_c), many efforts have been done to characterise their structural, magnetic and physical properties [1]. In last decade, the exciting magnesium diboride MgB_2 superconductor is a promising material for magnets and microelectronic devices at low cost. Some of their important characteristics are the light weight, higher critical current density, absence of weak links, longer coherence length of ~ 5 nm, weak thermal fluctuations and isotope effect. Bulk MgB_2 superconductors have been synthesized using several methods, such as high-pressure synthesis or sintering, hot isostatic pressure [2], mechanical alloying [3], self-propagation high-temperature synthesis method [4], spark plasma sintering [5], etc. The high critical current density is a crucial point in the use of superconductors in industrial technology. Especially, MgB_2 has no a weak-link effect which reduces the superconducting current density between grains [6]. This family is therefore the most promising candidate for the next industrial technology.

Excess Mg methods have been reported by [7-9] among others. Some advantages on superconductor properties are: an increased critical current density and enhanced mechanical properties, which specially have to do with the material fragility and the quantity of trapped magnetic field. The excess Mg method was used at first by E. Yanmaz [10], which modified the preparation technique, and this work was presented to get the patent of this novel method. To the best of our knowledge, high T_c superconducting properties can be enhanced by increasing connectivity between superconducting phases. The reported papers supported that MgB_2 superconductors could prove to be extremely useful in real applications.

In this paper, MgB_2 superconductors were produced using the excess Mg technique which was followed by a hot press. The magnetic and electrical properties of the obtained samples are described in detail herein.

2. Materials and methods

In this study, appropriate amounts of elemental magnesium (Mg) powder (Alfa Aesar, purity 99.8%, -325 mesh) and amorphous nano-boron (B) powder (supplied from Pavezyum Turkish co., purity 98.5%) were mixed in an agate mortar for 10 min. The size of the used B Sub-micron particle powder was (<250 nm). By

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using nano-boron powder, we are expecting enhanced connectivity and density, and superconducting phases will be high which results in high critical transport current [11].

The mixture was transferred into a chromium capsule and both ends of the capsule were tightly closed using chromium lids in Ar atmosphere. Subsequently, the closed chromium capsule was put into a preheated muffle furnace at 1000 °C, and held for 15 minutes in Ar atmosphere to allow the rapid reaction of Mg with B. This preparation method is described as follows: the amount of Mg and B were calculated according to the stoichiometric ratio of Mg/B, the quantity of B was kept as the calculated amount, more information about the preparation method and applications can be found in [3, 10].

Four different nominal compositions MgB_2, $Mg_{1.5}B_2$, Mg_2B_2 and $Mg_{2.5}B_2$ were produced by excess Mg method and followed by hot press. The aim of this method was to improve homogeneity of precursor materials Mg and B, as well as to improve rigidity and ductility of the final sample. The excess Mg is distributed in the superconducting grains, which are expected to work as pinning centers, and increases the capability of the trapped magnetic field in the samples. The target is to make a full reaction of B atoms in Mg and not to allow the superconducting grains growth. Reducing the reaction time by increasing temperature prevents the grain growth, lows down the normal state resistivity of the samples and the magnesium vapor pressure, which also affects the electron phonon interaction.

The amount of Mg and B quantity was calculated according to nominal compositions indicated above, and every mixture was relocated into a chromium tube in which both ends of the tube were closed with a chromium lid to prevent oxidation. The first reaction of these mixtures was performed at 10 mbar Ar pressure at 1000 °C for 15 minutes. These mixtures were then removed to room temperature to cool down. Each sample was ground separately by hand, and then compacted at 60 tones until the temperature reached 400 °C of hot pressed furnace.

After the hot pressure process, every sample was then transferred into a chromium tube again, in which both ends were strongly tightened, and put into furnace at 1000 °C for 15 minutes. Finally, after the heating process, the closed chromium tube was taken out of the furnace and cooled at room temperature.

The phase and crystal structure of the prepared samples were investigated by Rigaku Multiplex device [6]. The X-ray diffractometer system (XRD), with CuK_α target, provides a monochromatic beam target (k=1.54 Å) at room temperature. A XRD system was chosen to analyze the crystal structure of the samples by estimating the lattice parameters for tetragonal structure (a=b, c). The calculated values of the XRD patterns of MgB_2 samples, under hot press at 1000 °C for 1 h, were found to be a = 0.30797 (nm) and c= 0,346 (nm). The device parameters were set as follows: scan speed 5°/min and 0.02° as a step increment (in air atmosphere at the room temperature).

The surface morphology of the samples was analyzed by using Scanning Electron Microscopy (SEM) Jeol 6390LV at 20 kV.

Transition temperatures of each sample, $T_{c,onset}$ and $T_{c,offset}$, were determined by low temperature resistivity measurements under different magnetic fields (0.5T, 1T, 3T). The levitation forces of the samples were determined by measuring the magnetic force in the ZFC and FC regimes at 20 K using a homemade measurement system.

3. Results and discussion

Figure 1(a) and Figure 1(b) show the SEM micrographs of the nominal compositions MgB_2 and $Mg_{1.5}B_2$, respectively. In Figure 1(a), the surface morphology of the sample is the standard MgB_2; the particle size is significantly smaller than the sample $Mg_{1.5}B_2$. Moreover, both samples seem very dense. However, the excess of Mg produced more vacancies inside the sample in $Mg_{1.5}B_2$, as seen in Figuru 1(b). This is due to the fact that these samples are heated at 1000 °C and more Mg in the sample creates higher vapor pressure and, therefore, more vacancies. The micrographs illustrated that both samples are homogenous, in which the particle size of the samples were several hundred nanometers. As long as the Mg content increased, the morphology of samples changed and the homogeneity decreased. The phase analyses of this family (MgB_2) have been done in previous studies, such as [12-14], etc.

The powder X-ray diffraction patterns with different nominal compositions MgB_2, $Mg_{1.5}B_2$ and $Mg_{2.5}B_2$ are shown in Figure 2(a), Figure 2(b) and Figure 2(c), respectively. The highest intensity peak was observed at $2\theta = 42.6°$ as regards the main peak of MgB_2. Peak intensities at $2\theta = 30°– 40°$ represent the metallic Mg, which augmented regularly as a function of the metallic Mg content. As explained in the experimental procedure, the sintering temperature was 1000 °C which is a very high temperature for the formation of MgB_2 phase. The MgB_2 phase happen to be at around 650 °C, therefore, the excess Mg method was used in order to prevent the Mg evaporation. In this method, high Mg vapor pressure occurred in closed volume and all B atoms reacted with Mg, compulsory. The excess Mg was distributed homogenously in the main phase. Some amount of MgO was also observed in the XRD patterns. At the time that hot press process was applied, the oxidation phenomena happened in both samples.

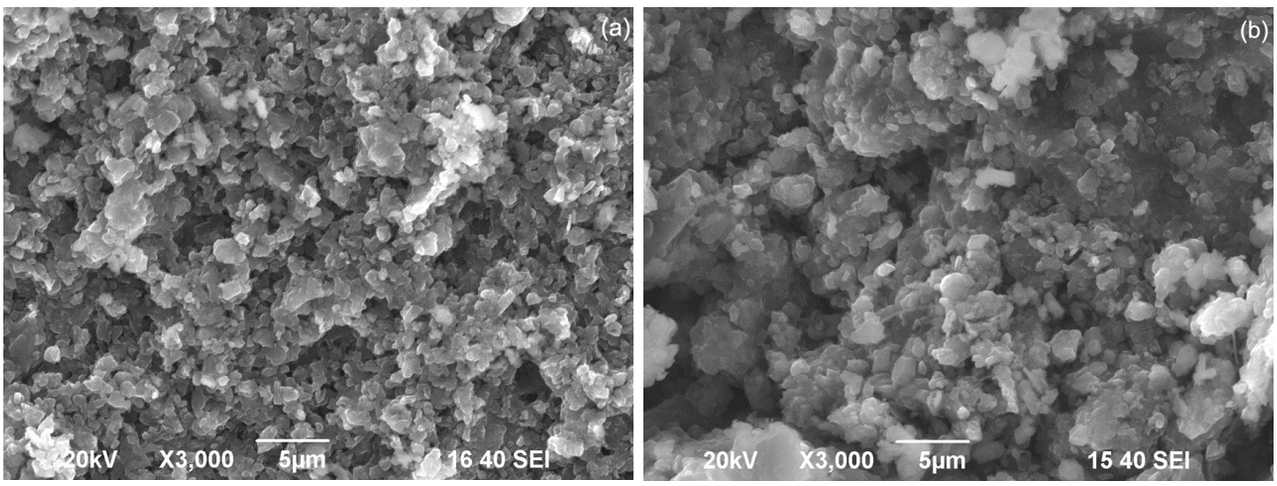

Figure 1. Nominal composition: (a) MgB_2 and (b) $Mg_{1.5}B_2$, SEM micrographs

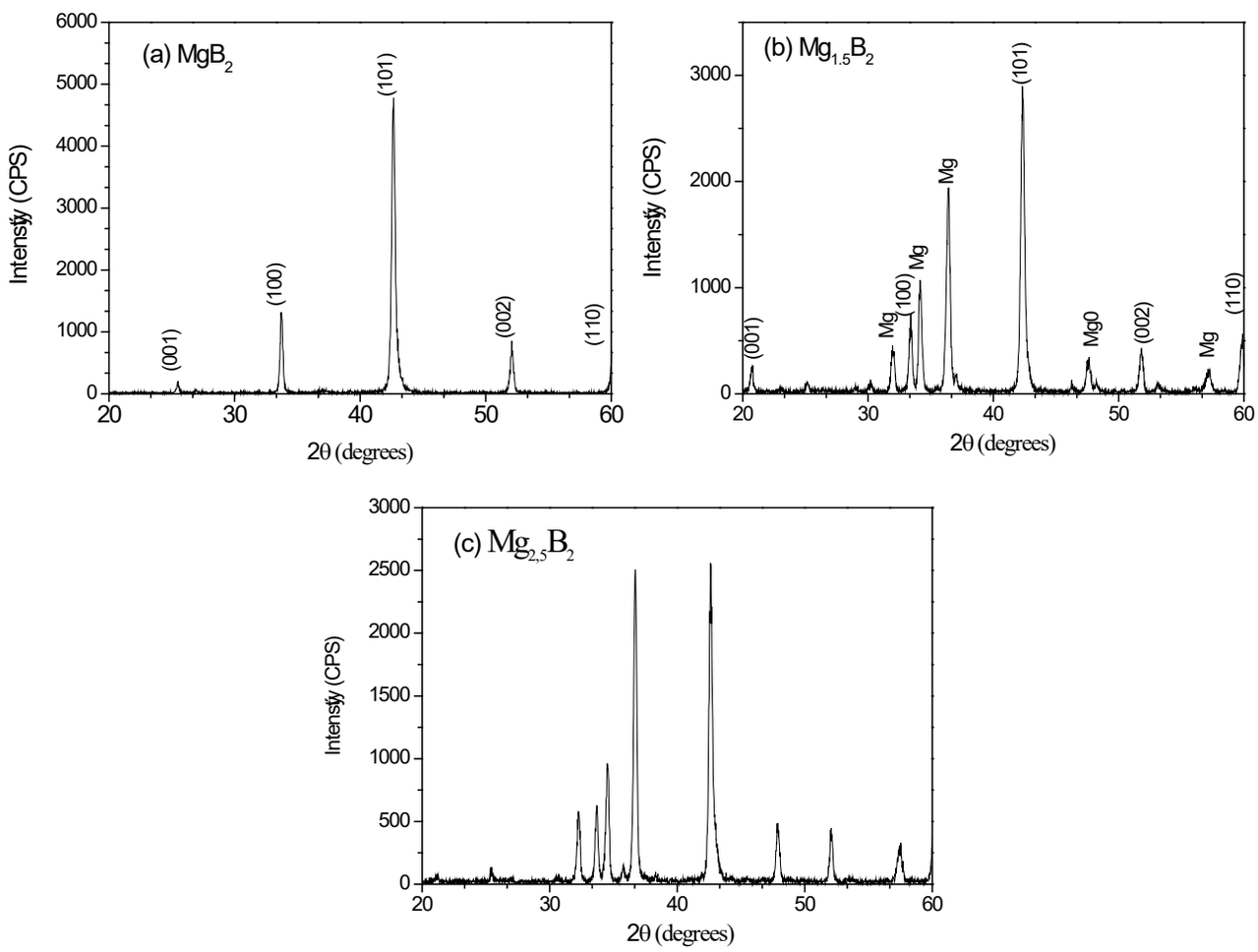

Figure 2. Powder X-ray diffraction patterns with different nominal compositions MgB_2, $Mg_{1.5}B_2$, Mg_2B_2 and $Mg_{2.5}B_2$ are shown in (a), (b) and (c), respectively

Figure 3-6 show low temperature resistivity measurements, which were represented under different magnetic fields in ZFC regime. In Fig. 3, the transition temperature MgB_2 were found to be 34.3 K for $T_{c,onset}$ and 32.0 K for $T_{c,offset}$ which indicate that the transition temperatures are less than the standard temperatures in literature. It is clearly seen that this values moved to lower temperatures under different magnetic fields, such as 3.0 T in which the temperature was reduced to $T_{c,offset}$ = 27.7 K. This result indicates that the quality of the sample was poor compared to a standard MgB_2, as reported in literature [15, 16], among others. When we compare all figures in terms of the transition temperatures, the sample $Mg_{1.5}B_2$ looks stronger

against the external magnetic field, see Figure 4. This sample shows a transition temperature around $T_{c,offset}$ = 37.0 K in zero magnetic field. The transition temperature moved to lower temperatures $T_{c,offset}$ = 29.5 K under 3 T, while in Figure 5, the Mg_2B_2 sample illustrates that the T_c under zero magnetic field was $T_{c,offset}$ = 36.5 K. This temperature value changed to 28.0 K at 3 T.

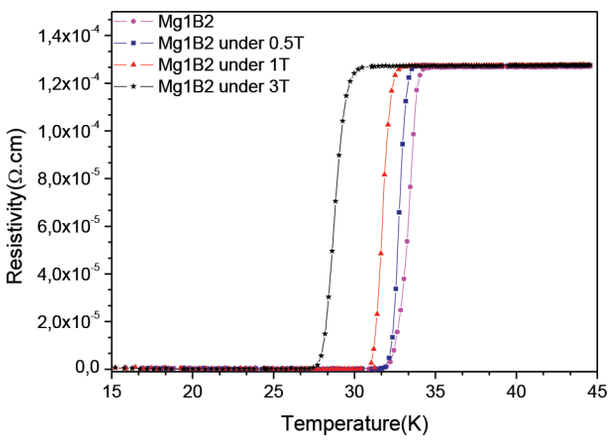

Figure 3. MgB_2 resistivity measurements at low temperature, under different magnetic fields in ZFC regime

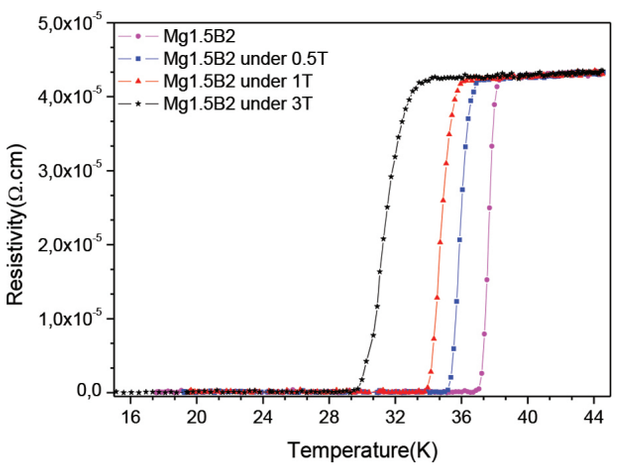

Figure 4. $Mg_{1.5}B_2$ resistivity measurements at low temperature, under different magnetic fields.

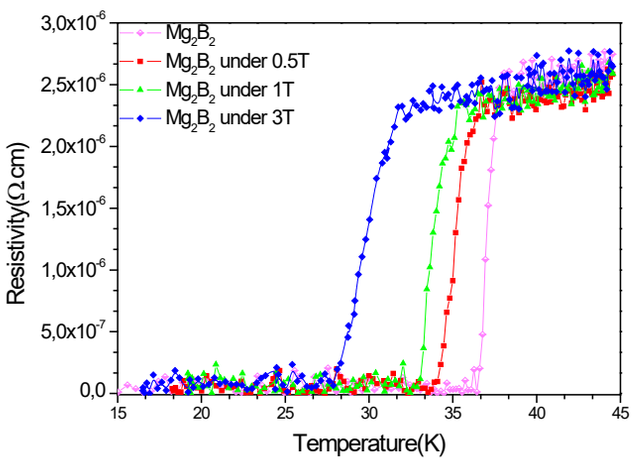

Figure 5. Mg_2B_2 resistivity measurements at low temperature, under different magnetic fields in ZFC regime.

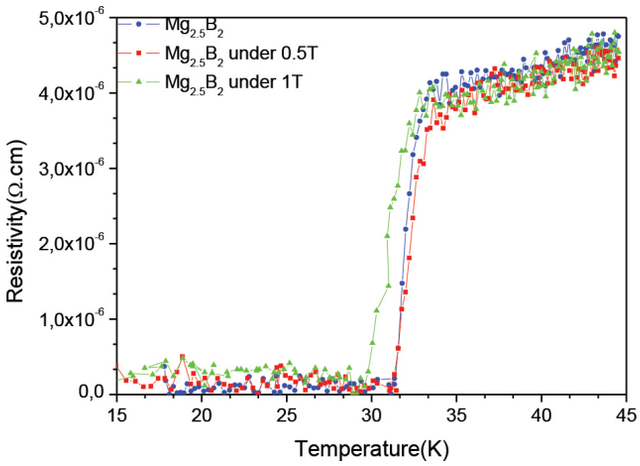

Figure 6. $Mg_{2.5}B_2$ resistivity measurements at low temperature, under different magnetic fields in ZFC regime.

Three nominal compositions MgB_2, $Mg_{1.5}B_2$ and Mg_2B_2 showed transition temperatures $T_{c,offset}$ at 27.7 K, 29.5 K, 28.0 K, respectively. However, the $Mg_{1.5}B_2$ sample shows better superconducting properties in this group.

The transition temperature of $Mg_{2.5}B_2$ could not be compared to the aforementioned three samples, as shown Figure 6. Furthermore, normal state resistivity happened to be very noisy for samples Mg_2B_2 and $Mg_{2.5}B_2$. Provided that Mg reduces the normal resistivity, the voltage dropped at inner contacts, which are already so small; therefore, noise becomes dominant in the measurement. In order over come to this problem, the applied DC current should be higher than the present working values.

Low temperature levitation force measurements were performed for each sample using a homemade device at 20.0 K in ZFC and FC. The diagrams of each sample are given in Figure 7(a) and Figure 7(b), in which the force is depicted for two different force scopes. In Figure 7(a), the force value goes from 0 N to 6 N, while Figure 7(b) shows a different scope that goes from -2 N to 2 N, in order to show attraction and the repulsive forces. These figures show that the highest levitation force was observed in the sample $Mg_{1.5}B_2$. In addition, a closed behavior compared to Mg_2B_2 was also achieved for the nominal composition. Once the content of Mg increases over two, the levitation, attraction and repulsion force dropped to the lowest level. In the light of these results, the excess Mg method had therefore affected the superconducting properties of the sample. Moreover, the levitation force values rose up to a significant Mg value. As a conclusion, the highest Mg values were determined for $Mg_{1.5}$ and Mg_2 superconducting samples.

This result indicates that excess Mg method is an alternative method to increase the super conducting properties. Especially, the number of pinning centers

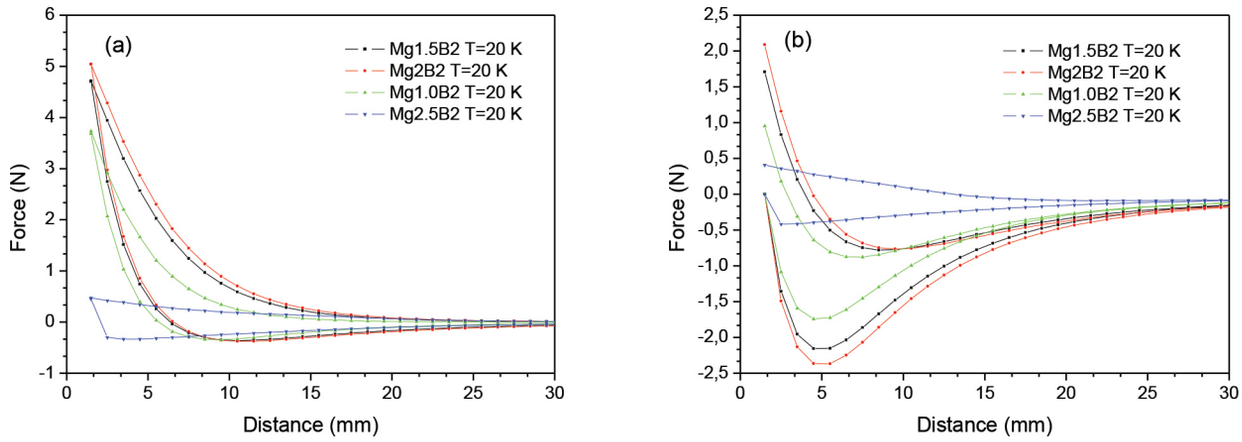

Figure 7. Low temperature levitation forces measured by means of a homemade device at 20 K, in ZFC and FC: (a) Force (0 N to 6 N) and (b) Force (-2 N to 2 N)

may increase to certain values; hence a high magnetic field is trapped. To the best of our knowledge, the critical current density of superconductors rises up with the number of pinning centers. The improved critical current density created stronger levitation forces in the repulsive and attractive regimes.

4. Conclusion

Four powder samples with different nominal compositions MgB_2, $Mg_{1.5}B_2$, Mg_2B_2 and $Mg_{2.5}B_2$ were produced by excess Mg method followed by hot press. In this process, as important characteristic, the samples are held for short time to in Ar atmosphere since the grains should be kept small to preserve the porosity of the samples. Another key matter is that the quantity of B in the samples never changed.

The samples MgB_2, $Mg_{1.5}B_2$ and Mg_2B_2 showed offset transition temperatures at 27.7 K, 29.5 K, 28.0 K, respectively. However, the $Mg_{1.5}B_2$ shows better superconducting properties. It was found that the excess Mg method in MgB_2 system enhanced the superconducting properties such as critical current density and low temperature levitation forces. The connectivity of superconducting grains is increased and the number of pinning centers rose to certain values, therefore, a high magnetic field is trapped. The improved critical current density created stronger levitation forces in the repulsive and attractive regime. Provided that the Mg content increased, the morphology of samples changed and the homogeneity decreased.

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