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Review on magnesium diboride (MgB_2) as excellent superconductor: Effects of the production techniques on the superconducting properties

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ABSTRACT

Although there is a wide variety of superconducting materials, only a few of them are suitable for practical applications. Nowadays, low temperature superconductors such as NbTi and Nb_3Sn are widely used. However, after discovery of MgB_2 with its considerably high critical temperature which has a simple crystal structure and cheap raw materials used in its production, renewed interests have emerged for employing MgB_2 in commercial application as well.

This study reports on the effects of production techniques on the superconducting properties of magnesium diboride and includes an introduction to MgB_2, its crystal and electronic structure and basics of superconducting properties. The production techniques would be explained as well as the probable problems during process and the way for optimizing superconducting property of MgB_2. Furthermore, the improvement of superconducting properties by oxygen reduction, doping elements as well as introducing of defects are covered. Finally, effects of starting materials and studies done by our research team in this regard are mentioned.

1. Introduction

Magnesium diboride (MgB_2) is a simple binary boride crystallizing in the well-known AlB_2 type [1] of structure. Although the compound and its crystal structure are known since 1953 [2], the superconducting properties of magnesium diboride have been discovered quite recently by Akimitsu and his group in 2001. The most striking novelty about this discovery was the astounding high critical transition temperature (T_c) of 39 K [3] conferring the new superconductor an intermediate position between the low temperature superconductors (LTS) such as NbTi etc. and the high temperature superconductors (HTS)- e.g. YBCO - with $T_c > 77$ K, which is the boiling point of liquid nitrogen. MgB_2 is not the first boron based superconductor. Already in 1994, a new class of quaternary transition metal boron carbides with complex structures were reported attaining a T_c of 23 K [4]. Until now, there are more than 50 superconductor boride compounds defined in current literature. The critical transition temperature (T_c) values of some metal borides are given in Table 1. Due to the outstanding T_c of MgB_2, many research studies have been done to improve the properties for potential applications [3]. The T_c is almost close to the theoretical value that BCS theory predicted such that MgB_2 can be considered as a non-conventional superconductor [5].

As seen in Table 1, T_c of MgB_2 is almost twice as much as Nb_3Ge [6] which was known to have the highest T_c among all binary superconductors, so far. Figure 1 shows the structural comparison of the most important superconductors, among which MgB_2 is occupying an outstanding position with its second highest critical temperature and the very simple crystal structure.

Together with the relatively small raw material costs it is attractive for several applications, such as in MRI-coils, wind generators or superconducting permanent magnets [6]. Compared with Nb-based superconductor, MgB_2 superconductor has shorter radioactivity decay time and higher running temperature. Therefore, MgB_2 has a great application prospect in international thermonuclear experimental reactor, to avoid the disadvantages of Nb-based and ensure the smooth running of the superconducting system [7].

MgB_2 based superconducting materials allow the use

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Table 1. The critical transition temperatures (T_c) values of some binary metal borides in comparison with Nb_3Ge^* [3,5,8].

Chemical Composition	Critical Temperature (T_c)
MgB_2	**39**
TaB_2	9.5
$Nb_{0.76}B_2$	9.2
$MoB_{2.5}$	8.1
$NbB_{2.5}$	6.4
ZrB2	5.5
BeB_2	0.79
NbB_2	0.62
Nb_3Ge	**23.2**

*: Explained in text

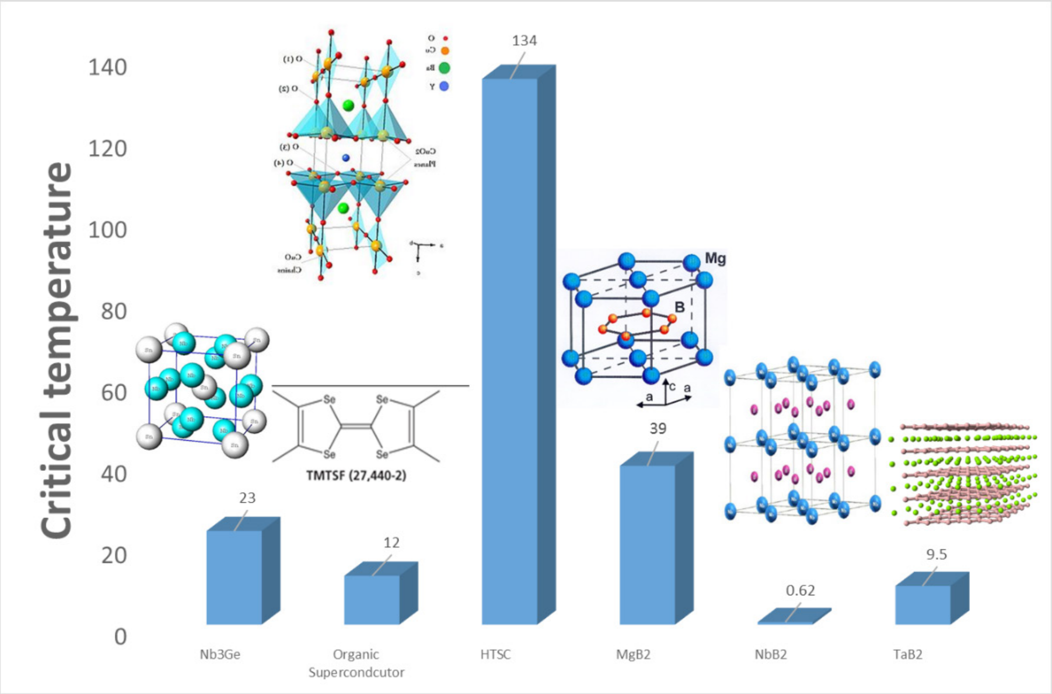

Figure 1. Comparison between the crystal structures of different classes of superconductors [8].

of helium-free cryogenic systems to cool-down the magnets below their critical temperatures. This is a big advantage against traditional low-temperatures NbTi/Nb_3Sn superconductors that need liquid helium for cooling. This is an important issue, hence since 2010 there are lively discussions on global shortage of helium and its increasing price with every year [8]. From economical and technical point of view, replacement of low temperature (LT) superconducting materials with MgB_2 has the following advantages [5,7,8]:

- Lower maintenance cost due to the price of liquefied hydrogen use instead of liquid Helium.
- Raw materials of MgB_2 are more abundant than LT systems.
- MgB_2 systems are way lighter than heavy LT materials which is a big asset in applications like wind-turbines.
- MgB_2 systems are more favorable for high-tech fusion applications. The superconducting magnets are exposed to heavy radiation during the fusion process and after their service time is finished LT superconducting materials have to be kept in special containers for thousands of years due to their very long half-time radioactive decay. For MgB_2, half-time is reported to be several years only.

2. General properties of MgB_2

MgB_2 has superior properties such as the thermodynamic and transport properties[9], the isotope effect [10], band structures [10, 11], promising critical current density [12, 13], ability of doping effect [15] and pressure effect [16]. However, after discovery of its superconducting properties in 2001, it has been a promising compound in superconductivity applications [3]. MgB_2 is competitive among high temperature superconductors (HTS) because it has fascinating advantages such as simple crystal structure, low material cost and small anisotropy [8, 10].

Structure refinement obtained from a single-crystal X-ray diffraction analysis indicated that MgB_2 crystallizes hexagonal in an AlB_2 type of structure with a = 3.0849 Å and c = 3.5187 Å [3,5]. As seen from Figures 1 and 2, the structure is characterized by hexagonal close-packed Mg atoms which are separated by graphite-like boron planes [17]. Like graphite, MgB_2 shows a strong anisotropy in the B-B bond lengths. The distances between B-B planes are considerably longer (d(B- -B) = 3.086 Å) than those in the B-B plane (d(B-B) = 1.782 Å) [8]. Overall, there are three different types of chemical bonding governing in MgB_2 ,i.e. (Mg-B), (Mg-Mg), (B-B), whereby the two band nature comes from the (B-B) bonding [11]. The final superconducting property of MgB_2 is a result of the metallic nature of 2D boron sheets with a phonon mediated BCS type mechanism [17].

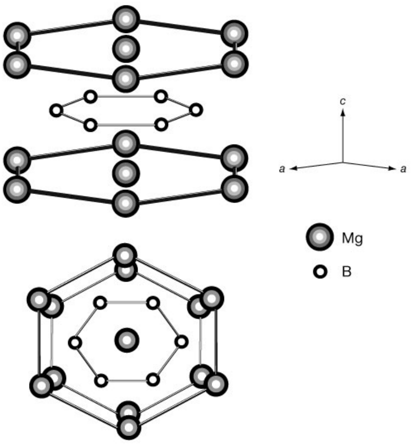

Figure 2. Crystal structure of MgB_2, adapted from Nagamatsu et. al. [3].

It has been demonstrated that T_c of MgB_2 varies about 1 K depending on which boron isotope (^{10}B or ^{11}B)[10] is used. However, the isotope effect for Mg is negligible, such that the B atom vibrations are more important for the superconducting property of MgB_2. The BCS mechanism can be confirmed by photoemission spectroscopy [18], scanning tunneling microscopy [19] and neutron scattering measurements [20].

There are two terms related to superconductive properties of MgB_2 which are of 'intrinsic' and 'extrinsic' nature [21]. Intrinsic properties are H_{c2} and flux pinning while extrinsic properties includes connectivity and porosity. By improvement any of this intrinsic and/or extrinsic features an enhancement of MgB_2 superconductor can be achieved [22]. Critical current density (J_c), critical magnetic field (H_c) (upper critical field (H_{c2}), irreversibility field (H_{irr})) and T_C are parameters which determine the basic superconducting characteristics of any superconductive material [23]. With a T_c of approximately 39 K [3], MgB_2 is a promising material for technical applications that require both a high upper critical field, H_{C2}, and ability of carrying a large supercurrent under presence of high magnetic fields. High critical current density and an upper critical field values for MgB_2 as semiconductor material have been reported to be 105 –106 A cm^{-2} and 40 T, respectively [24].

3. Production techniques of MgB_2

As a fabrication process of MgB_2, ''in situ'' and ''ex situ'' methods have been employed. In ''in situ'' technique, precursor materials are mixed with stoichiometric compositions and heat-treated under inert atmosphere to form the demanded shapes. On the other hand, in "ex situ" method, already synthesized MgB_2, MgB_2-reacted powders, used to form into desired shapes [25]. "Ex situ" is promising for obtaining homogeneous materials as well as dense cores. Since already reacted powders of MgB_2 are used in this method, the efficiency of sintering is poor and doping during process is not effective as compared with that observed in "in situ" methods. "Ex situ" production of MgB_2 usually suffers from poor grain conductivity which has a negative effect on critical current density. It has been reported that this can be overcome by decreasing MgB_2 grain size, carbon doping and presence of small amount of nano-sized MgO [23,24]. It has been reported that finer grains which were usually produced by high energy planetary ball milling resulted in extended grain boundaries. These are acting as pinning centers and lead to higher J_c [25,26], there are wide variety of specific production methods such as in situ preparation [26–28], powder in sealed tube method (PIST), hot isostatic pressing (HIP) [29], mechanical alloying [30,31], thin film[32,33], single crystal [34], and the most common one which is powder-in-tube (PIT) [35–41].

Canfield et al. has demonstrated a simple technique for the fabrication of MgB_2 wires from boron filaments and wires produced with this method had a high density and considerably low resistivity [42]. Figure 3 shows the temperature-dependent resistivity of MgB_2 wires fabricated with this technique.

It should be mentioned that most of the MgB_2 wires/tapes have been currently fabricated by powder-in-tube (PIT) technique either with or without heat treatment after deformation[43]. As demonstrated by HongLi Suo et al. [44], annealing improves the core density and increases sharpness of superconducting transition, and hence enhancement of J_c by a factor of 10 has been achieved. Y. Takano et al. [45] showed the improvement of intergranular critical current densities as well as magnetic flux pinning polycrystalline MgB_2 by using heat-treatment under high pressure [34,46]. As shown in Figure 4, sintering at 1000 °C has a sharper transition temperature onset at 39 K than that of the sample sintered at 775 °C.

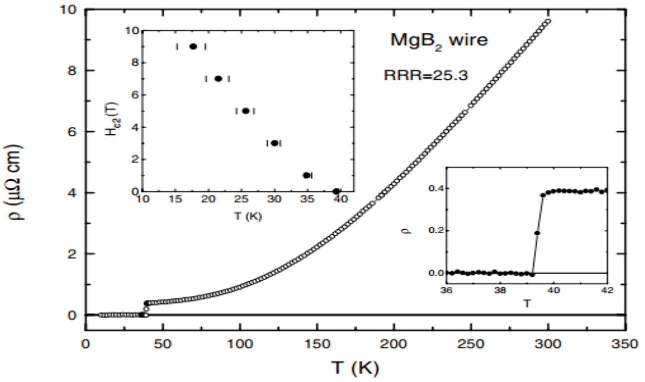

Figure 3. Temperature-dependent electrical resistivity of MgB$_2$ wire. Lower inset: expanded view for temperatures near T_c., adapted from Canfield et al. [42].

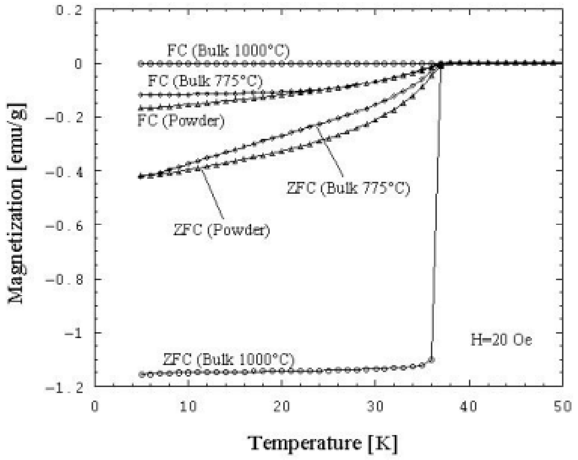

Figure 4. Temperature dependent magnetization curves for MgB$_2$ starting powder and the bulk samples sintered at 775°C and 1000°C under high pressure, adapted from Takano et al. [45].

Moreover, Giovanni Grasso et al. [35] fabricated "ex situ" PIT MgB$_2$ using Ag, Cu and Ni tubes and then cold worked the tubes by drawing and rolling. The pressure applied during cold working created additional strain in MgB$_2$ grains indicating the enhancement of intrinsic superconductivity. However, as presented in Figure 5, there is no change in texture of MgB$_2$ grains after cold working.

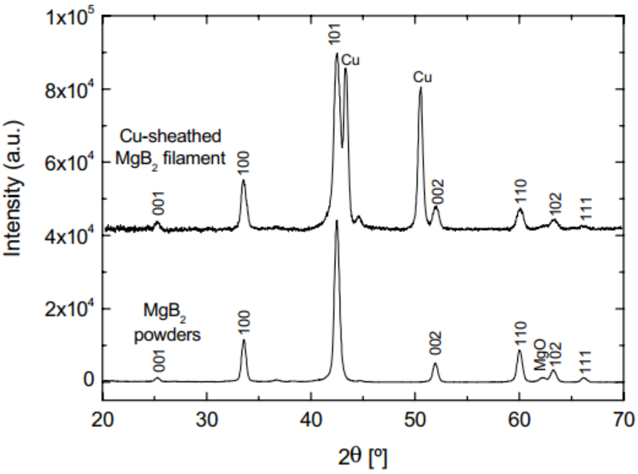

Figure 5. XRD patterns of the MgB2 powders before and after the cold working process, adapted from Grasso et al. [35].

Figure 6 shows susceptibility of MgB$_2$ before and after annealing for different tapes and cold working conditions. As can be seen, due to the induced deformation as-rolled tapes have lower critical temperature than others which is decreased about 1 degree. On the other hand, those which were annealed show higher T_c, because of the stress relieving due to thermal treatment [44].

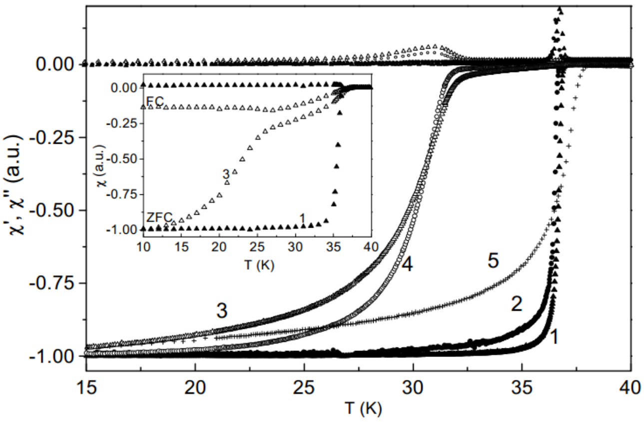

Figure 6. A.C. susceptibility and D.C. SQUID susceptibility - temperature for (1): MgB$_2$/Fe annealed; (2): MgB$_2$/Ni annealed; (3) MgB$_2$/Fe as-rolled; (4): MgB$_2$/Ni as-rolled; (5) starting powder, adapted from Suo et al. [44].

PIT includes two methods for fabrication of wires and tapes – that is – using stoichiometric composition of unreacted Mg and B powders (in situ PIT) [47], and MgB$_2$-reacted powder (ex situ PIT) [48]. However, all the fabrication methods have their own limitation, improvement techniques, and challenges which should be considered during processing. Some approaches have been developed for improving the superconducting properties such as the reduction of MgO phase, doping in MgB$_2$ and utilization of different boron sources. These considerations in MgB$_2$ production techniques are mentioned in the following subsections.

3.1. Effects of the MgO reduction on the superconductivity

MgO can limit the intergranular connection between grains by formation on surface of MgB$_2$ grains and as a result of which depression of the superconducting properties [49]. It has been demonstrated that MgO formation has two main sources [50]:

1- MgO forms when the Mg precursor powder sintered under oxygen atmosphere based on the following reaction:

$$2Mg(s) + O_2(g) \rightarrow 2MgO\ (s) \tag{1}$$

2- MgO also can form when B$_2$O$_3$ reacts with Mg based on the following reaction:

$$3Mg(s) + B_2O_3(s) \rightarrow 3MgO(s) + 2B(s) \tag{2}$$

It has been also reported that MgO formation occurs before the reaction of Mg and B such that MgO formed acts as a nucleation site~~s~~ for the growth of MgB_2 [51]. Qingzhi Shi et al. have shown that MgO forms under inert gases as well, as can be seen from the XRD patterns of Figure 7 [52].

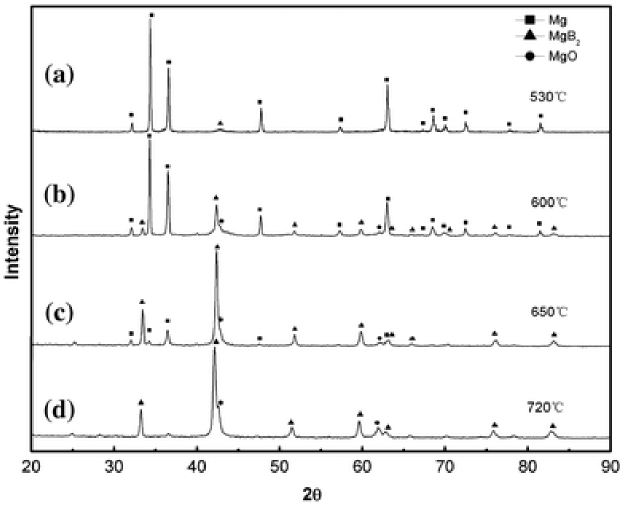

Figure 7. XRD patterns of the samples sintered at different temperatures. Each pattern is labeled with the sintering temperature, adapted from Shi et al.[52]

The presence of MgO impurity can limit intergranular connection between the grains and results the depression of superconductivity[1]. It has been shown that MgB_2 grains which are covered by MgO layer have a significant depression of critical current density (J_c) [53] due to the non-superconducting surface layer of MgO [54]. On the other hand, MgO may have some positive effect as well, as Jiang et al. found that light doping of MgO can improve the grain connectivity. As a result, the critical current density of MgB_2 should increase [55].

If MgO impurity sizes are comparable with the length of MgB_2 grains – 6-7nm –, they can be considered as a flux pinning centers. However, excess amount of MgO with large sizes can block grain boundaries and depress superconducting properties of MgB_2 [29,30]. Sigh, D.K., et al. have shown MgO amount also affects the transport and magnetic properties such that samples with larger volume fraction of MgO, 40%, have broader superconducting transition with critical temperature around 37.1K with paramagnetic Meissner effect. However, those have smaller volume fraction of MgO, 8%, exhibit sharper diamagnetic transition at around 38.8 K and also magnetization remains almost constant in temperature range of 35-20K [56]. It has been also mentioned that higher amount of MgO causes lower critical transition temperature as well as inhomogeneous of flux distribution [57]. Thus, the amount of MgO should be optimized between introducing pinning centers and the inter-grain connectivity [25].

Many efforts have been made toward reducing the amount of MgO in both ‘’in situ’’ and ‘’ex situ’’ processes. The effect of minor addition of Cu (<3 at%) on MgO reduction during ‘’in situ’’ sintering process has been investigated [1,58]. As seen from Figure 8, the amount of MgO decreases sharply from 16.5% to 12.5% as the amount of Cu addition increases from 0.0 to 0.03

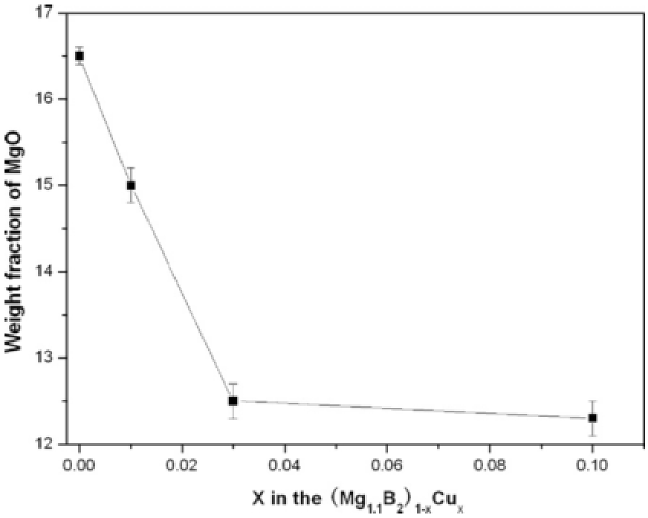

Figure 8. The weight fraction of MgO versus the amount of Cu addition in the Cu-doped samples sintered at 850°C for 30min, adapted from Ma et al. [1].

Likewise, Hiroki Fujii et al. have studied the effect of Ca-based compounds such as CaC_2 and CaH_2 in ‘’ex situ’’ process [59]. Figure 9 shows the effect of addition of Ca compounds on MgO formation, together with (102) reflection of pure MgB_2 as comparison.

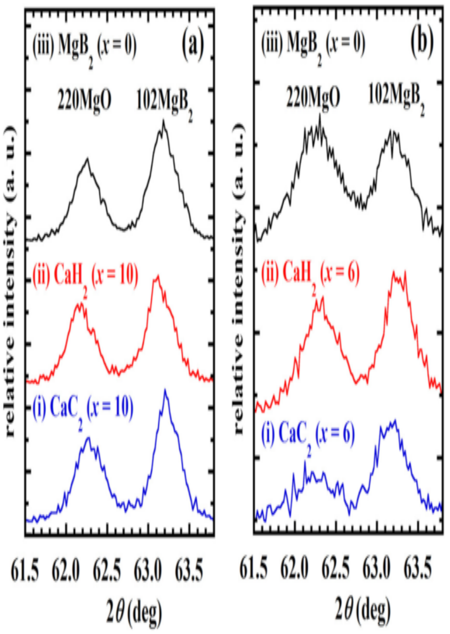

Figure 9. The profiles of XRD peak of MgB_2 and MgO for (a) sintered hand mixed powders with the additions of (i) CaC_2 and (ii) CaH_2 and (iii) without addition, adapted from Fujii et al. [59].

As afore mentioned, one of the main difficulties in MgB_2 production is the existence of MgO phases which depresses the superconducting properties. With this in mind, research studies by Inorganic Research Group in Koç University were focused on oxygen reduction of MgB_2 by different methods. Among them, the purification of boron by addition of elemental copper, treatment with reducing gas mixtures and reduction in copper tube are worth mentioning. It is important to note that the employment of all three purification techniques turned out to be successful and led to a significant reduction of oxygen impurities in MgB_2*.

3.2. Effects of doping elements on the superconductivity

It has been reported that defects in MgB_2 structure decrease the mean free path of the normal electrons then decreasing the coherence length ξ and accordingly increasing the H_{c2} values which is a limiting factor in MgB_2. Moreover, defects would introduce pinning centres in order to make the irreversibility line steeper [60]. On the other hand, it has been shown that doping in MgB_2 would decrease T_c. For instance, superconductivity of Al doped sample would disappear when around half of Mg are replaced by Al. It was mentioned that two different effects led to a T_c reduction as Al substitution increased:

1- A positive pressure effect—due to the smaller Al ionic

2- The increased number of electrons contributed by Al [61]

On the other hand, replacing Mg^{2+} by Al^{3+} will increase the population of the electrons in the two- dimensional (2D) σ-band. Therefore, substitution of Mg by Al would fill the σ-band completely even before a 100% substitution level. In this situation, only the π-band would take part in various physical processes so the system will no longer be a two- band (σ-band and π-band) system [62]. Amount of doping is related to changing in T_c value. It has been reported that light doping of C as well as Al (up to 2.5%) would keep T_c unchanged while increasing J_c by the factor of 2 [63].

In carbon doping, the carbon which stays at the grain boundary or at interstitial site can act as a pinning center (extrinsic pinning) and hence helps in enhancing the H_{c2}, H_{irr}, and J_c values. Additionally, the carbon into the structure creates disorder in the sigma band and causes intrinsic pinning to enhance the critical parameters. Therefore, doping carbon causes extrinsic/intrinsic pinning through additions/substitution- and enhances the superconductivity performance of MgB_2 in both ways [64] H_{c2} are obtained from this data based upon the criterion of 90% of normal resistivity i.e. H_{c2}=H at which Rho=90%Rho; where RhoN is the normal resistivity i.e., resistivity at about 40 K in our case. The Werthamer-Helfand-Hohenberg (WHH. So far, the application of MgB_2 are restricted since it has deficient mechanical properties as well as degraded J_c under high magnetic field [65]. Moreover, many experiments have been conducted on the substituting of Mg by different elements namely Al [66], Li [67] and most of the substitutions cause decrease in critical temperature. However, some of the element such as Zn do not show any improvement even the addition of 30% [68].

Although the various compound morphologies play a decisive role to control its properties, the synthesis method and doping process define additional, crucial parameters that markedly impact the nature and concentration of intrinsic or extrinsic defects and the materials' electronic properties [69]. As mentioned before, considerable number of efforts have been done to enhance both critical current field and current-carried capacity of magnesium diboride, carbon doping has the most significant effect among them [70]. Researches have demonstrated that H_{C2} (0)>50T for carbon doped MgB_2 films which makes MgB_2 a promising alternative for Nb_3Sn as a high-field magnet conductor [71]. Moreover, silicon carbide, SiC, by means of increasing of intergranular connection and pinning centers, is one the most sufficient dopant which has been used for improvement of J_C and H_{C2} [49][72]. Figure 10 shows the dependency of current density to different dopants. The Jc value of the all doped tapes have been improved with respect to the un-doped tape. This improvement is due to the effective pinning centers which have introduced by dopants [72].

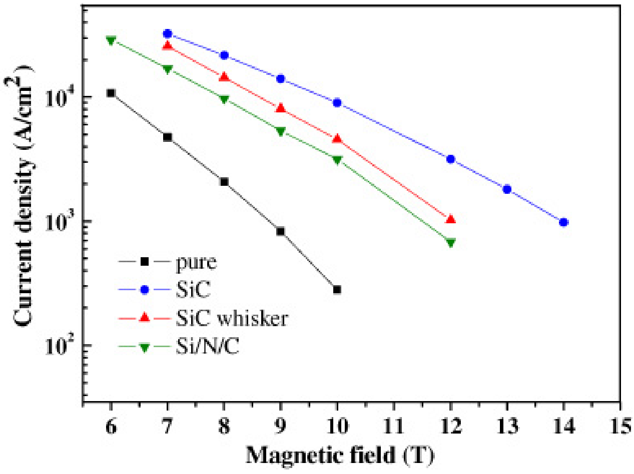

Figure 10. J_C–B properties of Fe-sheathed undoped and nano-SiC, SiC whisker and Si/N/C doped tapes heated at 650 °C for 1h. The measurements were performed in magnetic fields parallel to the tape surfaces at 4.2 K., adapted from Zhang et al. [73].

3.3. Effects of the starting materials on the superconductivity

The finding that the quality of the starting powder (purity, oxygen content and grain size distribution) influences strongly the final properties of the samples, runs like a threat through many papers [74]. The influence of the initial grain size of the powder was investigated

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*: Unpublished results done by Inorganic Research Group in Koç University

to understand the sintering mechanisms leading to higher intergranular connectivity in polycrystalline ex-situ MgB_2 as precondition for improved superconducting properties [75].

It is known that the quality of the starting materials, especially that of the boron powder, has great influence on the superconducting properties of MgB_2 wires and bulk materials. Inorganic Research Group in Koç University has been working on the development of amorphous boron and MgB_2 superconductor powders since 2010 with international/national collaborations. During these studies, MgB_2 samples were synthesized by using various elemental boron powders with different purity grades and particle sizes. Especially the collaboration with the national industrial partner Pavezyum Chemicals (Turkey) was quite fruitful resulting in a significant improvement of superconducting properties of MgB_2 powders by using amorphous elemental nano boron powders as starting material.

Elemental amorphous boron powders have been available and produced by Pavezyum in industrial scale in Turkey since 2010. The product development R&D phase was achieved with the support of National Boron Research Institute (Project No: 2010 – S244). Today, Pavezyum is globally the only producer of industrial scale fully amorphous elemental nano boron powder and this commercial product was developed with the support of BOREN granted projects (2008 – Ç388 and 2014 – Ç422). So called “PVZ Nano-Boron” is mainly used by MgB_2 based superconducting material producers and exported by Pavezyum to Columbus Superconductors SpA which is a world leader in cutting-edge MgB_2 technology. Among other elemental boron powders, MgB_2 made of nano size amorphous boron (d_{99} <350 nm - DLS) show excellent magnetic characteristics like 10-fold higher than the nearest pure elemental boron powder (95-97 % pure) does [40]. The difference is based on the following two reasons [30,38,71]:

- Amorphous nano boron powder has small particle size, spherical and has larger specific surface area (>40 m^2/g - BET) that leads to higher reactivity.
- Higher reactivity leads to lower reaction temperatures (around 700°C) for MgB_2 production that will result less crystallinity formation in the end product and enhances superconductivity.

4. Conclusions

The advantage of MgB_2 over LTS is a higher thermal stability due to a higher difference between operational and critical temperature. With a transition temperature of 39 K, MgB_2 occupies an intermediate position between the LTS and HTS. Intense efforts are undertaken for further enhancing of J_c. MgB_2 powders and bulk materials were fabricated using many different production techniques. The most crucial issue in the synthesis of high quality magnesium diboride powders are, however, amorphousness, purity and the particle size of the precursor boron material. From this point of view, nano-sized boron powder meets these requirements best, yielding high-performance MgB_2 with superior features. The superconducting properties of MgB_2 can be further optimized by doping, utilization of different boron sources and reduction of the main impurity phase MgO.

Among them, the reduction of MgO contributes to better grain connection, increase of critical temperature and hence to a general improvement of superconducting property of MgB_2. In addition, doping elements such as carbon by creation of defects have positive influence on superconducting performance of MgB_2, a method which is widely used.

From the applicative point of view, it seems possible to anticipate that the arrival of MgB_2 bulk superconductors will move superconductivity towards the design and realization of practical and cheap cryogenic systems at intermediate temperatures. For this target, the production techniques, performance and the low-price of MgB_2 will be the key issue.

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