

University of Wollongong

Research Online

---

Australian Institute for Innovative Materials -  
Papers

Australian Institute for Innovative Materials

---

1-1-2014

**Interplay between boron precursors and Ni-Co-B nanoparticle doping in the fabrication of MgB<sub>2</sub> superconductor with improved electromagnetic properties**

Mislav Mustapic

*University of Wollongong, mislav@uow.edu.au*

Josip Horvat

*University of Wollongong, jhorvat@uow.edu.au*

Zeljko Skoko

*University of Zagreb*

Md Shahriar Hossain

*University of Wollongong, shahriar@uow.edu.au*

S X. Dou

*University of Wollongong, shi@uow.edu.au*

Follow this and additional works at: <https://ro.uow.edu.au/aiimpapers>



Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

---

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: [research-pubs@uow.edu.au](mailto:research-pubs@uow.edu.au)

---

# Interplay between boron precursors and Ni-Co-B nanoparticle doping in the fabrication of MgB<sub>2</sub> superconductor with improved electromagnetic properties

## Abstract

The influence of different boron precursor powders on the critical current density of MgB<sub>2</sub> superconductor with added Ni-Co-B nanoparticles is investigated. Different types of boron have different morphologies, particle sizes and impurity content, all of which have a strong impact on the critical current density ( $J_c$ ). The boron samples investigated in this study include three different boron powders: semicrystalline boron (denoted as SC), with nanosized particles and high purity (99%) supplied from Specialty Materials, Inc. (USA); amorphous boron (denoted as AB), with nanosized particles and high purity (99%) supplied from Russia; and finally pure crystalline boron (denoted as CB), with micron-sized particles and 96% purity supplied from Tangshan WeiHao (China). The MgB<sub>2</sub> samples made from AB showed the best improvement of critical current with 2.5 wt.% Ni-Co-B doping;  $J_c$  was above 100,000 A cm<sup>2</sup> at 4 T and 5 K. Under the same conditions,  $J_c$  for MgB<sub>2</sub> made from SC was slightly worse than for the MgB<sub>2</sub> made from AB, 100,000 A cm<sup>2</sup>. On the other hand, MgB<sub>2</sub> made from CB presented sharply reduced  $J_c$  with Ni-Co-B doping at both measured temperatures, 5 K and 20 K.

## Keywords

improved, superconductor, mgb<sub>2</sub>, fabrication, nanoparticle, b, co, ni, precursors, boron, between, properties, doping, electromagnetic, interplay

## Disciplines

Engineering | Physical Sciences and Mathematics

## Publication Details

Mustapic, M., Horvat, J., Skoko, Z., Hossain, M. Al. & Dou, S. Xue. (2014). Interplay between boron precursors and Ni-Co-B nanoparticle doping in the fabrication of MgB<sub>2</sub> superconductor with improved electromagnetic properties. *Acta Materialia*, 80 457-467.

# Interplay between boron precursors and Ni-Co-B nanoparticle doping in the fabrication of MgB<sub>2</sub> superconductor with improved electromagnetic properties

Mislav Mustapić<sup>a</sup>, Josip Horvat<sup>a</sup>, Željko Skoko<sup>b</sup>, Md Shahriar Al Hossain<sup>a</sup> and Shi Xue Dou<sup>a</sup>

<sup>a</sup>Institute for Superconducting and Electronic Materials, AIIM, University of Wollongong, Squires Way, North Wollongong, NSW 2500, Australia

<sup>b</sup>Department of Physics, Faculty of Science, University of Zagreb, Bijenička c. 32, 10000 Zagreb, Croatia

Email: [mislav.mustapic@gmail.com](mailto:mislav.mustapic@gmail.com)

Key words: Magnesium diboride, Amorphous, Boron, Nanocrystalline nanostructure, X-ray diffraction (XRD), Differential thermal analysis.

## Abstract

The influence of different boron precursor powders on the critical current density of MgB<sub>2</sub> superconductor with added Ni-Co-B nanoparticles is investigated. Different types of boron have different morphology, particle sizes, and impurity content, all of which have a strong impact on the critical current density ( $J_c$ ). The boron samples investigated in this study include three different boron powders: semicrystalline boron (denoted as SC), with nanosized particles and high purity (99%) supplied from Specialty Materials, Inc. (USA), amorphous boron (denoted as AB), with nanosized particles and high purity (99%) supplied from Russia, and finally pure crystalline boron (denoted as CB), with micron sized particles and 96% purity supplied from Tangshan WeiHao (China).

The MgB<sub>2</sub> samples made from amorphous boron (AB) showed the best improvement of critical current with 2.5wt% Ni-Co-B doping;  $J_c$  was above 100,000 A cm<sup>-2</sup> at 4 T and 5 K. Under the same conditions,  $J_c$  for MgB<sub>2</sub> made from SC boron was slightly worse than for the MgB<sub>2</sub> made from AB boron, around 100,000 A cm<sup>-2</sup>. On the other hand, MgB<sub>2</sub> made from CB presented sharply reduced  $J_c$  with Ni-Co-B doping at both measured temperatures, 5 K and 20 K.

## 1. Introduction

Multiple applications, mostly for the military, high technology, and the aerospace industry, have made boron the focus of international interest. Only a few countries in the world have

large deposits of boron ore (borax) to meet the increased demand, including the countries mentioned in the abstract. High quality boron has become one of the most important requirements for achieving the best performing materials, especially for MgB<sub>2</sub> superconductor. Investigation of the features of different boron powders with a focus on the mechanism of reaction between boron and the other components, is one of the main aims of this article.

Characteristics of MgB<sub>2</sub> precursor boron powders, such as morphology, particle size, and purity, significantly affect the final performance of MgB<sub>2</sub> superconductors, as is clearly shown in this study. The boron production method and its crystallinity strongly influence the final MgB<sub>2</sub> properties.

Amorphous boron is usually obtained by the Moissan process [1], where boron oxide is mixed in a crucible with magnesium turnings ( $2\text{B}_2\text{O}_3 + 3\text{Mg} \rightarrow \text{Mg}_3(\text{BO}_3)_2 + 2\text{B}$ ). Pure amorphous boron can also be produced by thermal decomposition of diborane [2], chemical vapour deposition [3]. Amorphous boron contains B<sub>12</sub> regular icosahedra that are randomly bonded to each other without-long range order [4]. The boron obtained by the Moissan process contains a considerable amount of Mg impurity, which can be removed by different methods, such as acid etching, crystallization, etc.

On the other hand, crystalline boron is usually obtained by reduction of boron halides, such as BCl<sub>3</sub>, with H<sub>2</sub> gas. For this method, a high temperature is necessary for the production of boron, which is usually obtained by the use of an electric arc. A certain amount of amorphous boron can also be produced by this method, depending on the starting preparation conditions. The products of reaction are deposited directly on the tube, in larger crystalline plates, and as a dark-brown powder (amorphous). Amorphous boron obtained by this method has higher purity than boron obtained with the Moissan process. This reaction is reversible and can be written as  $2\text{BCl}_3 + 3\text{H}_2 \rightleftharpoons 2\text{B} + 6\text{HCl}$  [5].

The crystallization of amorphous boron powders can be conducted by pyrolytic or electrolytic processes at high temperature under inert atmosphere. The pyrolytic boron crystallizes as  $\alpha$ -B<sub>12</sub>, while electrolytic boron crystallizes as the thermodynamically most stable  $\beta$ -rhombohedral allotrope [6,7].

The investigation of MgB<sub>2</sub> samples with various boron precursors has been widely discussed in the literature by other groups [8-12]. The properties of the MgB<sub>2</sub> powders are strongly correlated with the quality of the boron precursor powders in terms of morphology, particle size, and purity. This report focuses on elucidation of the reaction mechanisms between

different boron powders, magnesium, and Ni-Co-B nanoparticles, coupled with analysis of the steps in the formation of new phases for different boron powders.

Good dispersion of nanoparticles (new phases) in the matrix of MgB<sub>2</sub> superconductor and the creation of pinning centres have a crucial role in improvement of the critical current density ( $J_c$ ). In previous research, Ni-Co-B nanoparticles were shown to substantially improve the critical current density of MgB<sub>2</sub> made from amorphous boron [13].

Furthermore, the influence of boron grain size on  $J_c$  properties was investigated, especially in a case of AB and SC boron powders with similar grain size (nano-size). Finally, a range of characterization techniques was used: transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), differential thermal analysis (DTA), and a physical properties measurement system (PPMS), together with a new software package, XBroad [14], which enables the grain sizes of different MgB<sub>2</sub> samples to be obtained based on the XRD patterns.

## 2. Experimental procedure

All measured MgB<sub>2</sub> samples were prepared in pellet form. The powders were mixed dry, first the Ni-Co-B nanoparticles and boron, and then the magnesium was added. The mixture was ground and pressed with a 10 tonne press into 10 mm diameter pellets. The resulting pellets were cut into small bar-shaped pieces with dimensions of  $1 \times 2 \times 3 \text{ mm}^3$ . All samples were enclosed in iron tubes and sintered at 850°C for 30 min under high-purity argon gas with a heating rate of  $5^\circ\text{C min}^{-1}$ .

All the prepared pellets were examined by X-ray powder diffraction. The XRD patterns were collected at room temperature using an automatic Philips powder diffractometer, model PW1820 (Cu K $\alpha$  radiation) in Bragg-Brentano geometry. The diffraction intensity for the MgB<sub>2</sub> samples was measured in the angular range of  $20^\circ \leq 2\theta \leq 70^\circ$ .

Rietveld refinement was performed using the program X'Pert HighScore Plus, version 2.1 (PANalytical 2004), using a pseudo-Voigt profile function and polynomial background model. Profile function parameters (full-width-half-maximum (FWHM), asymmetry, peak shape) and structural parameters for each phase were refined. Thermal displacement parameters were assumed and refined as isotropic. The preferred-orientation correction did not significantly improve the fit. The XBroad program [14] was used for crystalline size calculations.

Magnetization hysteresis loops were collected on a commercial Quantum Design Physical Properties Measurement System (PPMS), with the magnetic field applied parallel to the longest dimension of the sample. The magnetic critical current density  $J_c$  was estimated based on the critical state model using the formula  $J_c = 20\Delta M/(a-a^2/(3b))$  [15], where  $\Delta M$  is the height of the M(T) hysteresis loop, and  $a$  and  $b$  are the sample dimensions perpendicular to the applied field, with  $a < b$ . The magnetization was measured at 5 K and 20 K in a time-varying magnetic field with  $50 \text{ Oe}\cdot\text{s}^{-1}$  sweep rate and 9 T amplitude. Due to the large sample size effect on the magnetic  $J_c$  for  $\text{MgB}_2$ , all the samples for measurement were made to the same dimensions ( $1 \times 2 \times 3 \text{ mm}^3$ ) for comparison [16].

The microstructure of the  $\text{MgB}_2$  samples, and the grain size and morphology were studied with a JEOL JSM-6400 scanning electron microscope. Boron powders were examined using a JEOL 2011 TEM operating at 200 kV.

Differential thermal analysis (DTA) was performed on mixed powders of Mg, B, and Ni-Co-B nanoparticles, which were pressed and placed in an  $\text{Al}_2\text{O}_3$  pan. Samples were measured as the temperature was increased up to  $1000^\circ\text{C}$  at a rate of 5 K/min in an inert atmosphere of argon gas.

### 3. Characterization of boron precursor powders

A comparison of the XRD patterns of crystalline boron (denoted as CB) and amorphous boron (denoted as AB) is shown in Figure 1. The Figure implies a significant difference in the morphology of the two samples. The diffraction pattern of the CB sample shows two characteristic wide amorphous halos, approximately at  $2\theta \approx 21^\circ$  and  $35^\circ$ , and two sharp maxima belonging to  $\text{B}_2\text{O}_3$  at  $2\theta = 15^\circ$  and  $27^\circ$  (PDF-2/release card no. 2010 00-006-0297). The pattern of the CB sample shows distinct  $\beta$ -rhombohedral boron peaks at  $2\theta \approx 11.9^\circ$ ,  $16.5^\circ$ ,  $17^\circ$ ,  $18.2^\circ$ , and  $40.5^\circ$ , as well as  $\text{B}_2\text{O}_3$  peaks at  $2\theta = 15^\circ$  and  $27^\circ$ .

The intensity of the  $\text{B}_2\text{O}_3$  maxima for the AB sample is substantially smaller than for the CB sample, indicating that the CB sample has a substantial share of  $\text{B}_2\text{O}_3$  phase. The crystalline boron contained in the CB sample has the  $\beta$ -rhombohedral ( $\beta$ -rhB) structure. The  $\beta$ -rhB phase is stable even at high reaction temperature for  $\text{MgB}_2$ , so it is not easy to achieve full reaction before the Mg melts [17,18].

The XRD pattern of the sample consisting of semicrystalline nanosize boron powder (denoted as SC) is presented in Figure 2(A) [19]. The Figure shows the XRD patterns of two samples

of plasma synthesized boron (A, B) nanopowder, which are compared with the XRD pattern of fully crystalline  $\beta$ -rhombohedral boron (Fig. 2(C), with *hkl* Miller indices indicated) [19]. The nanopowder is a mixture of crystalline and amorphous phases. Diffraction lines are progressively broadened from C to A, consistent with powder A (SC, made at the lowest power and used in this experiment) having the smallest crystallite sizes and the lowest fraction of crystalline material [19].

The microstructure of the three boron powders was studied using transmission electron microscopy (TEM) [Fig. 3(a-c)]. Figure 3(a) shows that the crystalline boron (CB) is composed of micron-sized, angular particles. The indexing of the selected area diffraction pattern (SADP) in the inset is consistent with a  $\beta$ -rhB structure [12].

Figure 3(b) shows the amorphous boron powder (AB), which consists of spherical particles with diameters ranging between 100 and 300 nm. The selected area diffraction pattern consists of continuous diffuse rings due to short-range ordering, reflecting its amorphous nature. No distinct diffraction spots from crystalline regions were found.

The microstructure of the semicrystalline boron (SC) [Fig. 3(c)] [19] prepared by using lower plasma power resulted in a very small particles with diameters smaller than 70 nm. The SADP [inset Fig. 3(c)] shows distinct diffraction spots superimposed on diffuse rings, which indicates that the material is semicrystalline.

## **4. Characterization of MgB<sub>2</sub> made from different boron powders doped with Ni-Co-B nanoparticles.**

### 4.1 Electromagnetic properties

The critical current density was measured for pure MgB<sub>2</sub> and Ni-Co-B doped samples (1.25, 2.5, 5 wt%), made from the three different boron precursors. The  $J_c$  showed significant differences between the analyzed boron powders. MgB<sub>2</sub> made from amorphous AB (Fig. 5) and semicrystalline SC (Fig. 4) boron showed improvement of  $J_c$  with Ni-Co-B doping (1.25, 2.5, 5 wt%), while on the other hand, MgB<sub>2</sub> made from crystalline boron CB exhibited deterioration of  $J_c$  with any Ni-Co-B doping (1.25 and 2.5 wt%), as shown in Fig. 6.

The best improvement of  $J_c(H)$  is obtained at 5 K for AB and SC boron, where the  $J_c(H)$  is shifted to higher values as the concentration of Ni-Co-B increases to 2.5 wt%. For the highest doping level, enhancement of  $J_c$  was less than for the optimum doping value of 2.5 wt%, but the sample still shows an improvement in comparison to pure MgB<sub>2</sub>.

Substantially lower  $J_c$  values were obtained both for pure and doped  $\text{MgB}_2$  samples made from CB (Fig. 6). The doping for these samples led to no enhancement of  $J_c$  at 5 and 20 K. A possible explanation for this could be the low reactivity of crystalline boron and the slow formation of  $\text{MgB}_2$  phase caused by the large particle size with reduced reaction surface, while the phase of the crystalline boron is also the most thermodynamically stable allotrope,  $\beta$ -rhombohedral [17,18]. Furthermore, the large amount of  $\text{B}_2\text{O}_3$  impurities in crystalline boron (XRD results, Fig. 1), in combination with the doped Ni-Co-B nanoparticles (impurities), ultimately had a negative impact due to the enlarged percentage of non-superconductive phases in the specimen and the creation of barriers to supercurrent flow.

Detailed analysis of the results shows that doping with Ni-Co-B nanoparticles did not improve  $J_c$  at 20 K for any of the doped samples made with AB and CB boron precursor powders, but there was a slight improvement for  $\text{MgB}_2$  doped samples made from SC boron powder.  $\text{MgB}_2$  is a two-gap superconductor, with superconductivity occurring in 2-dimensional  $\sigma$ -bands and 3-dimensional  $\pi$ -bands, each of them having a different superconducting gap. Both gaps close at  $\sim 39$  K. An explanation for the improvement of  $J_c$  at 5 K, but not at 20 K could be in the way that each of these gaps is affected by the pinning centers. This could be associated with the reported charge transfer from  $\sigma$ -bands to  $\pi$ -bands below 15 K [20]. The use of different boron precursors, with different reactivity affects the way that the pinning centers are created in  $\text{MgB}_2$  samples, as well as their location.

Furthermore it is important to emphasize that the creation of new phases ( $\text{Mg}_2\text{Ni}$  and  $\text{Mg}_2\text{Co}/\text{Co}_2\text{Mg}$ ) reduces the percentage of MgO impurities in  $\text{MgB}_2$ , improving the grain connectivity, as explained in more detail previously [13].

Figure 7(a, b) presents the  $J_c$  values for pure and Ni-Co-B doped  $\text{MgB}_2$  samples synthesized from different boron powders at 5 T and 5 K, and at 2 T and 20 K. The values of the field at each temperature were chosen to avoid the artefacts associated with obtaining the  $J_c$  from magnetic measurements [16]. For  $\text{MgB}_2$  samples prepared from AB and SC boron precursor powders,  $J_c$  at both 5 and 20 K was improved by Ni-Co-B doping, while doping of  $\text{MgB}_2$  made from crystalline boron led to substantially decreased  $J_c$  values for both observed conditions (5 K, 5 T, and 20 K, 2 T). The highest  $J_c$  values were obtained for 2.5 wt% doped  $\text{MgB}_2$  samples made from AB and SC boron powders.



Figure 8 shows a comparison of  $J_c$  for the pure  $\text{MgB}_2$  samples made from the three different boron powders. At 5 K, the pure  $\text{MgB}_2$  samples made from crystalline boron (CB) give slightly better performance in the low field range than the pure samples prepared with AB and SC boron powders. The field dependence of  $J_c$  at higher fields is considerably better, however, for samples prepared from AB and SC boron powders. For high fields, the pure  $\text{MgB}_2$  samples prepared with AB powder show the highest improvement. The situation is similar at 20 K, where  $\text{MgB}_2$  samples made from crystalline boron present the best values in the low field range (1-2 T), while at higher fields, the pure  $\text{MgB}_2$  samples made from AB and SC boron powders provide substantially better results.

The reason for such a strong field dependence of  $J_c$  could be the grain size of pure  $\text{MgB}_2$ . As we can see from the SEM images [Fig. 16(a, b)], the grain size of pure  $\text{MgB}_2$  is related to the grain size of the starting boron precursor powders. Boron, as a high melting point material, does not melt at the sintering temperature (850°C) used in this work and, as a solid component in the reaction with magnesium, has more influence on the grain size of the resultant  $\text{MgB}_2$ . Especially for amorphous boron, the grain size of the starting boron powder [Fig. 3(b)] is very similar to the grain size of the  $\text{MgB}_2$  that is formed from it, with a uniform size distribution [Fig. 16(a)]. The pure  $\text{MgB}_2$  sample made from crystalline boron powder [micron size, Fig. 3(a)] shows a larger grain size with a broad size distribution and higher porosity [Fig. 16(b)] than  $\text{MgB}_2$  made from the other boron powders. The surface of  $\text{MgB}_2$  crystallites is associated with a large defect density, resulting in fewer pinning centres in large crystallites. This is the reason why the  $J_c$  values of  $\text{MgB}_2$  samples made from CB decrease faster than for  $\text{MgB}_2$  made from the boron powders with smaller grain size, AB and SC. In low magnetic field, pinning has a much smaller effect on  $J_c$  than in high field.

#### 4.2 Structural characterization

XRD patterns of  $\text{MgB}_2$  samples made from amorphous boron (AB) and semicrystalline (SC) boron precursors show almost identical results (Figs. 9, 10). The intensity of the MgO maximum at  $2\theta = 62.5^\circ$  (220) slightly increases with the amount of Ni-Co-B doping for  $\text{MgB}_2$  made from SC. Also, a very weak maximum of MgO is detectable at  $2\theta \approx 37^\circ$  (101) for the same sample. It is important to emphasize that only for the doped samples made from AB, does the amount of MgO phase slightly decrease compared to the pure sample.

The XRD patterns (Fig. 11) of pure  $\text{MgB}_2$  and 2.5wt% Ni-Co-B doped samples prepared from crystalline boron (CB) show considerable differences in comparison to  $\text{MgB}_2$  made from AB and SC (Figs. 9, 10). The amount of MgO phase significantly increases with doping, while for the pure sample, it has a similar value to what is obtained for  $\text{MgB}_2$  made from amorphous and semicrystalline boron powders. According to the XRD patterns of crystalline boron, Ni-Co-B doping considerably increases the amount of impurities in the  $\text{MgB}_2$  matrix, (Ni and Co compounds + MgO), which has a negative effect on  $J_c$  values.

According to Chen et al. [8], the formation of MgO phase starts with  $(\text{Mg})\text{B}_x\text{O}_y$  impurity phases. From the XRD patterns of the boron powders (Figs. 1, 2), it can be seen that CB contains more  $\text{B}_2\text{O}_3$  than the SC and AB powders. Besides the high presence of  $\text{B}_2\text{O}_3$  impurities in the crystalline boron precursor, the size of the boron particles and their morphology can have a strong influence on the formation of MgO.

The particles of CB are of micrometer size, while in the more amorphous boron powders AB and SC, the particles are much smaller, below 300 nm and below 70 nm, respectively. Small size of the boron particles means a larger surface area and better contact between the reacting powders which finally provides a complete reaction among them.

Furthermore, the amorphous morphology is more isotropic and equally reactive from all sides, as compared to the crystalline boron. The reactivity of the amorphous boron powders is much higher than that of the crystalline powders. Hence, when the crystalline B powders come into contact with Mg powder, the reaction to form  $\text{MgB}_2$  is relatively slow, and there is sufficient time for  $(\text{Mg})\text{B}_x\text{O}_y$  phases to form [8]. At the same time, the large amount of  $\text{B}_2\text{O}_3$  provides more oxygen for this reaction. Unreacted Mg was not detected in any of analysed samples due to relatively high sintering temperature, 850°C.

Figure 12(a) shows a shift in the position of the  $\text{MgB}_2$  maximum [002] for 2.5wt% doped samples made from AB and SC powders. The position of the [002] maximum is shifted towards smaller Bragg angles for these samples, which points to an increase in the unit cell parameter  $c$ . In the case of the 2.5wt% doped sample made from CB, a slight decrease in parameter  $c$  is detected [Fig. 12(a)]. The differences in lattice parameters can be explained as due to incorporation of a certain amount of Co and/or Ni atoms into the  $\text{MgB}_2$  crystal lattice, where the Co and/or Ni atoms substitute for Mg atoms. Nickel ( $r_{\text{Ni}} = 149$  pm) and cobalt ( $r_{\text{Co}} = 152$  pm) atoms in the lattice with larger radius size than Mg ( $r_{\text{Mg}} = 145$  pm) may be the reason for the change in the lattice parameters. As can be seen in Table 1, the larger lattice parameter  $c$  for the AB samples is also confirmed by the Rietveld refinement. Furthermore,

one can suppose that this effect will lead to increased density, since the atomic mass of the Ni/Co atom is almost twice as great as that of the Mg atom and this overcompensates for the larger unit-cell volume caused by the larger lattice parameter  $c$ .

The amounts of each phase, as obtained by Rietveld refinement, for the pure and Ni-Co-B doped  $\text{MgB}_2$  samples, are given in Table 2. A conclusive difference is observed in the amount of MgO between the  $\text{MgB}_2$  sample made from AB and the  $\text{MgB}_2$  made from CB. A high amount of MgO is very harmful for  $\text{MgB}_2$  superconducting properties due to the creation of insulating layers between superconducting grains and the reduction of the cross-sectional area for superconducting current flow [21].

$\text{MgB}_2$  made from amorphous and semicrystalline boron exhibits a low amount of MgO, with a slightly higher amount present in  $\text{MgB}_2$  made from SC. The explanation is likely to be the higher reactivity of these boron powders and some amount of crystalline phase in SC boron. No other impurities have been detected in the doped samples except for MgO. Unreacted Mg can be detected mostly in samples made at a low sintering temperature ( $650^\circ\text{C}$ ) and in samples with a high content of dopants in the form of nanoparticles [22,23].

Table 3 presents the crystallite sizes, calculated with the help of the XBroad program [14], in different [hkl] directions for the pure samples prepared from different boron powders.

This program performs Stokes deconvolution in order to separate pure diffraction and instrumental broadening, followed by Warren-Averbach and/or Williamson-Hall analysis. One of the main advantages of XBroad is its ability to determine the crystallite size in different crystalline directions, which provides more accurate information about the crystallite shape [14].

Table 3 shows that  $\text{MgB}_2$  prepared from CB has a much larger average crystallite size along the [002] direction and along the [100] direction, with crystallite size from 285 nm to 350 nm, respectively.  $\text{MgB}_2$  samples prepared from the amorphous and partially amorphous boron powders, SC and AB, are very similar in crystallite size, with the size  $\approx 230$  nm (along the [100] direction) and  $\approx 200$  nm (along the [002] direction). According to Table 2, the pure  $\text{MgB}_2$  sample made from crystalline boron has, on average, an approximately 100 nm bigger grain size than the AB and SC pure samples for the observed directions. Comparing the results of XRD analysis (Tables 2, 3) and SEM [Fig. 16(a, b)], a difference can be detected in the  $\text{MgB}_2$  grain size between the two applied techniques. XRD analysis takes all the grains

into account and gives an average value for all calculated grains, while SEM allows direct observation of grain size from images. The deviation from average grain size can be significant, especially for  $\text{MgB}_2$  made from crystalline boron with its broad grain size distribution.

#### 4.3 DTA analysis

Detailed differential thermal analysis (DTA) results on reactions between Ni-Co-B nanoparticles, magnesium, and amorphous boron (AB) have been explained in previous works [13, 24]. Briefly, two reaction steps have occurred between the nanoparticles, and the Mg and B precursors. The first is a solid state reaction (Fig. 13) between boron and magnesium (due to the formation of a eutectic system at  $\sim 570^\circ\text{C}$ ) [13,24], and the second and most important for  $J_c$  results is the reaction between Ni-Co-B nanoparticles and magnesium, accompanied by the formation of new phases (Mg compounds of Ni and Co) and their incorporation into the  $\text{MgB}_2$  matrix. This substantial exothermic reaction has a broad peak starting at  $730^\circ\text{C}$ , marked with a diamond at Figure 14.

The DTA results for  $\text{MgB}_2$  made from crystalline boron (doped and pure), however, show significantly smaller reaction intensity, which indicates slow and inhibited reactions between the components in comparison to the reaction with amorphous boron as a precursor (Fig. 14). An endothermic peak occurs in reactions of crystalline boron with magnesium and the dopant nanoparticles, due to the melting of magnesium at  $650^\circ\text{C}$ , which is present in all measured samples and serves as a reference peak for all obtained measurements.

Furthermore, the behaviour of the powder mixture for the doped sample with crystalline boron indicates a slow reaction to form  $\text{MgB}_2$  starting at  $700^\circ\text{C}$ , marked with a triangle, and a small exothermic peak at  $750^\circ\text{C}$  (star), which can be associated with the reaction of Ni-Co-B nanoparticles and Mg to form new phases with considerably smaller intensity in comparison to the AB doped sample. The explanation for the poor reaction between the Ni-Co-B nanoparticles, Mg, and crystalline boron is likely to be the lack of incorporation of the new phases into the matrix of  $\text{MgB}_2$  (simultaneous reaction). Several factors can play a role, such as the small surface area of crystalline boron and the large grain size (spatial limitation), as well as the low reactivity, of crystalline boron (Fig. 14).

The reaction curve of the doped sample shows an absence of eutectic system formation, which further indicates the highly inert nature of crystalline boron.

From the literature, it is well known that the  $\beta$ -rhombohedral boron phase is thermodynamically the most stable allotrope, even at high sintering temperatures, so it is hard to get it to react fully with Mg [17,18,25].

DTA analysis of the pure sample made from crystalline boron shows a long hump between 680 and 790°C (brackets in Fig. 14), which represents a slow and prolonged reaction between crystalline boron and magnesium, similar to what occurs in the doped sample (Fig. 14).

Finally, from the reaction curve of amorphous boron and magnesium, a peak corresponding to completion of the  $\text{MgB}_2$  formation reaction can be seen at  $\sim 740^\circ\text{C}$  (pentagon in Fig. 14).

A possible mechanism for the incorporation of new phases into the  $\text{MgB}_2$  matrix could be the Ostwald ripening process, which spontaneously drives small particles into large ones (Fig. 15) [26, 27].

Amorphous boron as the thermodynamically less stable allotrope with much larger contact area allows substantially better and more uniform incorporation of new phases than CB, which finally provides a better dispersion of pinning centers in the  $\text{MgB}_2$  matrix (Fig. 15).

Crystalline boron ( $\beta$ -rhombohedral) is the most stable allotrope, with large grain size and a substantial proportion of MgO phase, which may have a negative impact on  $\text{MgB}_2$  crystal growth and the incorporation of new phases by Ostwald ripening.

It is important to emphasize that although there is no direct reaction between the Ni-Co-B nanoparticles and boron precursor powders, the morphology and size of the boron has a crucial impact on improvement of  $J_c$ . The main formation reaction for  $\text{MgB}_2$  starts at 650°C with almost complete melting of magnesium; this reaction partly coincides with the formation of a new phase (Mg + Ni-Co-B) at temperatures above 730°C.

The overlap of these processes is critical for efficient incorporation of the new phases into the  $\text{MgB}_2$  matrix. During the formation of the final nanoparticle-doped  $\text{MgB}_2$  product, boron, as a solid, strongly influences the shape and size of the  $\text{MgB}_2$  particles, as well as the incorporation of the secondary phases.

The TEM images [Fig. 3(a-c)] of the starting boron powders show significant differences in morphology and particle size. CB has particle size of around 1  $\mu\text{m}$  with occasional larger grains, and non-uniform size and shape. On the other hand, the amorphous boron precursor (AB) is mostly composed of particles with a spherical shape, with a quite narrow size distribution between 100 and 300 nm.

The direct influence of the size of the boron precursors on the  $\text{MgB}_2$  morphology can be observed from the SEM images in Figure 16(a, b).  $\text{MgB}_2$  prepared from AB has a grain size between 100-300 nm (similar to the starting boron powder) and hexagonal shaped  $\text{MgB}_2$  crystals with a quite narrow size distribution. Figure 16(a) shows high density and relatively good connectivity between  $\text{MgB}_2$  grains.

In contrast,  $\text{MgB}_2$  made from crystalline boron has a much larger average grain size (more than 0.5 micron), with a broad distribution of particle sizes, leading to  $\text{MgB}_2$  grains with large differences in particle size and shape [Fig. 16(b)]. Amorphous boron with smaller and more uniform particles reacts efficiently with melted magnesium due to its large reacting area and forms a similar grain size in the  $\text{MgB}_2$ . In contrast, crystalline boron has a much smaller reacting area, and the reaction with melted magnesium is much weaker and slower, which finally results in non-uniform size and shape of the  $\text{MgB}_2$  grains. Also, the  $\text{MgB}_2$  sample made from CB has pronounced boundaries between the grains, while in the  $\text{MgB}_2$  sample made from AB, the boundaries are less noticeable, which can indicate better connectivity among the grains.

## 5. Conclusion:

In conclusion, the morphology and particle size of the boron precursor is of critical importance to the  $J_c(H)$  behaviour of  $\text{MgB}_2$  samples. Amorphous boron presents much better results in comparison to crystalline boron. The morphology has a stronger influence on critical current density than the particle size of the boron precursor when the grain size of the boron is on the nanoscale.

At temperatures higher than 730°C, Ni-Co-B nanoparticles react with Mg and produce new phases ( $\text{Mg}_2\text{Ni}$  and  $\text{Mg}_2\text{Co}/\text{Co}_2\text{Mg}$ ) [13,24]. Amorphous boron fully reacts with magnesium and uniformly incorporates newly formed phases into the  $\text{MgB}_2$  matrix, which finally provides good pinning centres and improves  $J_c$ .

Effective improvement of pinning with Ni-Co-B doping is only observed at the 5 K measurement temperature. This is likely to be associated with the charge transfer from  $\sigma$  to  $\pi$  bands at 15 K [20]. Improvement of grain connectivity with doping is explained by the competition between Ni-Co-B nanoparticles and traces of oxygen in the sample for magnesium, which finally results in less MgO in Ni-Co-B doped  $\text{MgB}_2$  samples with amorphous boron [13].

In comparing the two boron powders with nanosized particles, AB (100 to 300 nm) and SC (> 70 nm), it is important to note that with a size distribution on the nanoscale, the grain size of the boron does not have a strong impact on the MgB<sub>2</sub> properties. SC boron has a certain proportion of crystalline phase, which had a negative effect on  $J_c$  despite the smaller size of the grains.

The advantage of amorphous boron phase, as a less stable phase, is its high reactivity, which makes the reaction with magnesium complete with the maximal amount of created MgB<sub>2</sub> and, at the same time, incorporates magnesium compounds (pinning centres) into the matrix of MgB<sub>2</sub>.

Pure crystalline boron (CB) with microsize grains produced much weaker results, because the grain size and morphology have a common negative effect on  $J_c$ . Crystalline boron contains large amounts of other impurities, mostly B<sub>2</sub>O<sub>3</sub>, which consequently results in a larger amount of MgO, a non-superconductive phase in MgB<sub>2</sub>. Measurements of critical current showed that larger concentrations of impurities (Ni-Co-B and MgO) lead to decreased  $J_c$  for any type of boron.

### **Acknowledgments**

The lead author (M M) was recipient of a University of Wollongong PhD scholarship for the duration of the work presented in this paper. This work is built on the outcomes of Project UKF 1B 01/07, which was supported through the Unity Through Knowledge Fund, designed by the Croatian government, represented by the Ministry of Science, Education and Sport. This work was partially supported by the Australian Research Council (Grant No. DE130101247) and a 2013 Australian Institute for Innovative Materials – Community Reference Group (AIIM-CRG) grant. The authors acknowledge the use of facilities and the assistance of Mr. Darren Attard and Dr. David R. G. Mitchell at the University of Wollongong Electron Microscopy Centre. The help of Dr. Germanas Peleckis at ISEM is gratefully acknowledged. The authors would like to also thank Dr. Tania Silver for critical reading.

### **REFERENCES**

- 1 Moissan H. Ann. Chim. Phys. 1895;6:296–320.
- 2 Kohn JA, Nye WF, Gaule GK. Boron-Synthesis, Structure, and Properties. Plenum Press Inc; 1960.
- 3 Johansson S, Schweitz JA, Westberg H, Boman M J. Appl. Phys. 1992;72:5956

- 4** Delaplane RG, Dahlborg U, Howells WS, Lundström T. *J. Non-Crystal. Solids* 1988;106:66–69.
- 5** Srivastava AK, Jain PC. *Chemistry*, Vols. 1 & 2, 2<sup>nd</sup> ed. Delhi: Neekunj Print Process; 2006-2007.
- 6** Shalamberidze SO, Kalandadze GI, Khulelidze DE, Tsurtsunia BD. *J. Solid State Chem.* 2000;154:199-203.
- 7** Solozhenko VL, Kurakevych OO, Oganov AR. *J. Superhard Mat.* 2008;30:428–429.
- 8** Chen SK, Yates KA, Blamire MG, MacManus-Driscoll JL. *Supercond. Sci. Technol.* 2005;18:1473.
- 9** Mahmud MAA, Susner MA, Sumption DM, Rindfleisch MA, Tomsic MJ, Yue J, Collings WE. *IEEE Transactions on Applied Superconductivity*, 2009;19:3.
- 10** Häbler W, Birajdar B, Gruner W, Herrmann M, Perner O, Rodig C, Schubert M, Holzapfel B, Eibl O, Schultz L. *Supercond. Sci. Technol.* 2006;19:512–520.
- 11** Dongliang W, Ma Y, Yu Z, Gao Z, Zhang X, Watanabe K, Mossan E. *Supercond. Sci. Technol.* 2007;20:574-578.
- 12** Kim JH, Oh S, Kumakura H, Matsumoto A, Heo Y-U, Song K-S, Kang Y-M, Maeda M, Rindfleisch M, Tomsic M, Choi S, Dou SX. *Advanced Materials*, 2011;23:4942–4946.
- 13** Mustapić M, Horvat J, Hossain MS, Skoko Ž, Dou SX. *Supercond. Sci. Technol.* 2013;26:075013.
- 14** Skoko Ž, Popović J, Dekanić K, Kolbas V, Popović S. *J. Appl. Cryst.* 2012;45:594-597.
- 15** Bean CP. *Rev. Mod. Phys.* 1964;36:31-36.
- 16** Horvat J, Soltanian S, Wang XL, Dou SX. *Appl. Phys. Lett.* 2004;84:3109.
- 17** Kim JH, Heo Y-U, Matsumoto A, Kumakura H, Rindfleisch M, Tomsic M, Dou SX. *Supercond. Sci. Technol.* 2010;23:075014.
- 18** Xu X, Kim JH, Dou SX, Choi S, Lee JH, Park HW, Rindfleisch M, Tomsic M. *J. Appl. Phys.* 2009;105:103913.
- 19** Data provided by Specialty Materials Inc.
- 20** Muranaka T, Akimitsu J. *Z. Kristallogr.* 2011;226:385–394.
- 21** Kovač P, Hušek I, Melišek T, Grivel JC, Pachla W, Štrbík V, Diduszko R, Homeyer J, Andersen NH. *Supercond. Sci. Technol.* 2004;17:10.
- 22** Liu Z-K, Schlom DG, Li Q, Xi XX. *Appl. Phys. Lett.* 2001;78:3678.
- 23** Li WX, Zeng R, Wang JL, Li Y, Dou SX. *J. Appl. Phys.* 2012;111:07E135.
- 24** Mustapić M, Horvat J, Hossain MS, Sun Z, Skoko Ž, Mitchell DRG, Dou SX. *Acta Materialia*, 2014;70:298–306.
- 25** Wang CD, Ma YW, Zhang XP, Wang DL, Gao ZS, Yao C, Wang CL, Oguro H, Awaji S, Watanabe K. *Supercond. Sci. Technol.* 2012;25:035018.
- 26** Ostwald W. *Lehrbrück der Allgemeinen Chemie*, 1896;2:1.
- 27** Kahlweit M. *Adv. in Colloid and Interface Sci.* 1975;5:1–35.
- 28** Lee S, Mori H, Masui T, Eltsev Y, Yamamoto A, Tajima S. *J. Phys. Soc. Jpn.* 2001;70:2255.
- 29** Dou SX, Wang X L, Horvat J, Milliken D, Collings EW, Sumption MD. *Physica C* 2001;361:79.



### Figure captions:

- Fig. 1: XRD patterns of two different types of boron: crystalline boron and amorphous boron.
- Fig. 2: XRD pattern of plasma process boron powders: (A) semicrystalline (SC) boron produced at low plasma power; (B) semicrystalline boron produced at high plasma power. SC boron features nanosized particles with a mixture of amorphous and crystalline phases compared to (C) pure crystalline boron ( $\beta$ -rhB).[19] The XRD pattern for the SC boron used in our experiments, is shown in the top panel (A).
- Fig. 3: TEM images of the crystalline boron CB (a), amorphous boron AB (b), and semicrystalline boron SC (c). The insets are the corresponding selected area diffraction patterns.
- Fig. 4: Critical current density of  $\text{MgB}_2$  prepared from semicrystalline boron (SC) precursor, both pure and doped with Ni-Co-B nanoparticles (size  $\approx 5$  nm), with sintering at  $850^\circ\text{C}$ .  $J_c$  was measured at 20 K (solid symbols) and 5 K (open symbols).
- Fig. 5: Critical current density of  $\text{MgB}_2$  prepared from amorphous boron (AB) precursor with sintering at  $850^\circ\text{C}$ .  $J_c$  was measured at 20 K (solid symbols) and 5 K (open symbols).
- Fig. 6: Critical current density of pure and Ni-Co-B doped  $\text{MgB}_2$  prepared from crystalline boron (CB) precursor and sintered at  $850^\circ\text{C}$ .  $J_c$  was measured at 20 K (solid symbols) and 5 K (open symbols).
- Figs. 7:  $J_c$  values of  $\text{MgB}_2$  made from AB, SC, and CB with sintering at  $850^\circ\text{C}$  as a function of doping level: (a) measured at 20 K and 2 T; (b) measured at 5 K and 5 T.
- Fig. 8: Pure  $\text{MgB}_2$  samples made from different boron precursors and sintered at the same temperature,  $850^\circ\text{C}$ .
- Fig. 9: XRD patterns of pure (bottom) and Ni-Co-B doped (5wt% top)  $\text{MgB}_2$  samples made from SC sintered at  $850^\circ\text{C}$ . Miller indices for  $\text{MgB}_2$  are indicated in the figure.
- Fig. 10: XRD patterns of  $\text{MgB}_2$  made from AB for pure (bottom) and doped samples (5wt% at top). Miller indices for  $\text{MgB}_2$  are indicated in the figure.
- Fig. 11: XRD patterns of  $\text{MgB}_2$  made from CB for pure (bottom) and doped (2.5wt% at top) samples. Miller indices for  $\text{MgB}_2$  are indicated in the figure.
- Fig. 12: Selected regions presented in (a) and (b) show magnified views of peaks corresponding to [002] and [110] reflections, respectively, from the XRD patterns for pure and 2.5wt% Ni-Co-B doped samples (for all three analysed boron powders).
- Fig. 13: Schematic illustration of the reaction between Mg and B with the assistance of Ni nanoparticles.
- Fig. 14: DTA scans for Mg + 2B (CB), Mg + 2B (AB), Mg + 2B (CB) + 10 wt% Ni-Co-B, and Mg + 2B (AB) + 10 wt% Ni-Co-B powders. The open symbols and brackets are explained in the text.
- Fig. 15: Schematic illustration of  $\text{MgB}_2$  grain growth by the Ostwald ripening process.
- Fig. 16: (a) SEM image of  $\text{MgB}_2$  made from amorphous boron (AB). (b): SEM image of  $\text{MgB}_2$  made from crystalline boron (CB).

### Table captions:

- Table 1: Lattice parameters for pure and doped  $\text{MgB}_2$  samples made from three different boron powders.
- Table 2: Quantitative analysis by Rietveld refinement of pure samples (all boron types) and doped samples (2.5, 5 wt%).
- Table 3: Crystallite size,  $D_p$ , calculated in several [hkl] directions, from XRD line broadening for  $\text{MgB}_2$  samples made from different types of boron and sintered at  $850^\circ\text{C}$ . Crystallite size has been calculated by the XBroad program [14].