Formation of Higher Borides During High-Pressure Synthesis and Sintering of Magnesium Diboride and Their Positive Effect on Pinning and Critical Current Density

Tatiana A. Prikhna, Wolfgang Gawalek, Yaroslav M. Savchuk, Artem V. Kozyrev, Michael Wendt, Vladimir S. Melnikov, Vladimir Z. Turkevich, Nina V. Sergienko, Viktor E. Moshchil, Jan Dellith, Christa Shmidt, Sergey N. Dub, Tobias Habisreuther, Doris Litzkendorf, Peter A. Nagorny, Vladimir B. Sverdun, Harald W. Weber, Michael Eisterer, Jacques Noudem, and Ulrich Dittrich

***Abstract*—Critical current density (j_c) of high-pressure (2 GPa) manufactured MgB_2-based superconductors depends on the amount and distribution of higher borides (MgB_{12}) in MgB_2 matrix, which in turn are determined by the nature of the initial components first of all B or MgB_2 and the temperature of sintering or synthesis. Ti and Ta additions can improve j_c by promoting the higher boride formation via impurity hydrogen absorption, thus preventing MgH_2 detrimental for j_c being formed, which possibly increases the MgB_{12} nucleation barrier. SiC (0.2–0.8 μm) addition increases j_c of MgB_2, allowing us to get $j_c = 10^6$ A/cm^2 at 20 K in the 1 T field: pinning is increased by SiC and higher boride grains and there is no notable interaction between SiC and MgB_2. As the synthesis temperature increases from 800 to 1050°C, Ti and SiC additions may affect the oxygen segregation and formation of Mg-B-O inclusions enriched with oxygen as compared to the amount of oxygen in the MgB_2 matrix, which can also promote an increase in pinning. Materials high-pressure synthesized from Mg and B taken in 1:4, 1:6, 1:7, 1:8, 1:10, 1:12, 1:20 ratios were superconductive with T_c of about 37 K. High j_c ($7 \cdot 10^4 - 2 \cdot 10^4$ A/cm^2 in zero field at 10–30 K, respectively) showed materials with the matrix composition near MgB_{12} stoichiometry, they have doubled microhardness of MgB_2.**

***Index Terms*—Boron compounds, magnetic variable measurement, pressure effects, superconducting material growth.**

Manuscript received August 18, 2008. First published July 06, 2009; current version published July 15, 2009. This work was supported in part by the Projects STCU 3665, of Ukrainian-German Cooperation IB/BMBF UKR 06/004 (M84-2008), Ukrainian-Austrian Cooperation OEAD UA 07/2007 (M118-2007), Ukrainian-French Cooperation "Dnipro" 14186 XF (M121-2007), H.C. Starck GmbH, Germany.

T. A. Prikhna, Y. M. Savchuk, A. V. Kozyrev, V. S. Melnikov, V. Z. Turkevich, N. V. Sergienko, V. E. Moshchil, S. N. Dub, P. A. Nagorny, and V. B. Sverdun are with the Institute for Superhard Materials, National Academy of Sciences of Ukraine, 2, Avtozavodskaya Str., Kiev 07074, Ukraine (e-mail: prikhna@mail.ru; prikhna@iptelecom.net.ua).

W. Gawalek, M. Wendt, J. Dellith, C. Shmidt, T. Habisreuther, and D. Litzkendorf are with the Institut für Photonische Technologien, Albert-Einstein-Strasse 9, Jena, D-07745, Germany (e-mail: gawalek@ipht-jena.de).

H. W. Weber and M. Eisterer are with the Atomic Institute of the Austrian Universities, 1020 Vienna, Austria (e-mail: weber@ati.ac.at).

J. Noudem is with the CNRS/CRISMAT/ISMRA, 6, Bd du Maréchal Juin, CNRS UMR 6508, 14050 Caen, France (e-mail: jacques.noudem@ensicaen.fr).

U. Dittrich is with H.C. Starck GmbH, Goslar 38642, Germany (e-mail: ulrich.ditrich@hcstarck.com).

Digital Object Identifier 10.1109/TASC.2009.2018151

I. Introduction

Interest in the MgB_2-based materials can be explained by comparatively simple and cheap preparation technique and the intensive development of technologies that use liquid hydrogen. Preparation of the materials under pressure can surpass the evaporation of Mg and allows getting a dense structure with high j_c and mechanical characteristics. High coherence length (1.6–12 nm) of MgB_2 permits high j_c in polycrystalline material and grain boundaries can serve as pinning centers. The pinning in MgB_2 can be increased by chemical alloying with Ti, Zr, SiC, etc. According to the conception proposed in [1]–[3], when Ti or Zr is added, the pinning can be increased due to the formation of nanosized TiB_2 or ZrB_2 grains and in the case of nano-SiC adding due to the presence of SiC grains and co-substitution of Si and C in crystal lattice. It was shown [4] that pinning centers in MgB_2 can be $MgB_{2-x}O_x$ precipitates larger than 10 nm. We have found that additions of Ta, Ti, Zr can improve pining in high pressure (2 GPa) and temperature (HP-HT) synthesized MgB_2 [5]–[7], but the mechanism of their effect was different from that proposed in [2], [3]: their presence provoked an increase in the structure of inclusions with near MgB_{12} stoichiometry [8], [9]. The higher is the amount of these inclusions, the finer they are, and more homogeneously distributed, the higher is the j_c [10]. Up to now our attempts to improve j_c of HP-HT-synthesized MgB_2 by adding SiC with grains of sizes 20–30 and 200–400 nm were unsuccessful: j_c at 10–35 K decreased or remained unchanged [11]. Here our new results of complex study of HP-HT manufacturing of MgB_2 and higher borides using several types of initial boron and MgB_2 powders with and without adding of SiC (200–800 nm), Ti, and Ta, and the regularities of variations of j_c and pining are discussed.

II. Experimental

In the experiments on synthesis, metallic Mg chips (technical specifications 48-10-93-88) and amorphous B (Type I—1.9% oxygen (O), 1.4 μm, Type II—1.5% O, 4 μm, Type III—1 μm, 95–97% purity, 1.6–1.7% O, 0.8–0.84 μm, and Type IV—0.66% O, < 5 μm; Types I, II, IV—H.C. Starck,

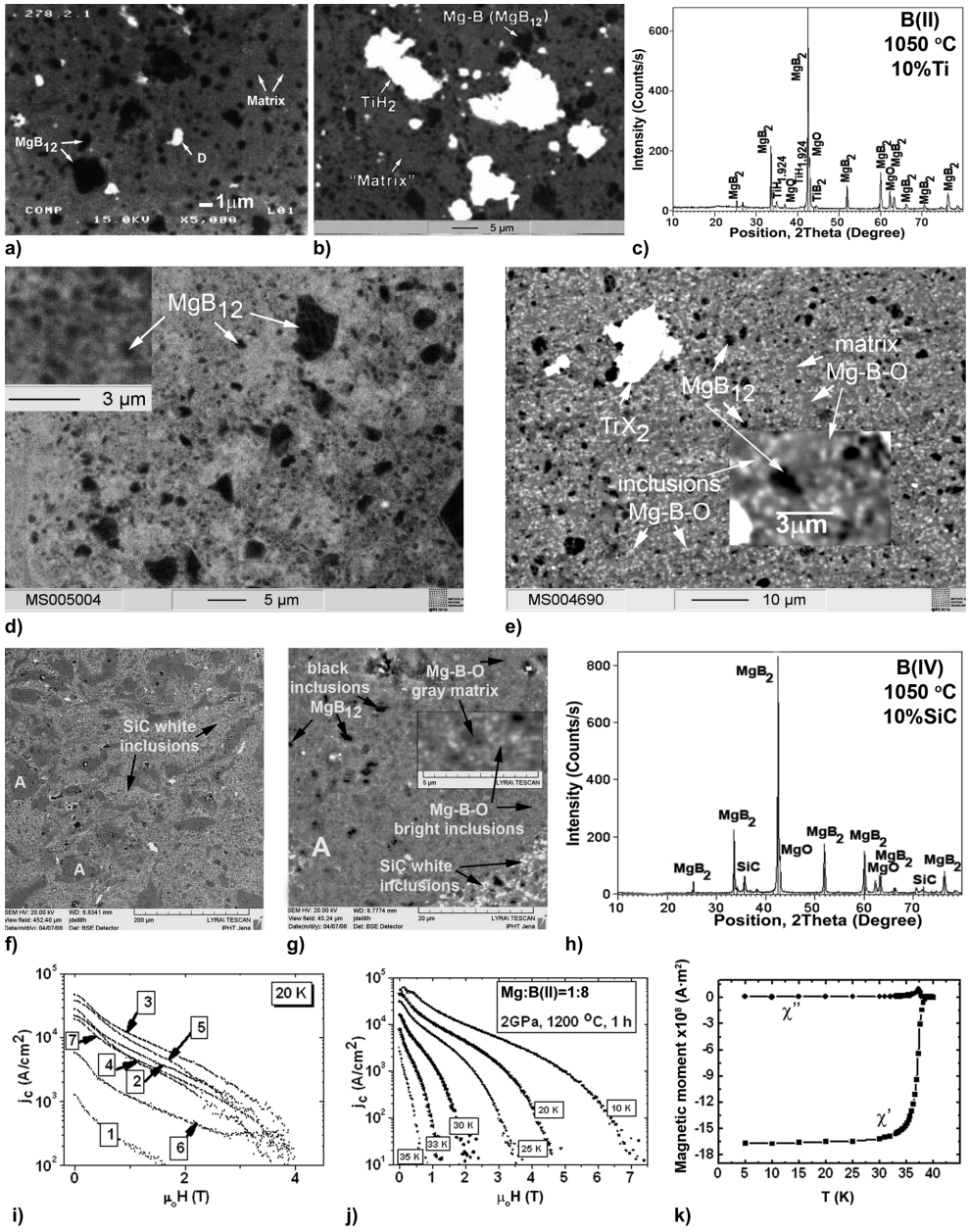

Fig. 1. Structures obtained by SEM (BSI—backscattering electron image) of MgB_2-based materials synthesized from Mg and B at 2 GPa, for 1 h: (a), (b)—from B(III) at 800°C without and with 10% Ti, respectively; (d), (e)—from B(II) at 1050°C without and with 10% Ti, respectively; (f), (g)—from B(IV) at 1050°C with 10% SiC, (Fig. 1(g) shows enlarged region A of Fig. 1(f), where there are no SiC inclusions); (c), (h)—X-ray patterns of the materials shown in Figs. 1(e), 1(f), and 1(g), respectively; (i) dependencies of j_c on the external magnetic fields, $\mu_o H$, at 20 K for the materials synthesized at 2 GPa for 1 h from magnesium and boron B(II) taken in the ratio Mg:B and synthesized at T_S: curves 1-1:12, $T_S = 1200°C$, curve 2-1:10 $T_S = 1200°C$, curve 3-1:8, $T_S = 1200°C$, curve 4-1:6, $T_S = 1200°C$, curve 5-1:4, $T_S = 1200°C$, curve 6-1:12, $T_s = 800°C$, curve 7-1:20, $T_s. = 1200°C$; (j, k)—characteristics of the material HP-HT-synthesized from $Mg : B(II) = 1 : 8$ at 2 GPa, 1200°C for 1 h: j_c vs $\mu_o H$ (j); imaginary (χ'') and real (χ') part of the ac susceptibility (magnetic moment) vs temperature, T, measured in ac magnetic field with 30 μT amplitude which varied with a frequency of 33 Hz (k).

Type III—MaTeck) have been taken in the stoichiometric ratio of MgB_2. In the experiments on sintering MgB_2 of Type I—H.S. Starck, 0.8% O, 10 μm and Type II—Alfa Aesar, 98% purity were used. A powder of Ti (30 μm, purity 95%), Ta (0.8–3.3 μm, Ta-207417061 H.C. Starck) or SiC (200–800 nm, SiC-28492000, H.C. Starck) has been added to the MgB_2 stoichiometric mixture of Mg and B in amounts of 10 wt%. The X-ray study of the initial Mg, Ti, Ta, and B showed no impurity phases with hydrogen (the method accuracy being about 3–5%). To study the synthesis of higher borides, the mixtures of Mg and Type II boron were prepared in 1:4, 1:6, 1:7, 1:8, 1:10, 1:12, 1:20 ratios. We mixed and milled the components in a high-speed activator with steel balls for 1–3 min and then compacted into tablets (all in the Ar atmosphere). The high pressure (2–4 GPa)—high temperature ($T_S = 700 - 1400°C$) conditions for 1 h were created in the recessed-anvil type high-pressure apparatuses (HPA) described elsewhere [8]. The structure of the materials was studied using X-ray diffraction and SEM. All j_c data were estimated using samples about 3 mm

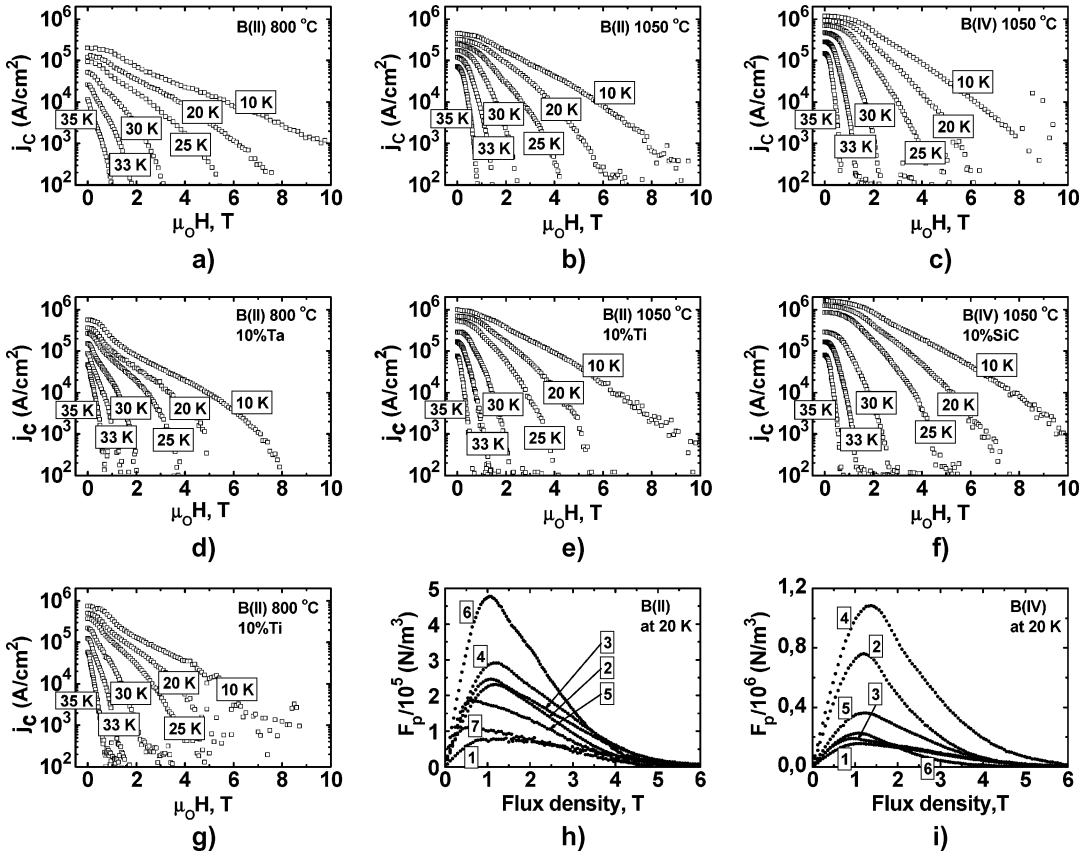

Fig. 2. Dependencies of critical current densities, j_c, on the external magnetic fields, $\mu_o H$, at temperatures of 10, 20, 25, 30, 33 and 35 K for the materials synthesized at 2 GPa for 1 h from magnesium and boron B(II)—(a), (b), (d), (e), (g) or B(IV)—(c), (f) without additions: (a) at 800°C, (b), (c) at 1050°C and with additions: (d) at 800°C with 10% Ta, (e) at 1050°C with 10% Ti, (f) at 1050°C with 10% SiC, (g) at 800°C with 10% Ti; (h, i)—dependencies of pinning force (F_p) on the flux density measured at 20 K for the materials synthesized at 2 GPa for 1 h from magnesium and boron B(II)-(h) and B(IV)-(i), without and with additions, curves 1—at 800°C without additions, curves 2—at 1050°C without additions, curves 3—at 800°C with 10% SiC, curves 4—at 1050°C, with 10% of SiC, curves 5—at 800°C with 10% Ti, curves 6—at 1050°C with 10% Ti, curves 7—at 800°C with 10% Ta.

in diameter, Oxford Instruments 3001 vibrating magnetometer and Bean's model.

III. Results and Discussions

Here we report the data for the initial 4 types of B and 2 types of MgB_2. But in our studies of the MgB_2 preparation at 2 GPa in $T_S = 700 - 1100°C$ range (with a 50°C step) 7 types of amorphous B and 8 types of MgB_2 powders (with 0.8 to 10 μm grains) with and without Ti, Ta, Zr and SiC adding were used, which allowed us to make the following conclusions. Superconducting (SC) properties of MgB_2-based material are largely determined by the quality of initial B or MgB_2. The average size of grains in the consolidated materials (estimated from the X-ray study) ranged from 15 to 37 nm. No correlations was found between the amount of oxygen in initial boron (0.66–3.5 wt% O) or MgB_2 (0.8–3.5 wt% O) and its amount in the HP-synthesized (7–15 wt% O) or sintered (4–9 wt% O) materials as well as the correlations with the material j_c. [9]. Usually SC properties of MgB_2-materials synthesized from B and Mg are higher than that of the sintered from previously prepared MgB_2. With MaTec boron and Alfa Aesar MgB_2 we could not increase the synthesis or sintering temperature above 950–1000°C, because the resultant materials were not SC, the optimal SC properties were exhibited by materials produced at 800–900°C. With the use of the H.C. Starck powders, the optimal SC properties in many cases were obtained in materials manufactured at about 1050°C. Practically for all types of H.C. Starck MgB_2 powders, sintering below 1000°C results in non-SC behavior down to 4 K (it is likely due to the absence of percolation). But when we used H.C. Starck boron, materials synthesized in the 700–1100°C range were SC and the highest j_c for the majority of boron types were obtained after synthesis at 1050°C, and only for two types B at 800°C. Usually materials synthesized at 800°C had higher j_c in higher fields (at 10–35 K) than those produced at 1050°C (Figs. 1(a) and 1(b)). The SEM structural study of the HP-HT-produced materials showed a correlation between j_c and the amount (Table I), size and distribution of inclusions (black in a SEM composition image) with near MgB_{12} stoichiometry (Fig. 1(a)). We cannot detect MgB_{12} by X-ray. It is known [12] that MgB_{12} reflexes can be absent in the X-ray pattern due to poor diffracted signals because of the low X-ray atomic scattering factor of boron, besides, MgB_{12} inclusions are dispersed in MgB_2, the etalon X-ray pattern of MgB_{12} is absent in the database and the literature data are contradictive.

Ti and Ta additions can increase j_c and pinning force (F_p). Compare Figs. 2(d), 2(e), and 2(g) and Figs. 2(a), 2(b); in Fig. 2(h) curves 1 with 5 (Ti), 7 (Ta) and curve 2 with 6 (Ti); in Fig. 2(i) curve 1 with 5 (Ti); data in Table I for materials

TABLE I
CRITICAL CURRENT DENSITY, j_c, VS. RELATIVE AMOUNT, N, OF "BLACK INCLUSIONS" WITH NEAR MgB_{12} STOICHIOMETRY

Type of the initial B or MgB_2	Manufacturing parameters: pressure, P, temperature, T, holding time, τ,	Name of addition, and its amount, wt.%	j_c in 1T , at 20 K kA/cm^2	N, %
MgB_2 (I)	P=2 GPa, T=1000 °C, τ=1h	without	5.2	1.8
MgB_2 (II)	P=2 GPa, T=900 °C, τ=1h	without	7.8	2.6
B(I)	P=2 GPa, T=800 °C, τ=1h	without	80	10.5
B(II)	P=2 GPa, T=900 °C, τ=1h	without	62	9.5
B(II)	P=2 GPa, T=1000 °C, τ=1h	without	240	12
B(II)	P=2 GPa, T=800 °C, τ=1h	without	520	19
B(III)	P=2 GPa, T=800 °C, τ=1h	Ta, 2%	90	10
B(III)	P=2 GPa, T=800 °C, τ=1h	Ta, 10%	310	12.5
B(III)	P=2 GPa, T=800 °C, τ=1h	Ti, 2%	95	10.7
B(III)	P=2 GPa, T=800 °C, τ=1h	Ti, 10%	360	14

[a]The amount of the "black" inclusions, N, was calculated as a ratio of the area occupied by the "black" inclusions at the COMPO image obtained at 1600× magnification to the total area of this image.

prepared from B(III). There were found no diffusion of Ti or Ta into MgB_2 under 2–3 GPa at 700–1100°C and the inclusions of phases contained Ti or Ta are rather big and randomly distributed to be pinning centers by themselves (Figs. 1(b) and 1(e)), but the presence of Ti or Ta causes an increase of the amount of inclusions with near MgB_{12} stoichiometry. Ta and Ti transform into hydrides by adsorbing impurity hydrogen (which may come from the high-pressure cell materials), thus preventing the MgH_2 formation harmful for j_c [5], [6]. The formation of $TiH_{1,924}$ only at 800°C, 2 GPa was confirmed by TEM and NanoSIMS ion mapping [13]. MgH_2 may increase the nucleation barrier of MgB_{12} restricting its formation, but this calls for further study. Why Ti adding to B(IV) and Mg decreases F_p after synthesis at 1050°C (Fig. 1(h) curve 6) is still the open question.

At higher T_S (1050°C) Ti forms hydrides and borides (Fig. 1(c)) and promotes the segregation of oxygen into Mg-B-O inclusions enriched with oxygen as compared to its amount in MgB_2 (or Mg-B-O matrix) and looks brighter in BSI, Fig. 1(e). In the matrix (in sites with low density of Mg-B-O inclusions) the average amount of oxygen was about 5 wt %, while at $T_S = 800°C$ when no segregation was observed it was about 8%. At higher T_S hydrogen evaporated, MgB_{12} grains became smaller and more homogeneously distributed (insert in Fig. 1(d)). In parallel the formation of Mg-B-O inclusions occurs, which can promote an increase of pinning and j_c.

We succeeded in increasing j_c of MgB_2 at 10–25 K adding 200–800 nm SiC and got highest j_c using B(IV) (Fig. 1(f)): $> 10^6$ A/cm^2 up to 2 and 1 T and $> 10^5$ A/cm^2 up to 5 and 3.5 T at 10 and 20 K, respectively. The material structure (Figs. 2(f)–2(h)) contains SiC grains, higher borides (MgB_{12}) and Mg-B-O inclusions, which can be relevant pinning centers. With addition of 20–30 nm and 200–400 nm SiC Mg_2Si was formed: the higher was the amount of Mg_2Si the lower was j_c [11], especially at 25–35 K (that can be due to carbon penetration into MgB_2 lattice promoting T_c decrease). The reactivity of SiC with coarser grains seemed to be lower and no notable interaction of SiC and MgB_2 (Fig. 2(h)) was observed.

HP-HT synthesized materials from Mg and B(II) taken in 1:4, 1:6, 1:7, 1:8, 1:10, 1:12, 1:20 ratios were superconductive (Figs. 1(i), 1(j), and 1(k)) with transition temperature, T_c about 37 K. The high j_c was shown by materials with near MgB_{12} composition of matrix, e.g., prepared from 1:8 or 1:20 mixtures (at 2 GPa, 1200°C, 1 h). Their Vickers microhardness (H_V) was twice as high as that of MgB_2 (25 ± 1.1 GPa and 12.1 ± 0.8 GPa, respectively, at a load of 4.9 N)

IV. CONCLUSION

Inclusions of higher borides can be pinning centers in MgB_2, additions of Ta and Ti promote the formation of MgB_{12} inclusions. At higher synthesis temperatures Ti and SiC seems to contribute to the formation of Mg-B-O inclusions (relevant pinning centers). SiC increases j_c of HP-HT synthesized MgB_2 when there is no notable interaction of SiC and MgB_2 (the pinning centers can be SiC, Mg-B-O and MgB_{12} inclusions).

REFERENCES

[1] S. X. Dou, S. Soltanian, and J. Horvat *et al.*, "Enhancement of the critical current density and flux pinning of MgB_2 superconductor by nanoparticle SiC doping," *Applied Physics Letters*, vol. 81, no. 18, pp. 3419–3421, 2002.

[2] Y. Zhao, Y. Feng, and C. H. Cheng *et al.*, "High critical current density of MgB_2 bulk superconductor doped with Ti and sintered at ambient pressure," *Applied Physics Letters*, vol. 79, no. 8, pp. 1154–1156, 2001.

[3] D. Goto, T. Machi, and Y. Zhao *et al.*, "Improvement of critical current density in MgB_2 by Ti, Zr and Hf doping," *Physica C*, vol. 392–396, pp. 272–275, 2003.

[4] R. F. Klie, J. C. Idrobo, and N. D. Browning, "Observation of coherent oxide precipitates in polycrystalline MgB_2," *Appl. Phys. Lett.*, vol. 80, no. 21, pp. 3970–3972, 2002.

[5] T. A. Prikhna, W. Gawalek, and A. B. Surzhenko *et al.*, "High-pressure synthesis of MgB_2 with and without tantalum addition," *Physica C*, vol. 372–376, pp. 1543–1545, 2002.

[6] T. A. Prikhna, W. Gawalek, and Y. M. Savchuk *et al.*, "High-pressure synthesis of MgB_2 with addition of Ti," *Physica C*, vol. 402, pp. 223–233, 2004.

[7] T. Prikhna, W. Gawalek, and N. Novikov *et al.*, "High-pressure synthesized nanostructural magnesium diboride-based materials for superconductive electromotors, generators and pumps," *Journal of Materials Processing Technology*, vol. 181, pp. 71–75, 2007.

[8] T. A. Prikhna, W. Gawalek, and Y. M. Savchuk *et al.*, "The inclusions of Mg-B (MgB12?) as potential pinning centres in high-pressure-high-temperature-synthesized or sintered magnesium diboride," *Supercond. Sci. Technol.*, vol. 20, no. 9, pp. S257–S263, 2007.

[9] T. Prikhna, W. Gawalek, and Y. Savchuk *et al.*, "High pressure and hot-pressing manufactured magnesium diboride. Inclusions of higher borides as possible pinning centers in the material," *Journal of Optoelectronics and Advanced Materials*, vol. 10, no. 5, pp. 1017–1020, 2008.

[10] T. A. Prikhna, W. Gawalek, and Y. M. Savchuk *et al.*, "Peculiarities of high-pressure and hot-pressing manufacture of MgB_2-based blocks with high critical currents for electrical machines," *Journal of Physics*, vol. 97, 2008, 012022.

[11] T. Prikhna, N. Novikov, and Y. Savchuk *et al.*, "High-pressure synthesis of MgB_2-based material with high critical currents," in *Innovative Superhard Materials and Sustainable Coatings for Advanced Manufacturing*, ser. NATO Science Series. II, J. Lee and N. Novikov, Eds. : , 2005, vol. 200, Mathematics, Physics and Chemistry, pp. 81–90.

[12] B. Birajdar, N. Peranio, and O. Eibl, "Quantitative electron microscopy and spectroscopy of MgB_2 wires and tapes," *Supercond. Sci. Technol.*, vol. 21, pp. 1–20, 2008, 073001.

[13] S. Haigh, P. Kovac, T. Prikhna, Y. M. Savchuk, M. Kilburn, C. Salter, J. Hutchison, and C. Grovenor, "Chemical interactions in Ti doped MgB_2 superconducting bulk samples and wires," *Supercond. Sci. Technol.*, vol. 18, pp. 1–7, 2005.