Structure and properties of oxygen-containing thin films and bulk MgB$_2$

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Abstract

Despite MgB$_2$ is oxygen-free superconductor the high affinity of Mg toward oxygen makes practically impossible to synthesize MgB$_2$-based materials free of oxygen.

The structural Auger spectroscopy study of MgB$_2$ thin (140 nm) oxygen-containing polycrystalline films obtained by magnetron sputtering with $j_c$(0-1T, 20K)=7.8-2.7 MA/cm$^2$

and 99% dense MgB$_2$ bulks synthesized at 2 GPa having $j_c$(0-1 T, 20 K)=0.9 – 0.7 MA/cm$^2$ or 0.4-0.3 MA/cm$^2$ (depending on initial boron),
up to 80% connectivity,
containing up to 94% of shielding fraction

allows to conclude that $j_c$ of MgB$_2$ to high extend depends on distribution of admixture oxygen.
$\text{Mg(B,O)}_2$ precipitation in $\text{MgB}_2$ (X. Z. Liao et al. J. Appl. Phys. 93, 6208 (2003))

$\text{MgB}_2$ grains to form coherently ordered $\text{MgB}_{2-x}\text{O}_x$ precipitates from about 5 up to 100 nm in size and that such precipitates can act as pinning centers.

Ordered replacement of B atoms by O and have the same basic structure as the $\text{MgB}_2$ matrix but with composition modulations.

No difference in the lattice parameters between the precipitates and the matrix can be detected in conventional electron diffraction patterns.

However, extra satellite diffraction spots were revealed by HREM study in some directions implying a structural modulation caused by the precipitates.

The periodicity of O atom ordering depends on the concentration of O atoms in the precipitate and primarily occurred in the (010) plane.

Longer exposure to trace amount of O at high temperatures also results in the transformation of the precipitates from the hexagonal $\text{Mg(B,O)}_2$ phase with compositional modulations to the face-centered cubic $\text{MgO}$ phase.

(a) An HREM image along [010] direction.

(b) Fourier transformation of the matrix.

(c) Fourier transformation of the precipitate showing satellite spots with a vector of $[-0.26, 0, 0.39]$.
The thin MgB$_2$ films were deposited by DC magnetron sputtering under 1 Pa Ar pressure on $8 \times 8 \times 0.2$ mm$^3$ sized substrates from leucosapphire in (0001) orientation having room temperature, which subsequently were annealed at 600-650 °C for 5 min in Ar under 10 Pa. For deposition we used MgB$_2$ target synthesized by hot pressing at 30 MPa, 800 °C, 1 h form Mg turning (Technical Specification of Ukraine 48-10-93-88) and commercially available precursor B powders HC Starck (grain size 4 μm, 1.5 wt% O, 0.47 wt% C, 0.40 wt% N, 0.37 wt% H).
Methods of preparation

High pressure (2 GPa) and hot pressure (30 MPa) synthesis of bulk MgB$_2$

ASEA (Sweeden) 140 MN effort
Structure of MgB$_2$ thin (140 nm) film deposited by magnetron sputtering (Type 1)

Structure of MgB$_2$ film after etching in Ar of oxidized surface layer in Auger spectrometer JAMP–9500F
(a) – SEI (secondary electron image showing the relief of the film) and (b) – COMPO (compositional electron image – the brightness increase with increase in Z )

Composition (Fig.a, at.%)
in point 1: 47.9 % B, 7.1 % C, 31.6 % O, 13.4 % Mg.
and in point 2: 58.3 % B, 10.8 % C, 16.6 % O, 14.3 % Mg.

The structure of film Type 1 which demonstrates the highest $J_c$ contains 16.6-31.6 at% of oxygen and nanostructural inhomogenities which can be pinning centers influencing $J_c$ are much smaller and more homogeneously distributed as compare to bulk MgB$_2$. 
Critical current density, \( j_c \), vs. magnetic field, \( B \), of thin MgB\(_2\) film (Type 1)

field parallel (\( H||ab \)) and perpendicular (\( H||c \)) to the substrate surface

\[ j_c(0-1T, 20K)=7.8-2.7 \text{ MA/cm}^2 \]

The thin MgB\(_2\) films were deposited by DC magnetron sputtering under 1 Pa Ar pressure on 8×8×0.2 mm\(^3\) sized substrates from leucosapphire in (0001) orientation having room temperature, which subsequently were annealed at 600-650 °C for 5 min in Ar under 10 Pa (Type 1)
Critical current density, $j_c$, vs. magnetic field, $B$, of thin MgB$_2$ films after repeated annealing

Type 2 repeatedly annealed at 720—750°C for 7 min in Mg vapor at $P = 100$ Pa

Type 3 repeatedly annealed at 720—750°C for 7 min vacuumed under $P = 0.1$ Pa.
X-ray of films deposited on substrates from leucosapphire in (0001) orientation having room temperature and then heated up to 600-650 °C for 5 min under 10 Pa of Ar (Type 1) and films which after this were repeatedly annealed at 720—750 °C for 7 min in Mg vapor at $P = 100$ Pa (Type 2) and in 0.1 Pa vacuum (Type 3)
Critical current density, $J_c$, vs. magnetic field, $\mu_0 H$, for thin films and bulk MgB$_2$:
1 – film as deposited in Ar from MgB$_2$ target (Type 1),
2 – the same film after repeated annealing in vacuum (Type 3); and
3-5 - bulk MgB$_2$ high-pressure (2 GPa, 1 h) synthesized at 1050, 800 and 600 °C, respectively;
Introduction

Critical current density, $j_c$, vs. magnetic field, $\mu_0 H$, of MgB$_2$ materials synthesized at 2 GPa for 1 h from Mg+2B at 800 and 1050 °C;

From B (1) with grain size <5 μm, 0.66 wt% O, 0.31 wt% C, 0.48 wt% N, 0.32 wt % H

From B (2) with grain size 4 μm, 1.5 wt% O, 0.47 wt% C, 0.40 wt% N, 0.37 wt% H

$j_c(0-1 \text{ T, 20 K})=0.9 – 0.7 \text{ MA/cm}^2$ $j_c(0-1 \text{ T, 20 K})=0.4-0.3 \text{ MA/cm}^2$

From B(1) with 10 wt% SiC

From B(2) with 10 wt% Ti

$j_c(0-1 \text{ T, 20 K})=1.2 – 1.0 \text{ MA/cm}^2$ $j_c(0-1 \text{ T, 20 K})=0.7-0.5 \text{ MA/cm}^2$
(a) Comparison of $J_c$ at 20 K in bulk MgB$_2$ prepared under various temperatures at 2 GPa:
1, 2: samples made of B(I) at 1050 °C, ($k=0.43$) and 800 °C, ($k=0.37$), respectively;
3, 4 of B(II) at 800 °C and 600 °C, ($k=0.32$), respectively.

(b) $B_{c2}$ of bulk MgB$_2$ prepared from Mg:2B:
1: B(II) at 2 GPa, 600 °C, 1 h, (HP);
2: B(III) at 30 MPa, 800 °C, 2h, (HotP);
3: B(III) at 50 MPa, 600-1050 °C, 1 h, (SPS);
4: B(III) at 2 GPa, 900 °C, 1 h (HP);
5: B(V)+10 wt.% Zr at 2 GPa, 800 °C, 1 h (HP);
6: B(V)+10 wt.% Ti at 2 GPa, 800 °C, 1 h (HP);
7: B(I)+10 wt.% SiC at 2 GPa, 1050 °C, 1 h (HP).

$B_{c2}$ (22 K)=15 T (No 1) and extrapolated $B_{c2}(0$ K$)=42.1$ T, as well, as irreversibility fields: $B_{irr}(18.5$ K$)=15$ T and $B_{irr}(0$ K$)=32.5$ T.
Structural transformations in bulk MgB$_2$ with manufacturing temperature increase from 800 to 1050 °C (under 2 GPa)

As Auger analysis shown

- material matrix (for the sample synthesized at 2GPa 1050 °C) showed near MgB$_{2.2-1.7}$O$_{0.4-0.6}$ stoichiometry as a result of multiple analyzing after multiple etching steps (providing depth profile)
  - bright Mg-B-O nanolayers (10-20 nm) had near MgB$_{1.2-2.7}$O$_{1.8-2.5}$ stoichiometry
  - separate bright Mg-B-O inclusions had near MgB$_{0.6-0.8}$O$_{0.8-0.9}$ stoichiometry
  - higher magnesium borides MgB$_x$ which appear the most black have near MgB$_{11-13}$O$_{0.2-0.3}$ stoichiometry

99% dense MgB$_2$

$j_c$(0-1 T, 20 K) = 0.4-0.3 MA/cm$^2$

up to 80% connectivity

up to 94% of shielding fraction
The size and amount of higher magnesium borides (black inclusions with near \( \text{MgB}_{11-13}\text{O}_{0.2-0.3} \) stoichiometry according to Auger study) decreasing with manufacturing temperature increase.

\[
\begin{align*}
\text{Mg:2B, 2 GPa, 800 °C, 1 h} \\
\text{Mg:2B, 2 GPa, 1050 °C, 1 h}
\end{align*}
\]

The Berkovich nanohardness and Young modulus of such inclusions as estimated under the 10-60 mn-load were 32.2±1.7 and 385±14 GPa, respectively, what were even higher than that for sapphire: 31.1±2.0 and 416±22 GPa.
We have applied the density functional theory [1] based on a full-potential linearized augmented plane wave method with the generalized gradient correction to exchange-correlation potential [2] (the program package WIEN2k [3]). In the nearest vicinity of the Fermi energy $E_F$ corresponding dependencies are not constant and their changes with $x$ are non-monotonous. But, in any case, all studied compounds are conductors with a non-zero density of states at the Fermi level. Large density of delocalized states proves the metallic type of the charge transport in them.

The work [G.Blatter, et.al, *Reviews of Modern Physics* 1994, v. 66, No. 4, p.p. 1125 – 1380] considers the models of Abrikosov vortexes behavior in HTS and the following types of their pining: $\delta T_C$ pinning (in the areas of fluctuation of critical temperature, $T_C$) and $\delta l$ pinning (in the areas of fluctuation of free path length, $l$), their combinations. The partial input of $\delta T_C$ and $\delta l$ into collective pinning was estimated based on the determination of temperature dependence $B_{SB}(T)$ from $J_C(B)$ temperature dependences using equation $B_{SB}(T) = P_1 B_{SB}^{T_C} + P_2 B_{SB}^{l}$, where $B_{SB}$ is the field in which replacement of single vortex pinning for pinning of small vortex bundle takes place.
The estimated contributions in pinning were:
1- \( P_1=0.5, P_2=0.5 \);
2- \( P_1=0.2, P_2=0.8 \);
3- \( P_1=0.7, P_2=0.3 \);
4- \( P_1=0.6, P_2=0.4 \);
5- \( P_1=0.4, P_2=0.6 \)

\((P_1 - \delta-T_C; P_2 - \delta-l)\)

1 – film as deposited in Ar from \( \text{MgB}_2 \) target (Type 1),
2 – the same film after repeated annealing in vacuum (Type 3);
and
3-5 - bulk \( \text{MgB}_2 \) high-pressure (2 GPa, 1 h) synthesized at 1050, 800 and 600 °C, respectively;

It has been shown that for attaining maximal \( J_C \) in low and medium magnetic fields in bulk \( \text{MgB}_2 \) the most effective is \( \delta-T_C \) pinning or combined \( \delta-T_C \) (dominant) with \( \delta-l \). For attaining high \( J_C \) in high magnetic fields the \( \delta-l \) pinning should be prevailed in bulk \( \text{MgB}_2 \). For nanocrystalline oxygen-containing films the increase of \( J_C \) in low and high magnetic fields correlates with increase of \( \delta-T_C \) pinning contribution. Films with combined type of pinning with equal partial contributions of \( \delta-T_C \) and \( \delta-l \) \((P_1=P_2=0.5)\) demonstrate the \( J_C(0 \text{ T})=1.8\times10^7 \text{ A/cm}^2 \) and \( J_C(5 \text{ T})=2\times10^6 \text{ A/cm}^2 \) at 10 K.
High-pressure (2 GPa, 800 °C, 1 h) treated wire from MgB$_2$

Panorama of MgB$_2$ filament after high pressure-high temperature treatment

**MgB$_2$ filaments**

**MgB$_2$C$_{0.2}$O$_{0.09}$**

**MgB$_{2.2}$C$_{0.7}$O$_{1.1}$**

**Ni, Ni$_2$Nb, Nb**

**Cover**
HPA cylinder-piston (V_p = 6300 cm^3)  P = 1-2 GPa,
T = 600-1100 °C, Press ASEA 140 MN effort

Items from MgB_2

D 150 mm

D 40 mm x 30 mm
MgB$_2$-based superconductors

working temperature 20-30 K

1-4, 8, 9 - High pressed (2 GPa); 5 – HIP (0.1 GPa); 7- Hot Pr. (30 MPa)
Conclusions

- The comparison of nanostructures of MgB$_2$ oxygen-containing thin film (with thickness of 140 nm) and highly dense oxygen-containing bulk materials demonstrating high SC performance gave us reasons to conclude that critical current density, $j_c$, of MgB$_2$–based materials to high extent depends on distribution of admixture oxygen what can be regulated by manufacturing conditions and by synthesis temperature, in particular.

- The higher $j_c$ of MgB$_2$ thin films as compared to bulk was explained by the higher density of finer oxygen-enriched Mg-B-O inhomogeneities in the film structure.

- The results of calculations of the electron density of states in MgB$_2$, MgB$_{1.75}$O$_{0.25}$, MgB$_{1.5}$O$_{0.5}$ and MgBO showed that all the compounds are conductors with metal-like behavior with maximum for MgB$_{1.5}$O$_{0.5}$ (what it is even higher than for oxygen-free MgB$_2$).

- The stoichiometry of the matrix of bulk MgB$_2$ materials having high SC performance was about MgB$_{2.2-1.7}$O$_{0.4-0.6}$ (according to Auger quantitative analysis), i.e. very near to the composition with calculated highest DOS: MgB$_{1.5}$O$_{0.5}$. The introduction of high amount of oxygen into MgB$_2$ structure cannot dramatically reduce material’s $T_c$ and allows obtaining high $j_c$.

- Films with combined type of pinning with equal partial contributions of $\delta$-$T_c$ and $\delta$-$l$ ($P_1 = P_2 = 0.5$) demonstrate the $J_C(10\text{K}, 0 \text{T}) = 1.8 \times 10^7 \text{ A/cm}^2$ and $j_c(10\text{K}, 5 \text{T}) = 2 \times 10^6 \text{ A/cm}^2$ at 10 K.
Thank you for your kind attention!
Estimation of MgB$_2$ density

Table 2. Characteristics (critical current density-$j_c$, maximal pinning force-$F_{p_{(max)}}$, amount of MgB$_2$, MgO and MgB$_4$ estimated from Rietveld refinements, and density-$\rho$) of MgB$_2$-based materials prepared under different $P$-$T$ conditions from Mg and B taken in MgB$_2$ stoichiometry or from MgB$_2$ powder using different methods: under high quasi-hydrostatic pressure – HP, by hot pressing HotP, by spark plasma sintering – SPS, by pressureless sintering under 0.1 MPa of Ar – PL.

<table>
<thead>
<tr>
<th>No</th>
<th>Preparation</th>
<th>Type of B</th>
<th>$P$, MPa</th>
<th>$T$, $^\circ$C</th>
<th>$j_c$, MA/cm$^2$</th>
<th>$F_{p_{(max)}}$, $10^9$(N/m$^3$) at 0-1 T, at 20 K</th>
<th>MgB$_2$/MgO/MgB$_4$, wt%</th>
<th>Density, $\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>in-situ, HP</td>
<td>I</td>
<td>2000</td>
<td>1050</td>
<td>0.9 – 0.7</td>
<td>7.6</td>
<td>94/6/0</td>
<td>99%</td>
</tr>
<tr>
<td>2.</td>
<td>in-situ, HP</td>
<td>I</td>
<td>2000</td>
<td>800</td>
<td>0.2 – 0.15</td>
<td>1.6</td>
<td>91/5.5/0</td>
<td>98%</td>
</tr>
<tr>
<td>3.</td>
<td>in-situ, HP</td>
<td>III</td>
<td>2000</td>
<td>1050</td>
<td>0.4 – 0.3</td>
<td>2.3</td>
<td>87/13/0</td>
<td>99%</td>
</tr>
<tr>
<td>4.</td>
<td>in-situ, HP</td>
<td>III</td>
<td>2000</td>
<td>1000</td>
<td>0.36-0.23</td>
<td>2.4</td>
<td>86/14/0</td>
<td>99%</td>
</tr>
<tr>
<td>5.</td>
<td>in-situ, HP</td>
<td>III</td>
<td>2000</td>
<td>950</td>
<td>0.3 – 0.2</td>
<td>2.1</td>
<td>-</td>
<td>98%</td>
</tr>
<tr>
<td>6.</td>
<td>in-situ, HP</td>
<td>III</td>
<td>2000</td>
<td>900</td>
<td>0.12 – 0.06</td>
<td>1.1</td>
<td>71/13/0</td>
<td>98%</td>
</tr>
<tr>
<td>7.</td>
<td>in-situ, HP</td>
<td>III</td>
<td>2000</td>
<td>800</td>
<td>0.12 – 0.07</td>
<td>0.8</td>
<td>73/12/0</td>
<td>97%</td>
</tr>
<tr>
<td>8.</td>
<td>in-situ, HP</td>
<td>II</td>
<td>2000</td>
<td>600</td>
<td>0.14 – 0.05</td>
<td>0.6</td>
<td>64/30/0</td>
<td>83%</td>
</tr>
<tr>
<td>9.</td>
<td>in-situ, SPS</td>
<td>III</td>
<td>50</td>
<td>1050</td>
<td>0.5 – 0.4</td>
<td>4.6</td>
<td>83/4.5/12.5</td>
<td>94%</td>
</tr>
<tr>
<td>10.</td>
<td>in-situ, SPS</td>
<td>III</td>
<td>50</td>
<td>800</td>
<td>0.4 – 0.36</td>
<td>2.7</td>
<td>-</td>
<td>74%</td>
</tr>
<tr>
<td>11.</td>
<td>ex-situ, SPS</td>
<td>-</td>
<td>50</td>
<td>1050</td>
<td>0.4 – 0.3</td>
<td>3.3</td>
<td>83/6.5/10.5</td>
<td>96%</td>
</tr>
<tr>
<td>12.</td>
<td>in-situ, HotP</td>
<td>III</td>
<td>30</td>
<td>1050</td>
<td>0.08 – 0.016</td>
<td>0.2</td>
<td>46/8.5/45.5</td>
<td>99%</td>
</tr>
<tr>
<td>13.</td>
<td>in-situ, HotP</td>
<td>III</td>
<td>30</td>
<td>800</td>
<td>0.3-0.2</td>
<td>0.6</td>
<td>-</td>
<td>72%</td>
</tr>
<tr>
<td>14.</td>
<td>in-situ, PL</td>
<td>IV</td>
<td>0.1</td>
<td>800</td>
<td>0.08-0.03</td>
<td>1.9</td>
<td>90/10/0</td>
<td>55%</td>
</tr>
<tr>
<td>15.</td>
<td>in-situ, PL</td>
<td>III</td>
<td>0.1</td>
<td>600</td>
<td>0.26-0.13</td>
<td>1.3</td>
<td>94.5/5.5/0</td>
<td>65%</td>
</tr>
</tbody>
</table>

Cold dens. 2 GPa, PL
Estimation of grain sizes in MgB$_2$

The average crystallite sizes were calculated from line broadening in X-ray diffraction pattern by the standard program in accordance with the following:

$$\text{Crystallite size} = \frac{K \cdot \lambda}{W_{\text{size}} \cdot \cos \theta} \quad \text{with} \quad W_{\text{size}} = W_b - W_s$$

where $W_{\text{size}}$ is the broadening caused by small crystallites; $W_b$ is the broadened profile width; $W_s$ is the standard profile width (0.08 °); $K$ is the form factor; $\lambda$ is the wavelength.

Table. Critical current density, $j_c$, vs. relative average grain size of crystallites of high-pressure sintered from MgB$_2$ and synthesized from Mg and B taken in 1:2 ratio materials

<table>
<thead>
<tr>
<th>High pressed at 2 GPa for 1 h at $T_s$, °C</th>
<th>average crystal sizes</th>
<th>lattice parameters</th>
<th>$j_c$, kA/cm$^2$ at 10 K</th>
<th>$j_c$, kA/cm$^2$ at 20 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a$ (nm)</td>
<td>0 T 1 T</td>
<td>0 T 1 T</td>
</tr>
<tr>
<td>From MgB$_2$ (10 μm and 0.8 % of O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>19.7 nm</td>
<td>0.30805 0.35188</td>
<td>- -</td>
<td>- -</td>
</tr>
<tr>
<td>800</td>
<td>18.8 nm</td>
<td>0.30822 0.35212</td>
<td>- -</td>
<td>- -</td>
</tr>
<tr>
<td>900</td>
<td>18.5 nm</td>
<td>0.30820 0.35208</td>
<td>56 14</td>
<td>36 8</td>
</tr>
<tr>
<td>1000</td>
<td>25.0 nm</td>
<td>0.30797 0.35200</td>
<td>28 8</td>
<td>19 5</td>
</tr>
<tr>
<td>From Mg chips and B (4 μm, 1.5 % O) mixed and milled in 1:2 ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>15.0 nm</td>
<td>0.30747 0.35188</td>
<td>245 142</td>
<td>138 79</td>
</tr>
<tr>
<td>900</td>
<td>21.0 nm</td>
<td>0.30819 0.35174</td>
<td>205 136</td>
<td>128 61</td>
</tr>
<tr>
<td>1000</td>
<td>37.0 nm</td>
<td>0.30808 0.35192</td>
<td>485 364</td>
<td>360 237</td>
</tr>
</tbody>
</table>
Estimation of connectivity, $A_F$

$A_F = \frac{9 \mu\Omega \cdot cm}{\rho_{300} - \rho_{40}}$

$\rho = \frac{V \cdot \sigma}{I \cdot \Delta l}$

$\rho_{300} = \frac{V_{300} \cdot \sigma}{I \cdot \Delta l}$  \quad $\rho_{40} = \frac{V_{40} \cdot \sigma}{I \cdot \Delta l}$

$\Delta l$ - distance between voltage contacts
$\sigma = a \cdot b$ - cross-section area of the sample, $a \cdot b \cdot c$ - sample dimensions
$V_{300}$ - arithmetic average of all $V$ data at room temperature
$V_{40}$ – voltage at 40 K
$I = 100 \text{ mA}$ - current

$\rho$ - by four probe method

$\rho_{300}$, $\rho_{40}$ perfect connectivity for MgB$_2$
Identification of the dominant pinning mechanism from the peak position of pinning volume force:

\[ k = \frac{B_{\text{peak}}}{B_n} ; \]

\[ B_{\text{peak}} - F_p(\text{max}) ; B_n - \frac{F_p(\text{max})}{2} \]

The dominant pinning mechanism was determined from the volume pinning force \( j_c B \) according to a scaling procedure proposed by M. Eisterer, which eliminates the influence of the intrinsic anisotropy of MgB\(_2\) on the field dependence of the volume pinning force. The field \( B_{\text{peak}} \), where the maximum of the volume pinning force occurs, was normalized by the field \( B_n \), at which the volume pinning force drops to half its maximum (on the high field side), instead of the upper critical field, \( B_{c2} \), as in the original approach for isotropic superconductors. For typical values for the anisotropy (4) and the percolation threshold (0.25) in bulk MgB\(_2\) samples, the position of the peak, \( B_{\text{peak}}/B_n \), is expected to be at 0.34 and 0.47 for grain boundary and point pinning, respectively. Changes in the anisotropy and the percolation threshold only slightly change the peak position, in particular in the realistic range of these parameters. Another advantage of this scaling approach is that \( B_n \) is easily available and no separate experiment for determining \( B_{c2} \) or any extrapolation to estimate the irreversibility (or Kramer) field is necessary to define the scaling field.
X-ray diffraction patterns of the materials prepared from Mg:2B under 2 GPa for 1 h without additions at 800 °C (a) and 1050 °C (b) and with 10 wt. % Ti at 800 °C (c) and 1050 °C (d).

Synthesis temperature increase
With synthesis temperature increase the shift from grain boundary pinning towards point pinning occurs (about what k-ration increase witnessed)

Estimation of connectivity, $A_F$, amount of shielding fraction, $S$, and type of pinning, $k$.

<table>
<thead>
<tr>
<th>No</th>
<th>Preparation</th>
<th>Type of B</th>
<th>$P$, MPa</th>
<th>$T$, °C</th>
<th>$k = \frac{B_{\text{peak}}}{B_n}$</th>
<th>$A_F$, %</th>
<th>$S$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>in-situ, HP</td>
<td>I</td>
<td>2000</td>
<td>1050</td>
<td>0.43</td>
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<td>-</td>
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<td>2.</td>
<td>in-situ, HP</td>
<td>I</td>
<td>2000</td>
<td>800</td>
<td>0.37</td>
<td>-</td>
<td>-</td>
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<td>3.</td>
<td>in-situ, HP</td>
<td>III</td>
<td>2000</td>
<td>1050</td>
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<td>79</td>
<td>94</td>
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<td>4.</td>
<td>in-situ, HP</td>
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<td>2000</td>
<td>950</td>
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<td>59</td>
<td>81</td>
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<td>5.</td>
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<td>2000</td>
<td>800</td>
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<td>6.</td>
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<td>18</td>
<td>90</td>
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<td>7.</td>
<td>in-situ, SPS</td>
<td>III</td>
<td>50</td>
<td>1050</td>
<td></td>
<td>98</td>
<td>91</td>
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<td>8.</td>
<td>ex-situ, SPS</td>
<td>-</td>
<td>30</td>
<td>1050</td>
<td>-</td>
<td>80</td>
<td>100</td>
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<td>9.</td>
<td>in-situ, HotP</td>
<td>III</td>
<td>30</td>
<td>1050</td>
<td>-</td>
<td>32</td>
<td>-</td>
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<td>10.</td>
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<td>30</td>
<td>800</td>
<td>-</td>
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<td>-</td>
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<td>11.</td>
<td>in-situ, 2 GPa, PL</td>
<td>III</td>
<td>0.1</td>
<td>600</td>
<td>-</td>
<td>-</td>
<td>75</td>
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<td>12.</td>
<td>in-situ, 2 GPa, PL</td>
<td>III</td>
<td>0.1</td>
<td>800</td>
<td>-</td>
<td>-</td>
<td>84</td>
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CONTRADICTIONS BETWEEN X-RAY DATA AND SEM OBSERVATIONS

(a), (b) structures of the samples obtained by SEM in COMPOsitional contrast:
(a) sintered from MgB$_2$ at 2 GPa, 1000 °C, 1 h;
(b) synthesized from Mg and B taken into 1:2 ratio at 2 GPa, 800 °C, 1 h;
(c), (d) –X-ray patterns of the samples shown in Figs. 5a, b;
(e) dependences of critical current density, $j_c$, on magnetic fields, $\mu_0H$, at different temperatures of the samples shown in Fig. e: open symbols – sintered from MgB$_2$ material and solid symbols - synthesized from Mg and B taken in 1:2 ratio

Structure of MgB$_2$-based material synthesized from amorphous boron and magnesium chips taken in Mg:B=1:2 ratio in contact with Ta foil at 2GPa, 800° C, 1h (BEI SEM image) shows that inclusions of black phase with near MgB$_{12}$ stoichiometry may crystallize in hexagonal habit or have near hexagonal cross-section (see, for example, inclusion marked “A”)

Each of the following non-superconducting higher magnesium borides in the Mg-B system can crystallize in the MgB$_2$ matrix and can influence pinning:

- MgB$_4$
- MgB$_7$
- MgB$_{12}$
- MgB$_{17}$

The method of preparation (pressure-temperature-time conditions) can affect the stoichiometry of the MgB$_x$ inclusions in MgB$_2$. (2 GPa – MgB$_{12}$)
Typical structures of MgB$_2$ prepared at 0.1 MPa – 2 GPa at low temperatures (a) - 600-800 °C and high (b) -1000-1100 °C and their compositions

0.1 MPa – 2 GPa

“L“ - MgB$_{0.9-3.5}$O$_{1.6-2}$ white layers, thickness (15-20 nm)

Auger spectrum

“J” - MgB$_{0.5-0.8}$O$_{0.8-0.9}$ white inclusions
MgB$_{11-13}$O$_{0.2-0.5}$ black inclusions
MgB$_{2.2-1.7}$O$_{0.3-0.6}$ gray matrix.

Auger study by JAMP–9500F

Zone of excitation being 10 nm in diameter and two lattice parameters in depth etching in Ar allows to exclude analyzing of oxidized layer on the surface!
Auger study by JAMP–9500F
zone of excitation being 10 nm in diameter and two lattice parameters in depth
Mg(I):2B(III), 1200 °C, 2 GPa, 1h

Place of analysis
MgB\textsubscript{0.5-0.8}O\textsubscript{0.8-0.9} white inclusions
MgB\textsubscript{11-13}O\textsubscript{0.2-0.5} black inclusions
MgB\textsubscript{2.2-1.7}O\textsubscript{0.3-0.6} gray matrix.

Comparing these results with that of X-ray structure analysis we can conclude that boron incorporated into the MgB\textsubscript{2} structure.
Repeated etching in Ar (in the JAMP–9500F chamber during study) and quantitative Auger analysis showed practically the same oxygen concentration in MgB\textsubscript{2} matrix of the structure after 30 cycles, which points to the oxygen incorporation into the MgB\textsubscript{2} lattice.
The critical current density of MgB\textsubscript{2} - based materials usually increases at low and medium magnetic fields with increasing manufacturing temperature, but lower manufacturing temperatures can result in a $j_c$ increase at high magnetic fields.

A shift from grain boundary pinning to point pinning was observed.

A positive effect in enhancing the critical currents of MgB\textsubscript{2} is played, by dopants, such as Ti, for example.
MgB$_2$ for fault current limiter

Transformer-type fault current limiter (Budapest University of Technology and Economics)

At fault event an increase in the circuit current causes a growth of the current in a superconductor higher than the critical value. The SC-or passes into the resistive state introducing a required for limitation impedance in the circuit (2–4 ms and 1 ms).
Smart application of HP and hot-pressed MgB$_2$-based materials

Characteristics of the MgB$_2$-based material synthesized at 30 MPa, 800 °C, 2 h from amorphous boron (III) (H.C. Starck, 1.5 % O, 4 µm grains) and magnesium (I) taken in the MgB$_2$ stoichiometry and of the ring cut from this material:

Typical oscilloscope traces of the current (solid lines) and voltage drop across the primary normal-metal winding (dashed lines) at 4.2 K. Arrows show the quenching current. Voltage of source was 170 V (c) and 125 V (d); e) ring: outer diameter – 45 mm, height - 11.6 mm, wall thickness – 3.3 mm.

Quenching current 24000 A. $j_c = 63200$ A/cm$^2$.

At 125 V losses till quenching are about 17 J. Power of the losses is about 200 W.
Experimental HTS Motor for 20 K Temperature

Cross-section of HTS Motor

General View of HTS Motor

Compound HTS-Ferromagnetic Rotor With YBCO Bulk Elements

General View of YBCO Samples

Rotor With YBCO Bulks

Compound HTS-Ferromagnetic Rotor With MgB2 Bulk Elements

General View of MgB2 Bulk Samples

Rotor With MgB2 Samples

Test results of reluctance motor with MgB2 blocks

Temperature: $T = 15 \ldots 20\ \text{k}$

Phase voltage: $U = 120\ \text{V}$

- efficiency, ○ - output power, ▲ - power factor

Test results of reluctance motor with YBCO blocks

Temperature: $T = 15 \ldots 20\ \text{k}$

Phase voltage: $U = 120\ \text{V}$

Phase voltage: $U = 160\ \text{V}$

Phase voltage: $U = 210\ \text{V}$

Phase voltage: $U = 215\ \text{V}$

- efficiency, ○ - output power, ▲ - power factor
Conclusions

- The distribution of nanostructural inhomogeneities, such as areas with a high concentration of B and impurity O, plays a key role in the variation of $j_c$ in MgB$_2$ materials.
- Auger and SEM studies show that with increasing manufacturing temperature oxygen enriched 15-20 nm thick nano-layers transform into distinct dispersed Mg-B-O inclusions.
- In parallel, the Ti addition results in a further increase in $j_c$, because Ti fosters the localization (or segregation) of oxygen and of higher magnesium borides and facilitates the formation of a homogeneous MgB$_2$ matrix with low oxygen content, but with Mg-B-O and MgB$_x$ pinning centers.
- At low synthesis temperature Ti can absorb hydrogen forming titanium hydrides, thus preventing the formation of MgH$_2$ and promoting the material densification.
- The positive effect of Ti addition results from the high ability of Ti to absorb H, O, and Mg.
Experimental

2 GPa - HP, 30 MPa- HotP, 50 MPa – SPS, 0.1 MPa Ar - PL

Initial materials

(I) *in-situ* from Mg:B=1:2 (MgB₂), from Mg:B=1:7 and 1:12 mixing and milling in a high speed activator for 3-5 min

✓ Boron (B) amorphous

**Characteristics of initial boron powders.**

<table>
<thead>
<tr>
<th>Type of B</th>
<th>Grain size</th>
<th>O, wt%</th>
<th>C, wt%</th>
<th>N, wt%</th>
<th>H, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>&lt;5 μm</td>
<td>0.66</td>
<td>0.31</td>
<td>0.48</td>
<td>0.32</td>
</tr>
<tr>
<td>II</td>
<td>&lt;1 μm</td>
<td></td>
<td>3.5</td>
<td>1.02</td>
<td>0.87</td>
</tr>
<tr>
<td>III</td>
<td>4 μm</td>
<td>1.5</td>
<td>0.47</td>
<td>0.40</td>
<td>0.37</td>
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</tbody>
</table>

✓ Magnesium (Mg)

Mg(I) turning (Technical Specifications of Ukraine 48-10-93-88)

Mg(II) powder 325 mesh (HyperTec, USA)

(II) *ex-situ* from MgB₂ powder

✓ Magnesium diboride (98% purity)