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Structure and properties of MgB_2 bulks, thin films and wires; effect of TiO_2 and TiC additions

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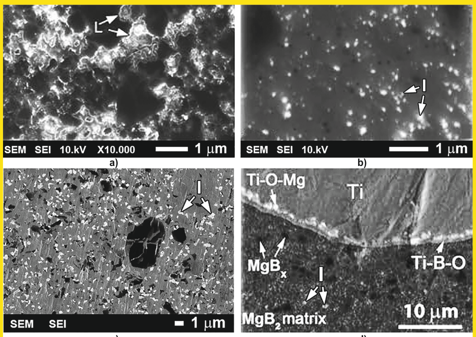
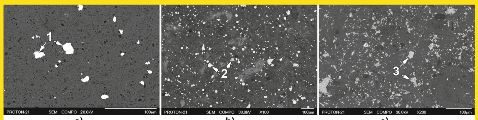
An x-ray analysis of MgB_2-based materials shows that they contain MgB_2 and MgO phases. According to a quantitative Auger analysis (taken after removing the oxidized surface layer by Ar ion etching in the microscope chamber) the MgB_2 phase contains some amount of oxygen that approximately corresponds to the composition $MgB_{2.2-1.7}O_{0.4-0.6}$. Rietveld refinement of the MgB_2 phase, based on EDX data with varying B/O content, leads to the composition $MgB_{1.68-1.8}O_{0.2-0.32}$. Ab-initio modelling of boron substitution by oxygen in MgB_2 (ΔH_f =-150.6 meV/atom) shows that this is energetically favourable up to the composition $MgB_{1.75}O_{0.25}$ (ΔH_f =-191.4 meV/atom). In contrast to oxygen substitution even very small amounts of carbon atoms in the MgB_2 structure can dramatically affect the superconducting characteristics causing essential changes in the electron density distribution. The formation of vacancies at the Mg site of both MgB_2 and substituted $MgB_{1.75}O_{0.25}$ was modelled as well, but has shown that such processes are energetically disadvantageous (ΔH_f of $Mg_{0.875}B_2$ and $Mg_{0.75}B_{1.75}O_{0.25}$ are equal to -45.5 and -93.5 meV/atom).

The experimental study of the structures (using SEM and Auger spectroscopy) and of the superconducting characteristics (J_c, B_{irr}, B_{c2}, T_c) of highly dense MgB_2-based materials (high pressure-high temperature synthesized) with additions of polyvalent titanium oxides, titanium carbide or titanium allows us to conclude that magnesium diffuses into the grains of additions during synthesis, which affects the redistribution of boron and of admixed oxygen in the superconducting matrices and thus provides pinning due to the formation of higher magnesium borides or oxygen enriched inclusions (containing Mg, B and O). The materials with additions of polyvalent titanium oxides, synthesized at 800 °C, and of titanium, synthesized at 1050 °C, showed an essential increase of B_{c2} and H_{irr} (but in the latter case B_{c2} and H_{irr} were somewhat lower). The TiC additions practically did not affect the critical magnetic fields of the material synthesized at 800 °C, possibly due to the diffusion of carbon into the matrix, while T_c and RRR were still high. The intensity of Mg diffusion into Ti-O or TiC grains is higher than that into Ti grains. Thus, in order to obtain high B_{irr} and B_{c2} in the case of Ti addition higher synthesis temperature (of about 1050 °C) and in the case of Ti-O lower (of about 800 °C) are to be used.

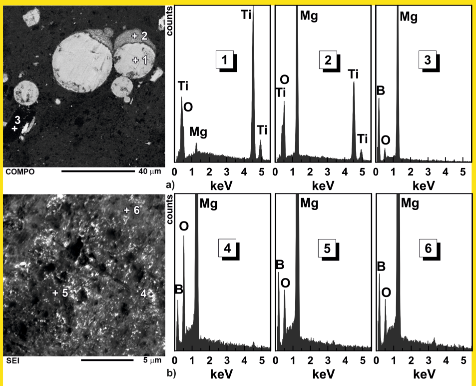


Structures (obtained by SEM in SEI regime) of MgB_2-based materials synthesized from Mg:2B at 2 GPa for 1h : (a) without additions at 800 °C; (b) with 10 wt% of Ti at 800 °C; (c, d) with 10 wt% of Ti at 1050 °C (different places under different magnifications). "L"- oxygen-enriched layers, "I" – oxygen-enriched inclusions, "MgB_x" – inclusions of higher magnesium borides with x>>2.

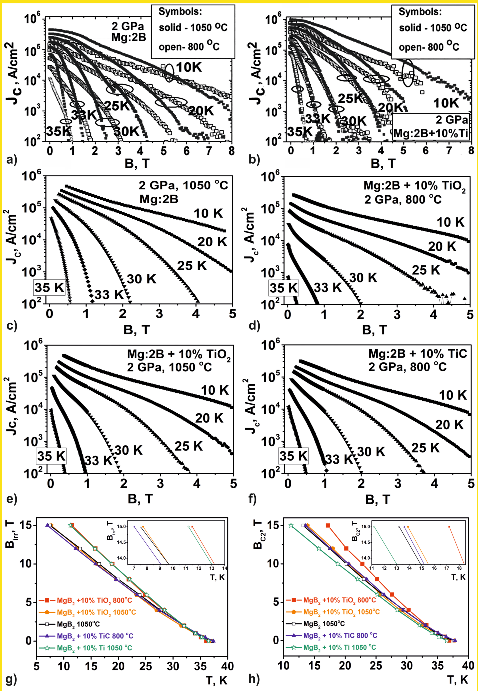


Structures of MgB_2-based materials (obtained by SEM in COMPO or BEI) synthesized from Mg:2B at 2 GPa at 800 °C for 1h: (a) - with 10 wt% of Ti (1); (b) - with 10 wt% of Ti-O (2) and (c) – with 10 wt% of TiC (3).

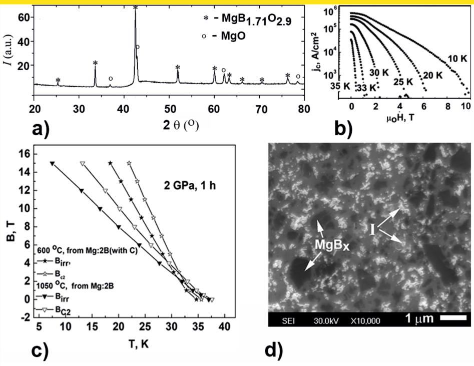
Initial mixture, preparation	Matrix	Black inclusions	Oxygen-enriched areas	Grains of additions
Mg:2B+(Ti-O), 2 GPa, 800 °C, 1 h	$MgB_{1.65}O_{0.22}$	$MgB_6O_{0.37}$	$MgB_{1.7}O_{0.4}$	$TiO_{0.8}C_{0.05}Mg_{0.02}$
Mg:2B+(Ti-O), 2 GPa, 1050 °C, 1 h	$MgB_{2.6}O_{0.1}$	$MgB_{6.4}O_{0.13}$	did not estimated	$TiO_{0.98}Mg_{0.5}$ – $TiO_{1.05}Mg_{0.8}$
Mg:2B+TiC, 2 GPa, 800 °C, 1 h	$MgB_{1.6}O_{0.34}$ – $MgB_{1.7}O_{0.47}C_{0.13}$	$MgB_{7.2}O_{0.18}$	did not estimated	$TiC_{0.63}Mg_{0.02}$



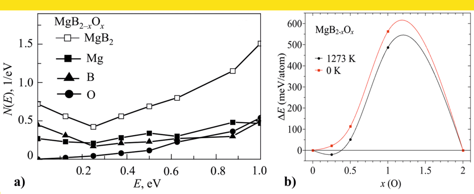
(a, b) -Structures (SEM, SEI and COMPO or BEI) and EDX spectra of the phases found in MgB_2-based material with Ti-O additions synthesized at 2 GPa, 1050 °C for 1 h. These phases are marked in the images by 1-6 and appeared with different colors.



Characteristics of magnesium diboride-based materials synthesized from Mg:2B at 2 GPa, for 1 h at different temperatures without and with additions of polyvalent titanium oxides (Ti-O), titanium (Ti) or titanium carbide (TiC). (a-f) – Critical current density, J_c, vs. magnetic field, $_oH$, of MgB_2-based materials without additions (a and c), with 10% of Ti (b) , with 10% TiO_2 (d, e), with 10% TiC (f) synthesized at 800 and 1050 °C (g, h) – fields of irreversibility, B_{irr} (g), and upper critical magnetic fields, B_{c2} (h), vs. temperature for MgB_2-based materials.



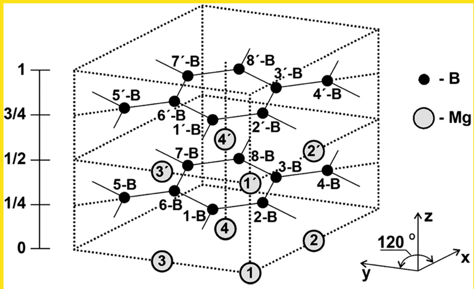
(a) - X-ray diffraction pattern, (b) – dependence of critical current densities, J_c, on magnetic field, μ_0H, at 10, 20, 25, 30, 33, 35 K and (d) - SEM (SEI mode) structure of the material synthesized at 2 GPa, 1050 °C for 1 h from Mg:2B mixture (approximate composition according to the quantitative Auger analysis: matrix – $MgB_{2.2-1.7}O_{0.4-0.6}$, "I" – oxygen enriched inclusions appear brightest - $MgB_{0.6-0.8}O_{0.8-0.9}$; and the boron enriched inclusions "MgB_x" appear darkest – $MgB_{5.1-13}O_{0.02-0.06}$); (c) - dependence of the upper critical magnetic field (B_{c2}) and of the irreversibility field (B_{irr}) of MgB_2-based materials synthesized at 2 GPa for 1h: at 600 °C from Mg:2B (amorphous, contained 3.5 wt% of C) and 1050 °C from Mg:2 B (amorphous, contained 0.47 wt% of C).



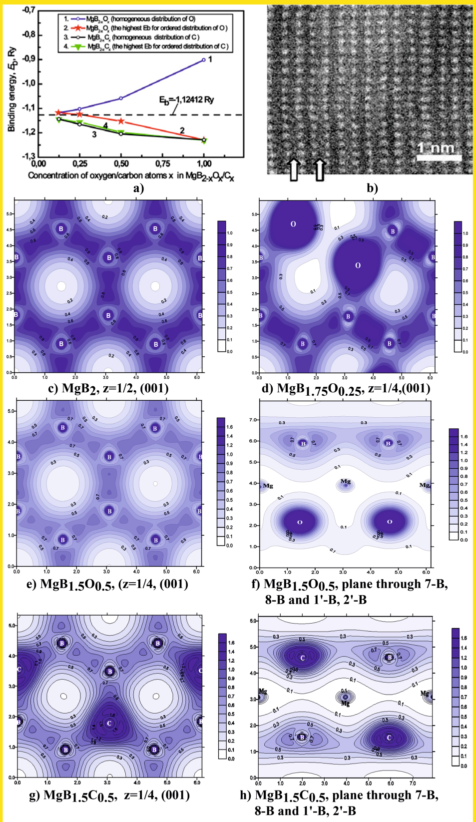
(a) Calculated DOS at the Fermi level N(EF) as a function of the oxygen concentration x in $MgB_{2-x}O_x$ compounds. Common DOS and partial contributions of Mg, B and O atoms;
(b) Results of Gibbs energy calculations for $MgB_{2-x}O_x$. For calculation of Gibbs energy two methods were used: full potential and psevdopotential. At 1273 K for X = 0.25 in $MgB_{2-x}O_x$ a deviation from an ideal behavior of Gibbs potential has been observed. It indicates that there is a solid solution of oxygen in MgB_2. When concentration of oxygen is big there exists two- or three-phase region. In the case of $MgB_{1.5}O_{0.5}$ the transition to lower symmetry takes place and the hexagonal structure destroys.

Calculated enthalpies of formation of MgB_2, MgO, $Mg_{1-x}B_2$, and $MgB_{2-x}O_x$

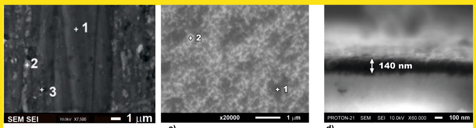
No	Compound	Enthalpy of formation, ΔH_f (meV/atom)
1	MgB_2	-150.6
2	$Mg_{0.875}B_2$	-45.5
3	$Mg_{0.75}B_2$	+74.6
4	$Mg_{0.75}B_{1.75}O_{0.25}$	-93.5
5	$MgB_{1.75}O_{0.25}$	-191.4
6	$MgB_{1.5}O_{0.5}$	-162.6
7	MgO	-2719.7
8	$MgO_{0.5}B_{0.5}$	-82.0



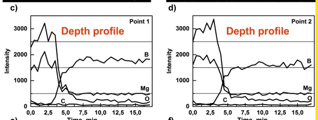
Scheme of MgB_2-2´2´2 supercell.
Boron positions are depicted as black small circles, Mg positions under consideration as gray big circles.
Mg positions are marked as 1, 2, 3, 4 and 1', 2', 3', 4' for z=0 and for z=1/2, respectively.
Boron positions are denoted as 1-B, 2-B, 3-B, 4-B, 5-B, 6-B, 7-B, 8-B and 1'-B, 2'-B, 3'-B, 4'-B, 5'-B, 6'-B, 7'-B, 8'-B for z=1/4 and for z=3/4, respectively.



(a) - Dependence of the binding energy, E_b, on the oxygen concentration, x, in $MgB_{2-x}O_x/C_x$: 1, 3- homogeneous oxygen and carbon substitutions for boron atoms, respectively; 2, 4 - the lowest binding energy for each x in the case of ordered oxygen and carbon substitutions (for example, in the nearby positions or in pairs), respectively; (b) - Z - contrast image of coherent oxygen-containing inclusions in MgB_2 [010] bulk. Bright atoms - Mg. The contrast increases in each second row and is due to the presence of oxygen in each second boron plane. The white arrows show the columns of atoms in which oxygen is present; (c) - (h) - maps of electron density distribution for: (c) - MgB_2 (z=1/2, (001)), (d) - $MgB_{1.75}O_{0.25}$ (z=1/4,(001)), (e) - $MgB_{1.5}O_{0.5}$ (z=1/4, (001)); z- coordinates of the plane of a 222 supercell, where z is given in units of the c parameter of a 222 MgB_2 supercell; (g) – $MgB_{1.5}C_{0.5}$ (z=1/4, (001)) z- coordinates of the plane of a 222 supercell, where z is given in units of the c parameter of a 222 MgB_2 supercell; (f, h) – map of the electron density distribution for $MgB_{1.5}O_{0.5}$ and $MgB_{1.5}C_{0.5}$, respectively, in the transversal plane under an angle to the basal boron planes of the hexagonal unit cell, in order to show the boron plane without imbedded oxygen atoms together with the Mg plane (i.e., the plane which goes through 7-B, 8-B and 1'-B, 2'-B positions of a 222 supercell) .



MgB_2 Hypertech raw wire in Ni-Nb coating after treatment at 800 °C, 2 GPa, 1 h
Average compositions in the points:
1 – $MgB_2O_{0.08}C_{0.2}Nb_{0.007}$ (core matrix),
2 – $MgB_{1.8-1.7}O_{1.2-0.78}C_{0.5}Nb_{0.004-0.008}$ (white inclusions),
3 – $MgB_{2.4}O_{0.08}C_{0.15}Nb_{0.004}$ (the darkest inclusions)



Film was deposited on the (0001) plane of sapphire substrate at room temperature by magnetron sputtering of MgB_2 target synthesized by hot pressing and then annealed at 640 °C for 5 min at 10 Pa of Ar by heating the substrate.