High gas pressure technology in practical use for MgB_2 applications

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Abstract. We report the effect of high gas pressure, up to 1 GPa of argon, annealing on the polycrystalline and single crystal samples of MgB_2 doped with nano-crystalline C, SiC and MgO additions.
The annealing temperature was in the range from 700 to 950 ^oC in the case of solid state diffusion process and up to 1700 ^oC in the case of liquid phase recrystallization and crystal growth of the doped single crystals.
By using XRD, SIMS and SEM we investigated the growth mechanism. It was observed that the samples doped with nano-sized powder of C, SiC and MgO showed a significantly enhancement of flux pinning effect, and by this way improved critical current, especially under high magnetic field over several thousand A/cm^2 at 8 T and 4,2 K.
The effect of the grain size of the doped elements on the superconducting parameters is shown and discussed. Some practical observations and conclusions for the future applications of the polycrystalline and single crystal materials in wires, tapes and bulk crystals are presented from the point of view of obtained results. The high gas pressure technology was found to be very promising one in the MgB_2 superconductors applications.

1. Introduction

MgB_2 is such a new material [1] which, just like all other superconducting materials, requires multi-disciplinary expertise (in basic material science, chemistry, physics and electrical engineering) to be developed into a technical conductor for use in a wide range of areas. For a superconductor, "extreme conditions" are defined in terms of current density, magnetic field and temperature i.e. transport parameters of superconductivity .

Although prototype MgB_2 conductors have already demonstrated the potential of the material, there is still considerable scope for performance enhancement in two respects: magnetic flux line pinning and thermal stability.

The magnetic field at which moving of the flux appears, can be increased by introducing pinning centres in the material, regions of modified electronic properties on a nano-metre scale which trap magnetic flux lines.

Thermal stability is related to the maximum current that a superconducting filament can carry. When the current becomes too high, j_c fluctuations on a micro-metre scale cause localised dissipation. Such hot-spots can grow and drive the whole wire non-superconducting.

In MgB_2, H_{irr} is typically about half of H_{c2}, so that lack of flux pinning seriously limits the material's performance.

However, this limitation can be overcome. Proton or neutron irradiation creates nanoscale amorphous regions in the MgB_2 crystal structure, which act as artificial pinning centres, trapping magnetic flux lines and enhancing j_c in high magnetic field significantly. These proof-of-principle results have been reproduced with scaleable metallurgical techniques, by introduction of nano-sized particles of Y_2O_3, MgO, TiB, SiC or diamond, which enhances the irreversibility field H_{irr} of MgB_2 powders substantially (by ~ 60 % in the case of SiC and diamond), e.g. [2,3].

Even more dramatic improvements are reported in Mg- and O-rich thin films, where the irreversibility field increased from 7 to 14 T at $T = 4.2$ K.

Finally, grain boundary pinning might also play an important role in MgB_2. In bulk samples with sufficiently small MgB_2 crystallites (~ 40 – 100 nm), the irreversibility field increases from $\mu_0 H_{irr} \approx 0.5\ \mu_0 H_{c2}$ to $\sim 0.8\ \mu_0 H_{c2}$. The starting powders for such fine-grained material are obtained through mechanical alloying, i.e. prolonged milling of a mixture of Mg and B powders [4].

Several methods to enhance magnetic flux pinning have been demonstrated, but in most cases the underlying mechanisms are not totally clear. In the case of nano-metric inclusions, for instance, the improved $j_c(H)$ behaviour could be due to direct core pinning, but also to smooth variations in the superconducting order parameter due to mechanical strain fields around the inclusions (so-called ΔT_c pinning).

MgB_2 offers certain advantages over both HTS and LTS superconducting materials.

By modifying the nano-structure of MgB_2 crystals, powders and bulk in a controlled way and correlating detailed structural and physical analysis of these materials, we try in our laboratory to identify individual pinning mechanisms and quantify their influence, by applying the high pressure high temperature technology.

The main goal of using HT-HP process is to apply very high strain to induce mechanical alloying (crystallites of 10–100 nm) sintering during the high deformation process of nano-particles of Mg and B by prolongated milling of the substrate.

The main advantages of such process are:

- greatly decreasing the temperature of annealing even below 600 ^{o}C,
- hot pressing and/or hot extrusion used for "one pass act technology" in obtaining superconducting wire,
- possibility to introduce to the bulk ceramics (i.e. wires or tapes) the pinning centers by doping of nano-scale hard inert particles (as SiC, BC, MgO or C) to enhance $\mu_o H_{irr}$ and therefore to increase j_c,
- sintering materials as a nano-crystals, growing them under high gas pressure to avoid the grain expansion and keeping the bigger particles inside serving as the inclusion and acting as pining centers.
- crystal growth of superconducting MgB_2 crystals with homogeneous distributions of inert inclusion dispersed as nano-crystals or amorphous material in it and acting as

nano-structural pining centers to enhance the transport parameters of superconductor.

2. Experimental procedures

2.1 High gas pressure in solid reactoin of MgB_2 bulk with Mg vapor

Taking account all the problems with the growth of MgB_2 we consider to use our high gas pressure trap system used previously for the HTc materials growth [5]. This system enabled us to isolate the several ccm of the Ar high pressure volume completely closed from the ambient at as high temperature as 1800 ^oC. The crucible was made from BN and had conical shape with diameter from 8 to 10 mm and length 70 mm. Outer diameter was 12 mm. At the equilibrium pressure on both sides of volumes in the range of 1.5 GPa the temperature was increased up to max. 1800 ^oC. The Mg vapour pressure was induced from the additionally magnesium placed in the crucible. At these conditions annealing of the pure boron or MgB_2 materials with the doping elements was performed at very high vapour pressure of magnesium. In all experiments MgB_2 powder made by Alfa Aesar was used.

The dopant materials were added by several methods:

- For carbon nano-sized grains, we use the method of mixing to the argon gas other hydro-carbide gas (propane or metan) which decomposes at high temperature in the closed volume space making very homogeneous gas mixture with the nano-size particles. The density of argon at such conditions is like water and its viscosity is high.
- For MgO particles, usually the MgB_2 materials with the MgO additions was used. The mixture was several days milled.
- For the SiC additives the nano-sized powders (from 9 up to 16 nm) were mixed and milled for several days with the apropriate amount of the MgB_2 powder.

2.2. High gas pressure in liquid phase grow of MgB_2 crystals from flux

As it was shown by Lee *et al.* [6], MgB_2 melts congruently at 2430 ^oC with Mg pressure over 65 bar. This makes practically impossible to grow crystals from the stoichiometric melt. For the temperature range from 650 ^oC to 1107 ^oC the liquid phase of Mg can be obtained in a closed crucible. At higher temperature the magnesium vapor pressure increase up to 60 bars at 1700 ^oC. This with the great reactivity of magnesium especially to oxygen makes almost impossibly the growth of pure crystals of MgB_2 phase. The most serious problem in MgB_2 synthesis is the formation of MgO phase.

Additionally, solubility of the MgB_2 phase in the Mg vapor even at such extremely high temperature is negligible, so it is no melt to grow the crystals from the liquid. Several fluxes were used for grow of MgB_2 i.e. Al, Ga, all without success. From the high pressure of Mg in the gas state it is possible to grow the layer of MgB_2. The experimental way is presented on the Fig.1.

For the liquid phase crystallization all dopants were additionally well mixed by the process itself at the temperature gradient and convection during melting of the MgB_2 materials. In our process performed with the specially prepared flux neither reaction, nor melting with the BN crucible was found. The inner surface of the BN crucible remained clean. The $MgNB_9$ phase was not found.

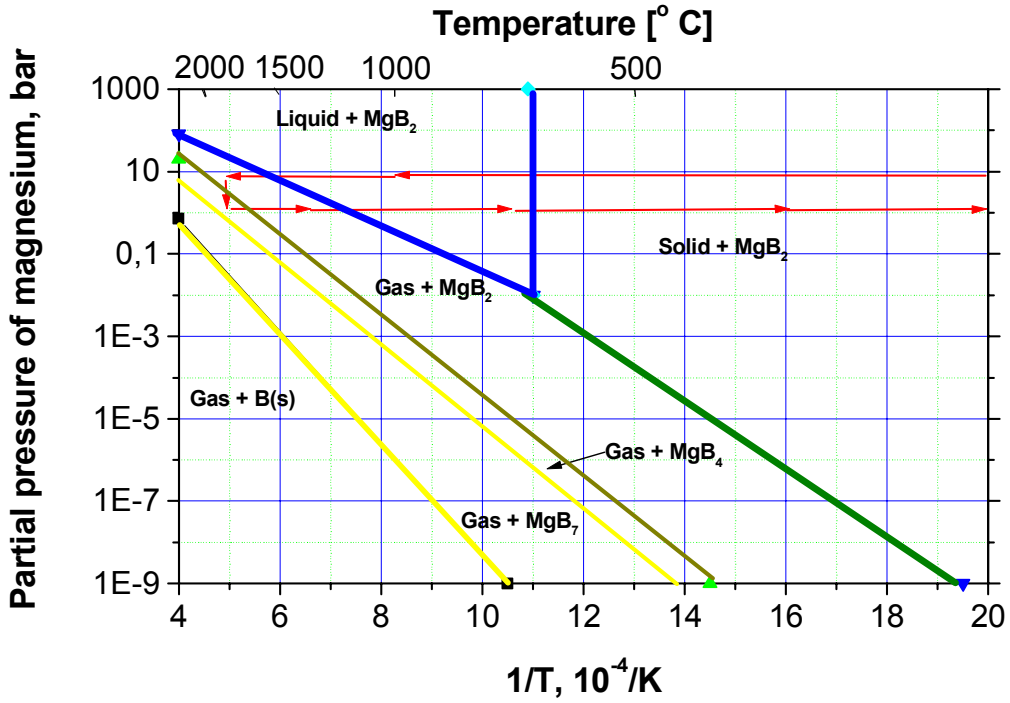

Figure 1. The phase diagram of Mg vapor pressure over Mg-B system is taken from the work of Liu *et al.* [7]. The red arrows show our experimental conditions adapted to the phase diagram.

3. Results

To determine the good conditions for growth of MgB_2 crystals the DTA measurement under high gas argon pressure was applied. To obtain the large single crystals the melt with the special additions was necessary. These experiments will be described elsewhere.

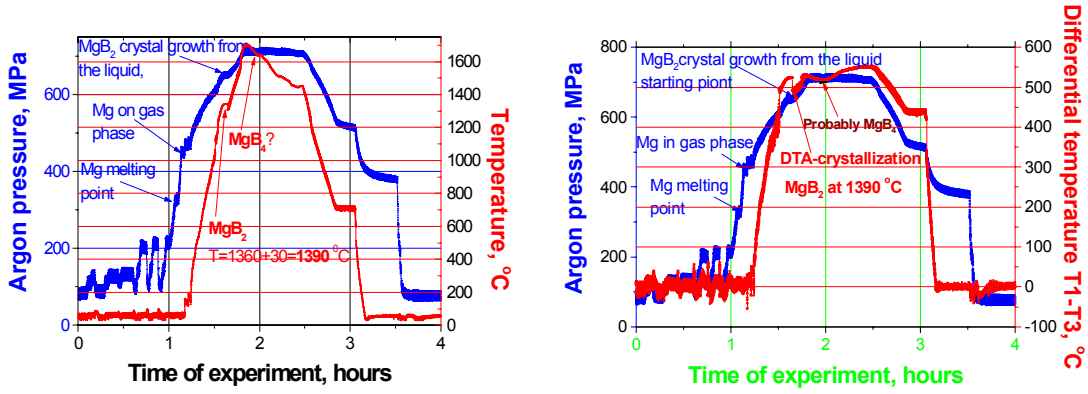

Figure 2. DTA results of MgB_2 single crystals growth from the liquid flux under high gas pressure in the vessel volume closed by the gas-trap system [5].

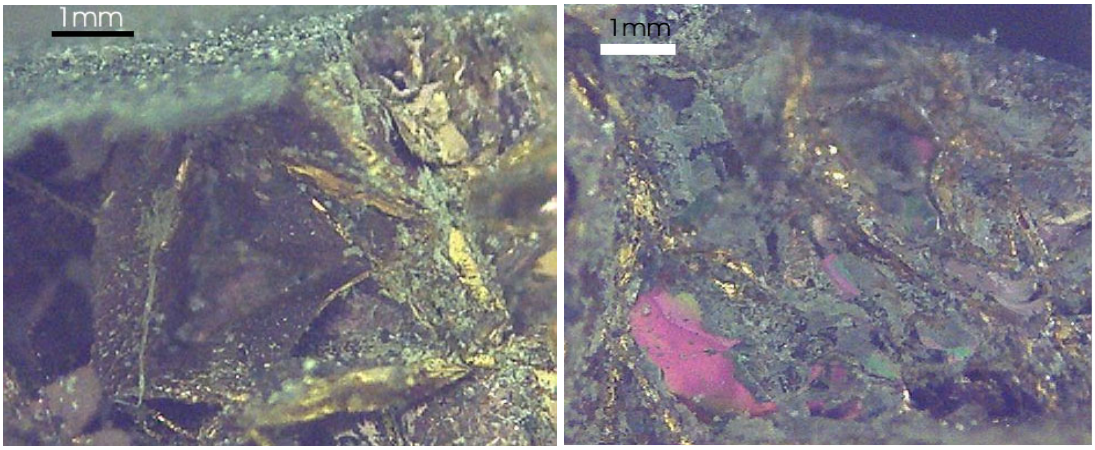

Figure 3. On the left: one of the optically isolated single crystals of MgB_2 obtained by the high gas pressure technology (3x2x0.3 mm) with the melted batch around. On the right: another batch with included single crystals of MgB_2, both obtained by the flux method. Images taken by optical micrscopy.

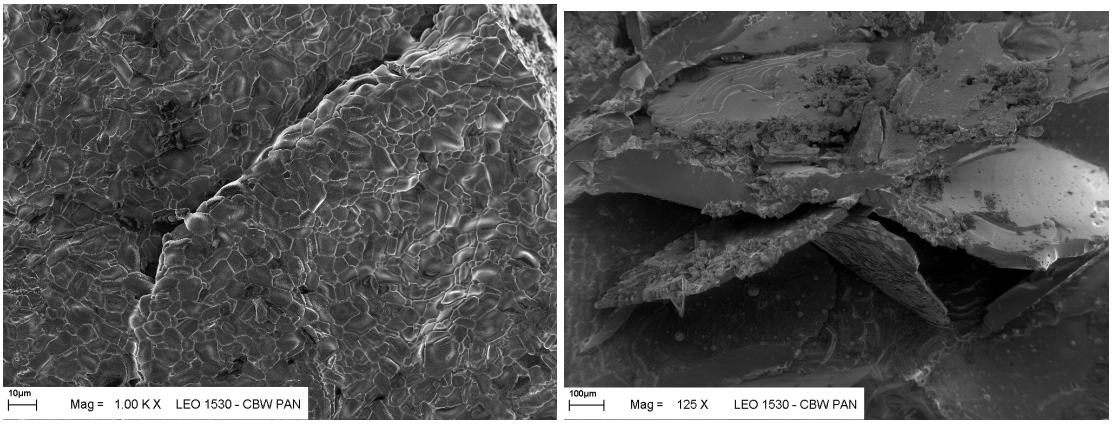

Figure 4. On the left: SEM micrograph of the polycrystalline sample of MgB_2 as obtained after high gas vapor crystallization without melt. On the right: SEM micrograph of the batch obtained by the flux method at high gas pressure of argon (1 GPa, 1700 ^{o}C).

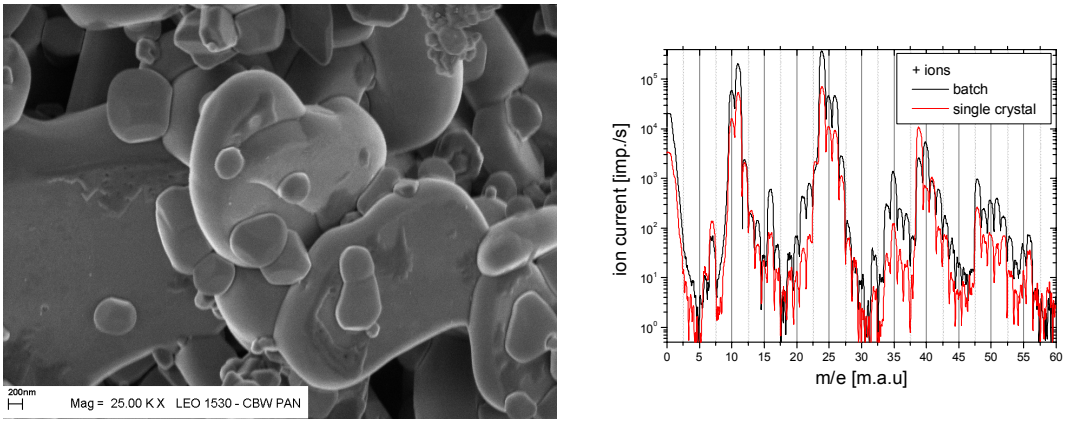

Figure 5. SEM micrograph of the polycrystalline sample of MgB_2 with 5% of SiC nano-powder, obtained by high gas pressure annealing in Mg vapor, and SIMS results for the single crystals obtained by flux high argon pressure method.

The crystals were measured by AC susceptometry as obtained so there are some differences among the obtained values. The sharp transitions in the temperature range of 32-33 K through 34-36 K, see Fig.6, visible within the imaginary part of the susceptibility curves, prove high superconducting properties of the samples.

As seen within the imaginary part of all susceptibility curves, there is the wide maximum near temperature 18 K, although it is not connected with the corresponding decrease in the real part of the susceptibility curve. The increase in the real part at temperature below 15 K may be caused with some, unknown, paramagnetic inclusions in the crystals.

The shape of the imaginary part of the susceptibility curves recorded for various field orientations indicates that T_c remains unchanged at 33 K, but height of the maximum differs, see Fig 6. The 17 K peak is the same for all crystal samples. From this initial search one may conclude that the anisotropy ratio is close to the published value, i.e. 2 through 8, depending on the temperature range and measurement mode.

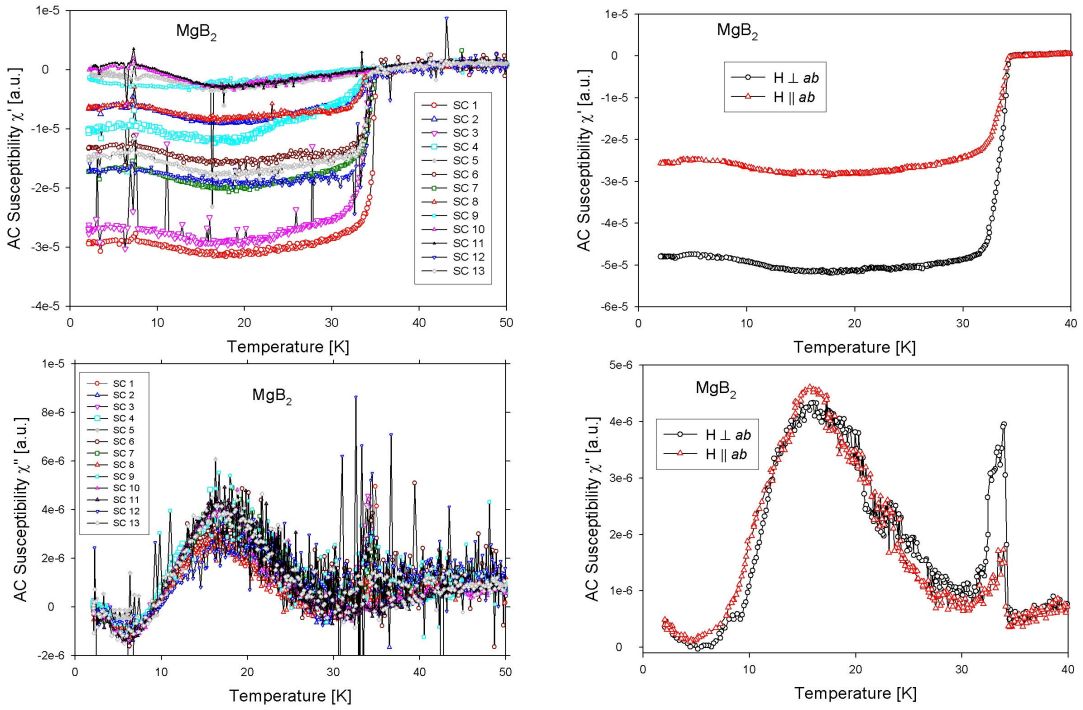

Figure 6. The AC susceptibility of the crystals taken from one batch, the homogeneity of different crystals. On the right: susceptibility for various field orientations.

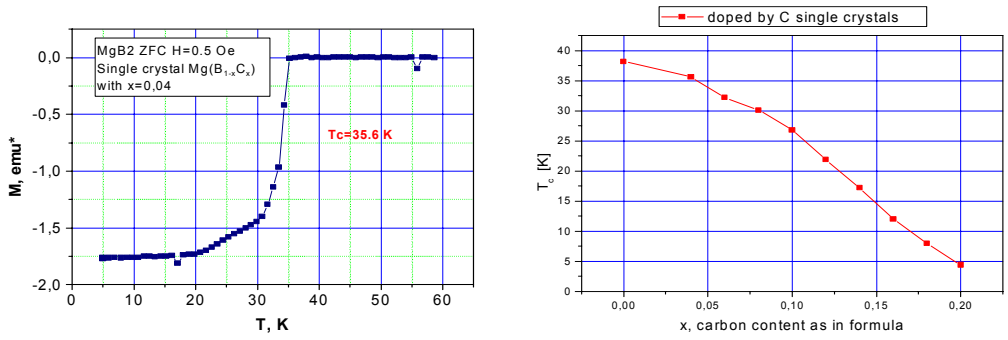

Figure 7. On the left: T_c for the MgB_2 single crystals sample with carbon content x=0.04, on the right the T_c dependence on carbon content for samples obtained by the hydrocarbide gas decomposition method under high argon pressure crystallization.

4. Conclusions

1. The high gas pressure technology enables to grow MgB_2 crystals at equilibrium high pressure from the liquid flux.
2. By high pressure high temperature reactions of boron with gaseous Mg it is possible to grow either polycrystalline sample or single crystals of high purity (with essentially low MgO inclusions).
3. High gas pressure technology allows to introduce extremely homogently carbon, or nano-crystalline additives from the gas state (hydro carbide gas by thermal decomposition in a closed vessel). Such nano-inclusions serve as excellent pining centers and significantly increase the J_c, especially at higher magnetic fields.
4. The sequence of the hydroextrusions processes applied for the rapid deformation of MgB_2 materials (e.g. wires) results in generation very good pinning centers, perfect microstructure of materials, and in consequence, enables to produce long wires samples with good parameters (J_c over 200000 A/cm^2 at 4 T and 4.2 K).
5. Additionally recently used hot extrusion method to process the wires or samples with nano-sized powder of MgB_2 and additives effected in self reactions during extrusion, without necessity of additional final annealing. These experiments are now in progress at the HPRC.

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Acknowledgements

This work was financially supported by The Polish State Committee for Scientific Research Project No.4 T08 A00123