Nucleation and growth of dense phase in compressed MgB$_2$

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Abstract. We report nucleation and growth of dense MgB$_2$ phase in two advanced methods for compacting MgB$_2$ powder: hot isostatic pressing (HIP) and resistive sintering (RS). Both methods produce a compact with nearly theoretical mass density and high critical current density: up to $8 \times 10^5$ A/cm$^2$ at 20 K. A liquid phase is responsible for the propagation of dense MgB$_2$. The additions of Mg and Ni are beneficial for rapid formation of dense compact. The process of compacting is further improved by introducing single crystal-dense MgB$_2$ seeds.

MgB$_2$ is a superconducting material with a high critical temperature, twice above the boiling point of liquid hydrogen. The impact of introducing MgB$_2$ into future liquid hydrogen-based energetics could be enormous. The main requirement for this, however, is a cheap and simple method for preparation of dense material, preferably ex-situ, from non-reactive MgB$_2$ powder. Historically MgB$_2$ was mainly produced in-situ starting with amorphous boron and highly reactive fine magnesium powder [1]. The high reactivity of Mg ensures the quality of the final product, but Mg could also react with other elements, especially oxygen. An ex-situ process could be used in preference to an in-situ process provided it results in high enough density of critical current. In this paper we explore the ex-situ process and report on a new phenomenon: nucleation and rapid growth of dense MgB$_2$. The control of the growth could lead to a cheap and effective route for bulk MgB$_2$ manufacture. We further found a similar process in in-situ prepared samples.

The phenomenon of nucleation and growth of dense MgB$_2$ has been found simultaneously in two different methods: hot isostatic pressing and resistive sintering. Hot isostatic pressing (HIP)[2] is already a traditional method for preparation of bulk MgB$_2$. In this method a pre-compacted powder is enclosed in a steel container, evacuated and pressed in a high pressure (1 kbar) argon atmosphere at a temperature 950 - 1000 °C for 3-4 hours.

Resistive sintering (RS) is a novel method for the preparation of MgB$_2$. The RS comprises of a high pressure graphite die and tungsten rods that create a uniaxial pressure and simultaneously act as electrodes to carry high electrical currents, up to about 500 A. The inner diameter of the die used was 5 mm, and the applied pressure is about 500 bar. The densification of powder takes place in vacuum with a remnant pressure below $10^{-4}$ Torr. The electrical current heats the sample up to 1000 °C. The RS is similar to the plasma synthesis method described in [3] but uses direct instead of a pulse current. The main advantage of the method is a short processing time to prepare dense MgB$_2$: typically one to five minutes. The RS produces MgB$_2$ of low porosity and provides abundant sub-micron inclusions of MgO that could add to a high density
of critical current ($J_c$). Starting with pre-compacted powder, we reached $J_c = 8 \times 10^5$ A/cm$^2$ at 20 K in both HIP and RS.

The RS method is effective due to the rapid growth of dense MgB$_2$. Due to a large processing time in HIP, the details of the formation of the dense compact cannot be observed after the opening of the can. However, if the steel cans are filled with loose powder, it is possible to slow the process and see development of the dense phase as well as investigate the boundary between the dense and non-dense MgB$_2$. Fig. 1 shows development of the dense phase in the cross-section taken from the bottom of a loosely filled HIP can. The dense phase nucleates at the points of largest deformation, on the surface of the steel and propagates inside the can. The porosity of this phase is low, 3 - 7 %, whereas porosity of the adjacent non-dense phase is high and varies from 27 to 44 %. Fig. 2 shows the boundary between the dense (grey in the top of the plot) and non-dense (dark, bottom) MgB$_2$ powder. An intermediate layer with multiple white inclusions is situated between these two.

**Figure 1.** Cross-section of hot isostatic pressure can showing the growth of dense MgB$_2$ phase. 1 - dense MgB$_2$; 2 - non-dense precursor; 3 - steel can; 4 - bakelite pellet. The diameter of bakelite pellet is 3.1 cm.

**Figure 2.** Boundary between dense phase (grey) and non-dense (dark) MgB$_2$. The site marked "Spectrum 1" is the area used for the element analysis.

Electron dispersive x-ray analysis was used to identify phases in all specific areas of the sample. The dense area is nearly pure MgB$_2$ with some inclusions of MgO. The element content in the area indicated "Spectrum 1" in Fig. 2 is: B - 52.77 atomic %, Mg - 35.11 % and O - 11.73 %. Surprisingly, we found a small amount of Ni, about 0.38 atomic %, in this area. The dark area of non-dense powder is Ni-free, but the intermediate layer contains a considerable amount of Ni, up to 5.5 atomic %. Ni has not been added to the MgB$_2$ powder. Its origin may have been from the surrounding stainless steel can. We can suggest that during HIP Ni dissolves into MgB$_2$ and creates a liquid that spreads into the can leaving behind a fully dense MgB$_2$ with small traces of Ni.

Another feature of the intermediate layer, except of the higher Ni content, is a high content of Mg seen in Fig. 2 as an enhanced density of white spots. Extra 10.56 atomic % of Mg has been added to this sample to replace Mg loss during the processing and facilitate the formation of dense phase. We can conclude that both added Mg and extracted Ni are beneficial for creation
of a liquid phase, an important factor in the process of densification of MgB$_2$. The control of the liquid phase could be crucial for the production of MgB$_2$, including drawing of commercial wire. The advanced methods for preparation of MgB$_2$ wire could combine pressure with precise control of the chemical content of the liquid phase. An additional advantage of adding extra Mg is that it is partially left in MgB$_2$ in the form of sub-micron MgO inclusions that act as effective pinning centers for superconducting vortices.

To analyze superconducting properties, small rectangular slabs have been cut from the dense and non-dense regions. The temperature and field dependence of the magnetic moment of these samples has been measured in a commercial magnetometer Quantum Design MPMS5. Figs. 3 and 4 show the field dependence of magnetic moment ($m$) at a temperature of 10 K for non-dense and dense samples, respectively. Magnetic moment was recalculated into critical current density ($J_c$) according to the formula $J_c = 4m/(a^2bc(1 - a/3b))$, where $a$, $b$ and $c$ are width, thickness and length of the sample, respectively. $a$ is the lowest dimension of the sample in the direction perpendicular to the magnetic field. The expression above is the exact formula for magnetic moment of the sample in the critical state. It is quite accurate for the most parts of Fig. 4 except the area around the jumps in magnetic moment. In Fig. 4 the magnetization loop is symmetrical with respect to field axis and the effects of the trapped field are not too strong. In Fig. 3, a strong reversible component is present and the expression above should be applied to the width of hysteresis loop rather than to $m$ (with a coefficient of 2). The real critical current density is about half the maximum value for the points in the plot.

Figs. 3 and 4 show that samples with low density can have a critical current density more than three orders of magnitude lower than a fully dense sample. The main reason for this is high porosity and poor contact between the grains. In accordance with this, the dense sample shows a much narrower superconducting transition. Fig. 5 shows the temperature dependence of magnetic moment for non-dense (1) and dense sample (2) in a magnetic field of 20 Oe measured after a zero field cooling procedure. Both samples in the plot are superconducting with nearly equal critical temperature, but the non-dense sample has a much wider superconducting transition than the dense one.

![Figure 3](image1.png)  
**Figure 3.** Field dependence of magnetic moment recalculated into critical current density ($J_c$) for non-dense part of HIP sample at temperature 10 K.

![Figure 4](image2.png)  
**Figure 4.** Field dependence of magnetic moment recalculated into critical current density for dense part of HIP sample at temperature 10 K.

The value of ($J_c$) in the dense sample shown in Fig. 4 is large and it could potentially be even higher in a sample produced from the well pre-pressed powder, which usually results
in fully dense phase only. Fig. 6 shows current progress in the preparation of HIP and RS samples at 20 K. Cutting small pieces we are able to avoid the development of the jumps in the field dependence of magnetic moment. The best samples prepared to date have critical current density of $8 \times 10^5$ A/cm$^2$ at 20 K in zero magnetic field in both HIP and RS. This value of critical current density is already suitable for a large range of application in liquid hydrogen, neon or helium.

In order to facilitate formation of the dense phase, we introduced small pieces of HIPed MgB$_2$ into the pressed RS powder. The resultant samples were homogeneous and showed higher $J_c$ than many samples grown at the same conditions without seeds. For instance, at the low RS pressure of 400 bar $J_c$ of the seeded sample was $2 \times 10^5$ A/cm$^2$ at 20 K and zero magnetic field, whereas many other samples show $J_c$ in the range $1.0-10^5 - 1.7 \times 10^5$ A/cm$^2$. Our preliminary conclusion is that HIPed MgB$_2$ pieces impose their grain structure on the RS MgB$_2$ sample. The resultant grain size is typically on the micron and sub-micron level and apparently smaller than in the samples without seeds. We consider the small grain size as the main reason for the increased flux pinning in the dense MgB$_2$. We suggest the grain boundary dislocations as the main defects that provide pinning in MgB$_2$. The ability to vary the grain size means that seeded growth could be a valuable tool in the preparation of dense MgB$_2$.

In conclusion we observed an effect of nucleation and growth of dense MgB$_2$ phase in pressed MgB$_2$ powder. We found that the growth takes place due to spread of a liquid phase, and the additions of Mg and Ni are beneficial for densification of MgB$_2$. The value of critical current density in prepared samples is high and could be used in a range of high current applications.

References
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Figure 5. Temperature dependence of magnetic moment for non-dense (1) and dense (2) areas of a hot isostatically pressed sample in field 20 Oe. The curves have been recorded after a zero field cooling procedure.

Figure 6. Field dependence of magnetic moment expressed as critical current density ($J_c$) for a range of HIP and RS samples at temperature 20 K.