Preparation and Properties of New Superconductor Material MgB_2

D. Marinha[1,a] , F.J. Oliveira[1,b], M. S. Reis[2,c], F. M. Costa[3,d], M. F. Carrasco[3,e], J. P. Araújo[4,f], J. B. Sousa[4,g], J. M. Vieira[1,h] and V. S. Amaral[2,i]

[1] Departamento de Engenharia Cerâmica e do Vidro and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

[2]Departamento de Fisica and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

[3] Departamento de Física, Universidade de Aveiro, 3810-193 Aveiro, Portugal

[4] Departamento de Fisica and IFIMUP, Rua do Campo Alegre, 4169-007 Porto

[a]daniel.marinha@netvisao.pt, [b]filipe@cv.ua.pt, [c]marior@fis.ua.pt, [d]flor@fis.ua.pt, [e]fcarrasco@fis.ua.pt, [f]jearaujo@fc.up.pt, [g]jbsousa@fc.up.pt, [h]jvieira@cv.ua.pt, [i]vamaral@fis.ua.pt,

Keywords : superconductors, hot isostatic pressing, critical current, MgB_2

Abstract. Bulk MgB_2 samples were synthesized by hot isostatic pressing under pressures up to 200MPa at 950ºC. In these conditions, full densification of samples was obtained (~98% of theoretical density). SEM, EDS and XRD analysis on final dense bodies were used to evaluate samples, and show increasingly better control over the amounts of secondary MgO (down to ~10%) and complete prevention of formation of MgB_4 by using simple glass encapsulation techniques and addition of Mg(s) to the capsule. The samples display superconducting properties, including a narrow critical transition in electrical properties (Tc ~36-38K). Magnetic studies were performed, allowing the determination of the superconducting fraction and critical current density J_c of the materials. Contrary to the Tc, the J_c is quite sensitive to the processing and microstructure and values from 0.3 to $0.6x10^6$ A/cm^2 are obtained at 10K. The reduction of J_c with the applied magnetic field requires further improvements to reduce weak links.

Introduction

Although the covalent compound MgB_2 has been studied for a long time, its superconducting properties were only discovered in 2001[1]. This has opened new opportunities for superconductor applications because of its intermediate Tc (39 K), weak link free grain boundaries, low materials cost and processability. It has high potential for application at the cryocooler temperature range (20–30 K). An overview of the physical properties of MgB_2 can be found in [2]. It was soon realized that since Mg is extremely volatile at elevated temperatures, it is very difficult to prepare a bulk material with high density and low porosity for electrical transport applications by sintering at ambient pressure. Hot isostatic pressing (HIP) has been reported to improve the superconducting properties of MgB_2, by introducing more pinning centers and overcome the poor connectivity between grains, caused mainly by porosity [3]. Pressures up to 3.5 GPa have been used [4, 5]. In this work we present a study of HIP preparation and properties of dense materials, starting from commercially available MgB_2 powder.

Experimental

Commercial MgB_2 powder from Alfa-Aesar was used as starting material for all sample preparations. Particle size was determined using laser diffraction, which showed a bi-modal distribution with peaks around 0,4μm and 3μm. This starting material is superconducting and

contains ~5% MgO contamination. Samples were weighed and pressed into pellets with about 13mm diameter and 8mm height with relative green density of 65%, using a uniaxial press, and then encapsulated in vacuum using tantalum foil to wrap the samples [6]. Capsules were put into Al_2O_3 crucibles in a graphite powder bed for the hiping cycles.
To create a magnesium-enriched atmosphere, which will minimize and compensate the loss of magnesium through the superconducting phase dissociation reaction, metallic magnesium flakes were added to the capsules. Part of this magnesium will oxidize during cooling thus forming MgO.
Two HIP cycles with the same hold time and temperature (4 hours at 950ºC) but different pressures, were programmed: HIP_LP ~300 bar and HP_ HIP cycle at ~1900 bar. Technical problems related to the equipment forced the high-pressure cycle to be reduced to 85 min and an oscillation in the maximum pressure value occurred. Pressure applied had a peak at 1900 bar and reached its minimum at 1450 bar. The cycles are described in figure 1.

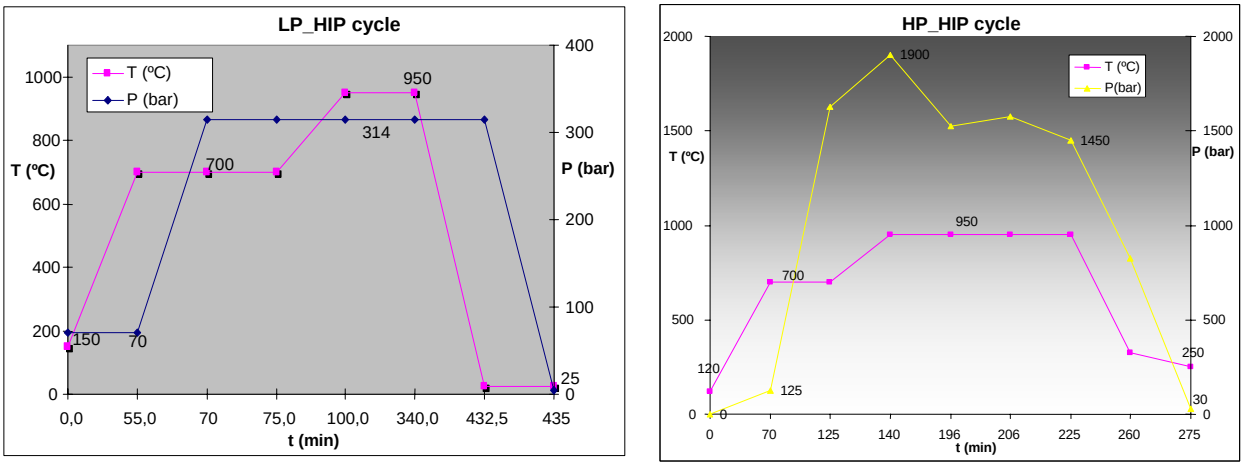


Figure 1. Temperature and pressure parameters of the HIP cycles.

Phase identification was made using standard XRD and phase quantification performed by Rietveld-based refinement. Bulk samples were observed using optical microscopy, SEM and X-ray energy dispersive spectroscopy (EDX). For SEM observation, samples were polished with disc diamond abrasive films down to 1μm. Electrical resistivity measurements were performed using standard 4-point probe technique in a closed cycle refrigerator, down to 10K. Magnetization (M) measurements as a function of the magnetic field (H) and temperature (T) were carried out using a Quantum Design MPMS SQUID magnetometer. Magnetic susceptibility (χ=M/H) was determined as a function of temperature, after zero field cooling procedure. Hysterisis cycles were performed at several temperatures (10-40K) with magnetic fields up to 5.5 Tesla. From the magnetic irreversibility (ΔM, the height of the hysterisis loop) at a given magnetic field, the critical current density J_c (H) can be evaluated (in c.g.s. units) using the critical state model [7] for a long parallelepiped of section *2a* x *2b*

$$J_c(H) = \frac{10\Delta M}{a\left(1-\frac{a}{3b}\right)}. \qquad (1)$$

Results and discussion

Table 1 summarizes the phase analysis of the samples, the experimental and theoretical densities (according to the composition) and the calculated porosity. One finds that the HP cycle was much more efficient in improving the densification from ~90% to ~98%. The addition of magnesium, allowed a better control over the formation of secondary phases, especially MgB_4 in agreement with

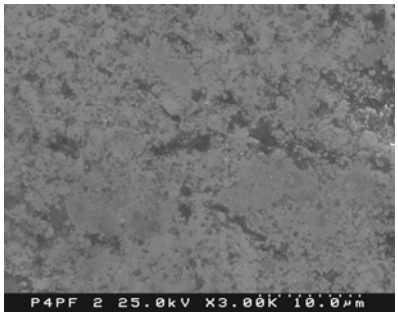
ref. [8]. This influence is further supported by the fact that the samples closer to the extra magnesium were the ones which showed the least amount of MgB_4. MgB_4 weight fraction increases for increasing distance from the extra magnesium source in the capsules.

Sample	Phases present (weight %)			ρ_t	ρ_{exp}	ρ_r	Π
	MgB_2	MgO	MgB_4	(g/cm^3)	(g/cm^3)	(%)	(%)
MB1-3	84	12	4	2,707	2,407	88,9	11,1
MB1-4	80	12,4	7,6	2,704	2,366	87,5	12,5
MB1-5	80,7	13	6,3	2,709	2,390	88,2	11,8
MB1-6	78	14	8	2,715	2,450	90,2	9,8

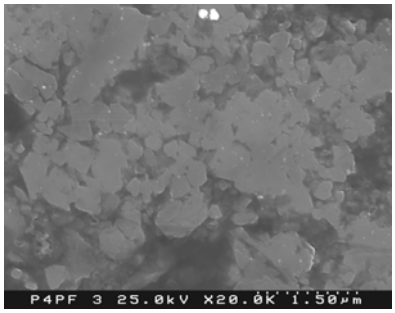
Sample	Phases present (weight %)				ρ_t	ρ_{exp}	ρ_r	Π
	MgB_2	MgO	MgB_4	Mg	(g/cm^3)	(g/cm^3)	(%)	(%)
MB1-7	77	15	8	0	2.726	2.469	90.6	9.4
MB1-8	79	13	8	0	2.710	2.558	94.4	5.6
MB1-9	89	11	0	0	2.702	2.659	98.4	1.6
MB1-10	86	13	0	1	2.700	2.652	98.2	1.8

Table 1. Phases, density and porosity of the samples prepared using the LP-HIP cycle (left) and HP-HIP cycle (right).

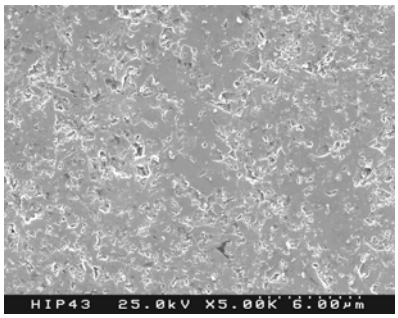
All samples were prepared for SEM observation. During the time period between preparation and observation, oxidation was found to occur at the sample's surface. All samples but one (MB1-10) were polished again in order to remove the oxidized layer. Sample MB1-9 was surface-etched with HCl 0.1N for 10 seconds in an attempt to better distinguish its grain boundaries. Though SEM images for this sample show differences from the non-etched, grain boundaries were not revealed. Figure 2 shows SEM images of some samples.



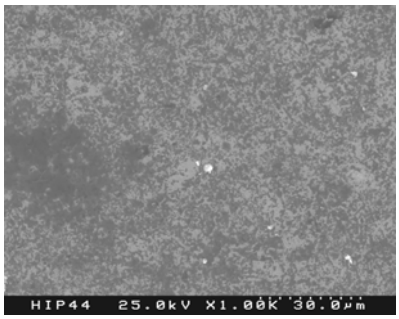
a) MB1-7



b) MB1-7 (higher amplifiation)



c) MB1-9 (HCl 0,1N etched for 10s)



d) MB1-10 (oxidized surface)

Figure 2. SEM images of selected HP-HIP cycle samples

Electrical transport measurements were performed using standard 4-point probe DC technique. The samples display superconducting properties, including narrow critical transition (Tc ~36-38K).

The temperature dependence of the electrical resistivity of one LP-HIP samples is shown in figure 3. The HP-HIP samples present lower values of the resistivity at the onset of the transition: 8μΩcm for sample MB1-9, about half the value found in sample MB1-4.

Magnetic susceptibility measurements at increasing temperatures, after cooling the sample in zero magnetic field from well above Tc allow the observation of the Meissner effect and the determination of the superconducting volume fraction of the sample. Figure 4 shows the temperature dependence of magnetic susceptibility of selected samples. After correcting for demagnetizing effects, the superconducting fractions obtained agree with the phase determination: 96, 91 and 94%, respectively for samples 4, 6 and 9.

To study the superconducting critical current density, the magnetic field dependence of the magnetization was measured at some representative temperatures in the superconducting phase: T=10K, 20K, 30K and 35K, very close to Tc. The initial negative (almost linear) part is associated with the Meissner state (no magnetic flux), which ends at the first critical field Hc1. The hysteresis loop traced is associated with the flux penetration in the sample. Figure 5 shows a representative case.

The irreversibility effects shown in the magnetic hysteresis are quite sensitive to the processing and microstructure.

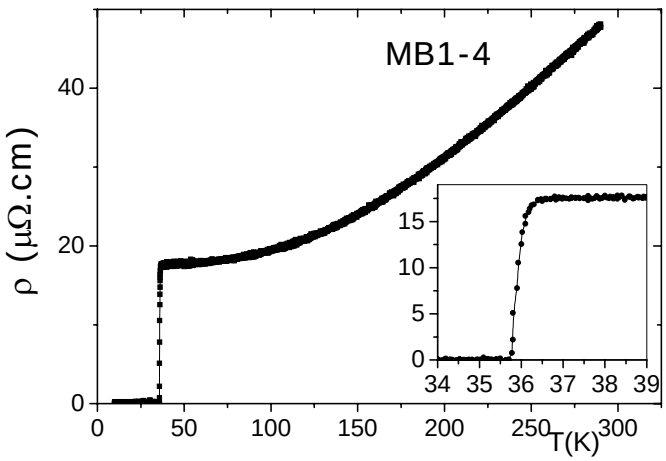


Figure 3. Temperature dependence of the electrical resistivity of one LP-HIP cycle sample. Inset: detail near Tc.

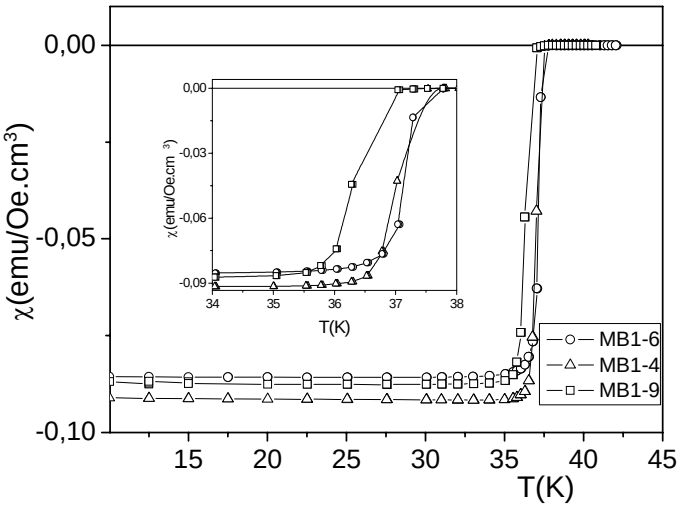


Figure 4. Temperature dependence of the magnetic susceptibility. Inset: detail near Tc.

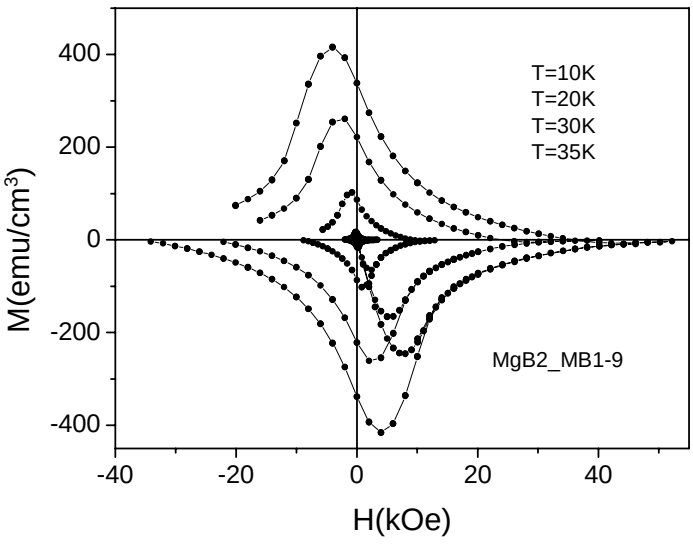


Figure 5. Magnetic hysteresis cycle of one HP-HIP cycle sample.

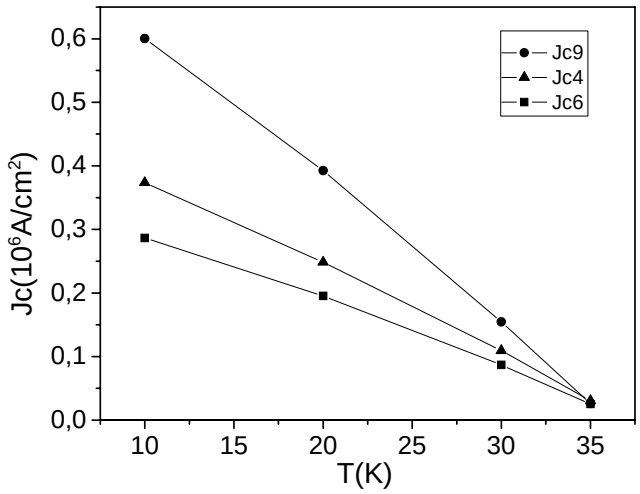


Figure 6. Temperature dependence of the critical current density determined at zero field using equation 1.

Using equation 1 at zero magnetic field (in the low field range is an approximation) one can estimate Jc and values from 0.3 to 0.6 x10^6 A/cm^2 are obtained at 10K. The temperature dependence is shown in figure 6 for some representative samples. These data show that the higher densification leads to higher values of Jc, due to higher density of pinning centers.

The magnetic field dependence of Jc is approximately exponential with field [9], and leads to a high reduction: For sample MB1-9, with highest Jc, 0.6x 10^6 A/cm^2 at 0 Tesla, it reduces to 0.3x 10^6 A/cm^2 at 1 Tesla and to 0.11 x 10^6 A/cm^2 at 2 Tesla. This reduction is comparable to the one found in other studies and shows that improvements have still to be done in the materials processing in order to reduce the weak links. Another effect observed in our study is the dependence of the magnetic properties on the sample dimensions (besides demagnetising effects), also reported in other studies [10,11]. Such behaviour is characteristic of an inhomogeneous current distribution inside the material, with magnetic screening with different length scales. In conclusion, it is found that samples prepared with HP-HIP cycle and composition control through Mg addition lead to improved normal state and superconducting properties (lower onset resistivity near Tc and higher Jc) when compared with the LP-HIP samples. On the other hand, Tc and the superconducting fraction do not vary appreciably.

Acknowledgements

This work was financially supported by FCT/Portugal and FEDER (POCTI/CTM/39340/01). M.F.C. thanks the Research Institute of the University of Aveiro for a research grant. M.S.R thanks a scholarship from CNPq/Brazil.

References

[1] Jun Nagamatsu, Norimasa Nakagawa, Takahiro Muranaka, Yuji Zenitani and Jun Akimitsu, *Nature* 410 (2001) 63
[2] P. C. Canfield, S. L. Bud'ko, D. K. Finnemore., *Physica C* 385 (2003) 1
[3] N. A. Frederick, S. Li, M. B. Maple, V. F. Nesterenko and S. S. Indrakanti, *Physica C* 363 (2001) 1
[4] Y. Takano, H. Takeya, H. Fujii, H. Kumakura, T. Hatano, and K. Togano, *Appl. Phys. Lett.* 78 (2001), 2914
[5] C. U. Jung, Min-Seok Park, W. N. Kang, Mun-Seog Kim, Kijoon H. P. Kim, S. Y. Lee, and Sung-Ik Lee, *Appl. Phys. Lett.* 78 (2001), 4157
[6] V. F. Nesterenko ,Y. Gu, *Appl. Phys. Lett.* 82 (2003) 4104
[7] D. X. Chen and R. B. Goldfarb, *J. Appl. Phys.* 66 (1989) 2489
[8] R. A. Ribeiro, S. L. Bud'ko, C. Petrovic and P. C. Canfield, *Physica C* 385 (2003) 194
[9] S. Senoussi, *J. Phys. III France* 2 (1992) 1041
[10] M. J. Qin, *Phys. Rev. B* 69 (2004) 012507
[11] J. Horvat, S. Soltanian, A. V. Pan, and X. L. Wang, *J.Appl. Phys.* 96 (2004) 4342 ; *Appl. Phys. Lett.* 84 (2004), 3109