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THE MECHANICAL PROPERTIES OF THE MgB_2 BULK MATERIALS OBTAINED BY REACTIVE LIQUID Mg INFILTRATION

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ABSTRACT

The Reactive Liquid Infiltration technique (RLI) allows to produce very dense MgB_2 bulk material, useful as superconductor in many electro-technical devices. The resulting MgB_2 product presents a composite structure characterized by large grains, reminiscent of the grain size of the precursor Boron powders, embedded in a matrix of the same material but with smaller grains, of the order of a micron size. This composite structure of the product presents peculiar mechanical properties characterized by high flexural strength and fracture toughness, as far as a ceramic material is concerned, and very high hardness. We have measured the room temperature mechanical properties as a function of the main RLI manufacturing parameters of the materials and we attempted a correlation with the grain size of the precursor B powders and the residual content of impurities in the materials. The obtained values compare favourably with that of the same material produced by other manufacturing techniques and with that of the other HTS bulk materials.

KEYWORDS : MgB_2, Bulk superconductor, Elastic modulus, Microhardness, Flexural strength
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INTRODUCTION

The mechanical properties of the High Temperature Superconductors (HTS), like the ceramic cuprates, are greatly affected by the porosity of the sintered material. This fact, together with the need of improvement of the critical current density, forced to obtain textured mono-crystalline bulk materials, like that one obtained by the YBCO

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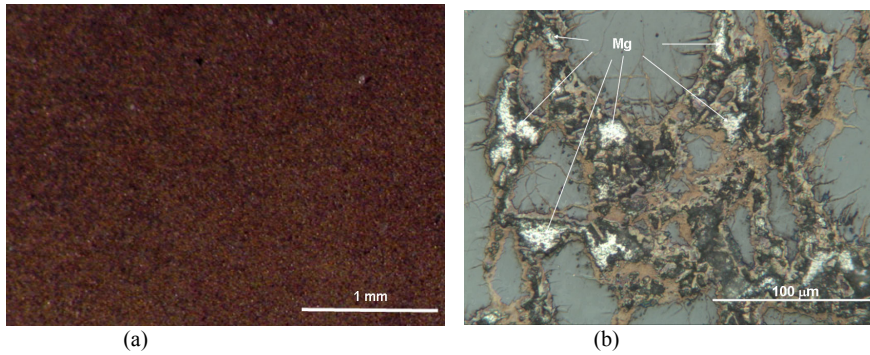
melt texturing process [1]. But, even if the textured YBCO can reach a density near to the theoretical one, it cannot avoid the intrinsic brittleness of the ceramic materials built by macroscopic grains. To alleviate these difficulties, that are particularly important at the higher magnetic fields, the state of the art is considering the addition of metallic silver between the grains or the use of external composite reinforcements. These hurdles appear less dramatic if one considers an alternative high temperature bulk superconductor, the MgB_2. Indeed this material, even if ceramic in nature too, may be manufactured in a polycrystalline form that, without loosing the superconductive properties, imparts much more friendly mechanical characteristics. The aim of our actual study is to elucidate some mechanical characteristics of typical MgB_2 high density materials. Among the different sintering routes to highly densify the MgB_2, the two main processes available are the Hot Pressing (HP) [2] and the Reactive Liquid Mg Infiltration [3], the only two that can reach densities of the order of 90% of the theoretical value (2.63 g/cm^3). In the EDISON R&D Laboratory the RLI process was invented [4] and now is developed in the light of the substantial benefit that the ease of the RLI process can offer with respect to the HP one, aiming to exploit the bulk MgB_2 superconductors at the industrial level. In particular we have considered two types of MgB_2 bulks of very different granularity, resulting by the use of B powders of different grain size in the RLI process. These two types of materials have already demonstrated different superconducting properties [5], with a preference for the samples of micron size granularity. Also the mechanical characteristics of these two kinds of MgB_2, here considered, show some important differences. A rationale to interpret the found differences will be presented.

MgB_2 SAMPLES PREPARATION AND THEIR STRUCTURE

Two different kinds of bulk MgB_2 samples have been prepared by the RLI process, following the normal recipe elsewhere reported [3]. The main morphological difference between the two samples is their different grain size, induced by the use of B powders of different granularity. The other main processing variables have been chosen similar, so the reaction temperature and time were about 850°C and 1 hour and the starting reactants composition was over stoichiometric (Mg/B weight ratio =1.4).

The typical morphologies of the two MgB_2 types are reported in the pictures of FIGURE 1, as observed by optical microscopy on diamond polished surface, using a Leica DFC290 and the Application Suite: multifocus software LAS modulus.



(a) (b)

FIGURE 1. Typical morphologies of MgB_2 bulk samples obtained by the RLI process:
a) sample A-type ; b)sample C-type (see text)

In particular the sample denoted by A, FIGURE 1a, has been derived by microcrystalline B powders (Starck AG, Amorphous grade I, 95 % purity) and is characterized by a very fine grain structure.

The other sample denoted by C, see FIGURE 1b, has been derived by macrocrystalline B powders (Starck AG, Crystalline Grade, 99% purity) mechanically grinded to a granular dimension < 100 micron. The morphology of sample C is highly non homogeneous, with the presence of large compact grains embedded in a matrix of finer grains. As reported elsewhere [6], to these two kind of morphologies corresponds also a significant variation in the presence of the impurity phases distributed around and inside the grains. The Mg_2B_{25} phase [7] is embedded inside the large grains of sample C and is practically absent in sample A. The metallic Mg residue is hardly visible with the optical microscopy in sample A, even if present in a significant amount, instead it is clearly visible in the intergrain region of sample C, FIGURE 1b. Through the powder X-Ray diffraction analysis [6] the presence of the Mg_2B_{25} phase in the sample C is estimated to be 1.8 molar % and is absent in sample A. Regarding the metallic Mg, the same analysis gives about 18 molar % for sample C and even a larger amount for sample A, but hardly to quantify.

The larger amount of Mg detected in the A sample correlates with the experimental evidence that at the end of the infiltration process, no metallic Mg residue is present in the reaction container, even if we started with an over stoichiometric amount of Mg. Instead for sample C some Mg residue was present around the MgB_2 sample.

With the aid of the X-ray powder diffraction we have evaluated also the crystallite dimensions of the various samples, by the use of the Debye-Scherrer formula [8] (assuming K=0.9). In TABLE 1 we collected the mean values of the crystallite dimension for MgB_2 ((100) and (101) crystallographic plane) and for Mg ((101) plane). The mean value has been calculated on a plurality of samples of the two types of material.

The A-type samples (without Mg_2B_{25} phase) present larger crystallite dimensions, even if their morphology is characterize by much smaller grains (micron size). This fact is probably due to the absence of the impurity phase Mg_2B_{25}, that may impede a regular crystal growth. The different crystallite dimensions may be also due to a different reaction kinetics of the MgB_2 crystal growth from microcrystalline boron and from already formed Mg_2B_{25}.

The samples used for the mechanical measurements were cut with a diamond saw from larger bulks in shape of bars or beams of the following thickness:

a) MgB_2 by crystalline boron (# T92 & #T106)

C1: 33.5 x 0.43 x 0.91 mm
C2: 33.0 x 0.41 x 0.9 mm
C3: 40.6 x 0.41 x 0.89 mm
C4a &C4b: 28.0 x 2.50 x 2.0 mm

b) MgB_2 by microcrystalline boron (#T123)

A1: 17.6 x 0.38 x 2.5 mm
A2: 18.7 x 0.34 x 2.0 mm
A3: 28.0 x 2.50 x 2.0 mm

TABLE 1. Crystallite dimension (Å)

	MgB_2(100)	MgB_2(101)	Mg (101)
C-type	215	165	190
A-type	300	215	230

MECHANICAL MEASUREMENTS

The two series of MgB_2 samples have subjected to several complementary mechanical tests :

a) Vickers Microhardness (Load F=1.961 N) have been performed on samples A and C using a Leitz Miniload microindenter. The microhardness HV is related to the diagonal of the squared indentation, d:

$$HV \approx \frac{1.854F}{d^2} \tag{1}$$

The stress intensity factor K_{IC} is related to the formula [9]:

$$K_{IC} = 0.016\left(\frac{E}{H}\right)^{1/2}\frac{F}{c^{3/2}} \tag{2}$$

where E is the Young modulus (GPa), H is the Vickers Hardness and c is the half diagonal of the indentation, including the cracks at the edges.

b) 4-point flexural test on thick bars A-type and C-type gives information on flex strength (σ_f):

$$\sigma_f = \frac{Fa}{bd^2} \tag{3}$$

where the geometrical parameters a,b,d are defined as in FIGURE 2:

c) A non conventional compressive/flexural test (buckling beams) on thin beams have been performed to have indication on the critical stress(σ_{tot}), the Young modulus (E) and the elongation to break. The maximum tensile stress on "external fibers" of the beams, evaluated from the buckling test, have been compared to those obtained with 4-point flex test to verify the consistency of the results.

In the buckling experiment the elastic modulus of the thin beams have been evaluated using the Euler equation describing the critical inflection load for buckling beams [10]. The load applied to the beam is monitored by a conventional dynamometric apparatus, see FIGURE 3.

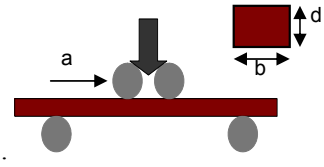


FIGURE 2. Geometry of the 4-point flexural test and of the cross section of the MgB_2 bars.

FIGURE 3. The supporting beams of the dynamometer equipment for the buckling measurement

In this approach the maximum load before inflection, F_{max}, is related to the Young modulus, E, by the equation:

$$F_{\max} = \frac{E\pi^2 J}{L^2} \tag{4}$$

where J is the area moment of inertia and L is the length of the beam.

$$E = \frac{F_{\max} L^2}{\pi^2 J}; \quad J = \frac{1}{12} bh^3 \tag{5}$$

where b and h are the smaller and larger dimensions of the cross section of the beam, respectively.

To evaluate the ultimate stress of the material we assume to be valid the super-imposition effect of a pure compressive load and a pure flexural moment. Within this approach the compressive and flexural contribution can be evaluated independently and summed up. Obtaining:

$$\sigma_{tot} = \sigma_c + \sigma_f = \frac{F}{hb} + \frac{Mz}{J} \tag{6}$$

where : M = Fc; F is the buckling load ; z = h/2 ; c (inflection arrow at the half length) has been calculated assuming a circular deformation of the beam.

With the same assumption, an estimation of the deformation of the "external fibers" of the beam, ε*, at half height, has been performed. ε* = Δl/L with Δl being the displacement of the dynamometer's cross bar.

RESULTS AND DISCUSSION

Microhardness and Toughness

The microhardness HV has been measured in several zones of the sample C-type, see FIGURE 4, obtaining quite different values according to the chosen zone. The typical measured mean values are HV= 35 GPa inside the large grains, and HV=1.9 GPa in the intergrain region. Such a big difference is due to the presence of the Mg_2B_{25} impurity phase inside the larger grains. Indeed this phase will be very hard, having the same structure of the β-rhombohedral crystalline boron, one of the hardest materials ever known.

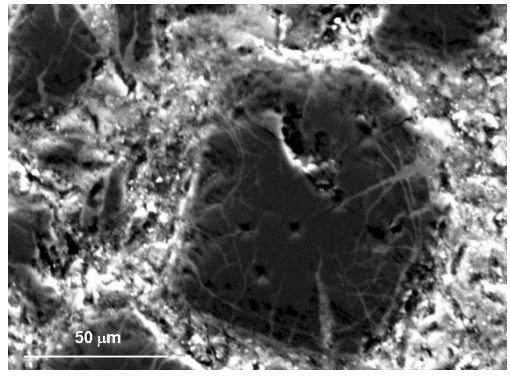


FIGURE 4. SEM micrograph of the indentations inside a grain of MgB_2 (sample C-type)

TABLE 2. 4-points flexural strength

	σ_f (MPa)
A3	278 ± 43
C4a	259 ± 28
C4b	251 ± 12

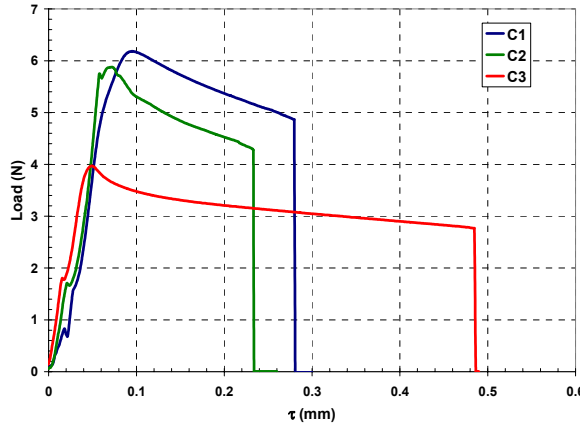
For the A-type samples we obtain a mean value of HV= 6.5 GPa. The Stress Intensity Factor K_{IC} value goes, for sample C-type, from 1.8 MPa $m^{1/2}$ inside the large grains and 2.6 MPa $m^{1/2}$ in the intergrain region and for sample A-type the almost constant values of 2.8 MPa $m^{1/2}$ is measured.

4-point flex

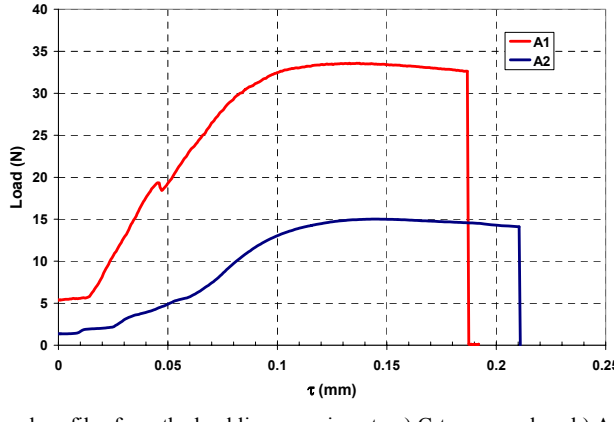
Mean values resulting from a test on series of 6-8 samples (A3,C4a, and C4b) are reported in TABLE 2

Beams buckling

The loads curves, corresponding to the two series of samples (A and C) , are reported in FIGURE 5 .



(a)



(b)

FIGURE 5. Load profiles from the buckling experiment : a) C-type samples : b) A-type samples

TABLE 3. Results from the buckling experiments

	Fmax(N)	E(GPa)	σ_{tot} (MPa)
C1	6.18	121	352
C2	5.87	125	345
C3	3.97	129	326
A1	33.6	92	658
A2	15	80	467

The values of the Young modulus and total strength, resulting from the load curves of the buckling experiment, are reported in TABLE 3.

We have compared in the graph of FIGURE 6 the stress σ_{tot} versus ε^* curves, resulting from the elaboration of the corresponding load profiles of the samples A1 and C1.

These data of the buckling experiment show a clear difference between A-type and C-type materials. The A-type samples have a substantial lower elastic modulus, higher total strength and larger elongation to break. So it is confirmed the difference between A and C sample found in the 4 point flexural strength, with even larger absolute values.

Another substantial difference is represented by the elongation to break, which is much higher for sample A-type. This elongation to break behaviour correlates well with the finer granularity of the A-type material and with its lower hardness but can be partially due also to the presence of a larger amount of metallic Mg in the intergrain region.

This compositional feature, of a larger amount of Mg in A-type material, at least for the actual samples, is very puzzling also with regard to the superconducting properties. Indeed the previous measured transport and magnetic characteristics in the superconducting state of analogous materials are far better with respect to the C-type MgB_2 [11]. As far as the comparison with other mechanical measurements on the MgB_2 bulk samples is concerned , the data are very sparse due to the difficulties to obtain high density materials, enough large in size to perform all the mechanical tests. The HP materials were generally studied with additives, like Ta, limiting the analysis to microhardness [12]. In such a case a HV value is reported having a value of 12.8 GPa, which can be considered similar to our mean value derived by the different points of the C-type sample(1.8÷35 GPa). The elastic properties (shear and bulk modulus) of a pure HP MgB_2 sample in the temperature range between 4-300K have been reported in [13], being 115 and 142 GPa, at RT, respectively.

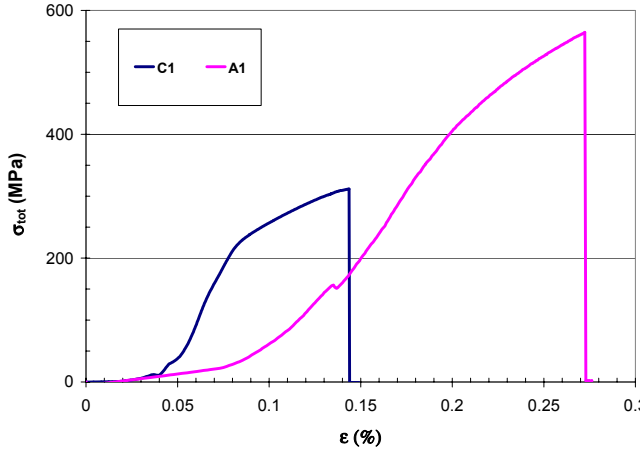


FIGURE 6. σ_{tot} curves derived from the load curves of A-type and C-type MgB_2 beams.

These values should be compared with the Young modulus evaluation on an early MgB_2 sample obtained by our RLI process [14] ,164 GPa, and the actual measured sample A and C mean values of 86 and 125 GPa, respectively. We may interpret these differences in terms of a different Mg metallic contents.

Regarding the comparison of the mechanical properties with the competing HTS, YBCO type material [15], it is reported that its Young modulus is varying from 109 to 132 GPa , according to different measurements and different sample composition. We can consider these values in the range of our present values. But in the same paper, substantially lower tensile and flexural strength are reported for YBCO, in the range of 40 – 75 MPa; to be compared with our actual mean values which range from 250 to 500 MPa, according to the particular mechanical test.

CONCLUSIONS

In this paper we present the first data of a wide mechanical analysis of the bulk MgB_2 superconductors, as derived by the RLI process. The two very different morphologies corresponding to crystalline B derived material (C-Type) and to microcrystalline B derived materials (A-type), correlate with different mechanical characteristics. The differences can be summarized observing that the A-type material is more soft, more ductile, but of better overall strength. Comparing with other bulk MgB_2 preparations, we can state that our actual data are similar to the best HP products. With respect to the other HTS competing material, like YBCO, the RLI MgB_2 appears to have a substantial higher mechanical strength.

The present mechanical characteristics of the RLI MgB_2, even if preliminary, must be considered as a base to further improvements in future within the light of better impurity control of the material

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