Effects of Sheath Materials and Thermo-mechanical Treatments on the Superconductivity of MgB$_2$ Wires and Tapes

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Abstract. In this work a combination of stainless steel, copper, titanium and silver are used as sheath materials to fabricate SiC doped MgB$_2$ wires and tapes by the powder-in-tube (PIT) method. The samples are cold deformed to the final dimension with several intermediate and final heat treatments between 200°C and 900°C. The microstructure and phase composition of the tapes are followed during the deformation and heat treatment processes by Scanning Electron Microscopy (SEM) and X-Ray Diffractometry (XRD). Critical current densities ($J_c$) were determined by magnetization. The correlation between the superconducting properties and the microstructural characteristics is discussed.

Index Terms— MgB$_2$, critical currents anisotropy, material synthesis effects.

1. Introduction

The strong potential for commercial applications of MgB$_2$ is due to a unique combination of characteristics, such as a high transition temperature $T_c$ ~39K, chemical simplicity, lightweight and low cost of the raw materials. In addition, the absence of weak-link behavior at grain boundaries in polycrystalline samples allows the use of simple Powder In Tube (PIT) methods to fabricate wires and tapes [1]. SiC doping is also one of the best-known ways to increase $J_c$ in MgB$_2$ [3], and a very promising $J_c$ result has already been achieved by combining in a coil the addition of SiC and HIPing [6].

Several fabrication parameters seem to affect the superconducting properties of PIT wires and tapes [2]. The desired conditions include: a sheath material that has no or little reaction with MgB$_2$, but also provides a reasonable solution to thermal stabilization; a mechanical deformation process that produces a final density as high as possible and, intermediate treatments performed at temperatures as low as possible but high enough to relax stresses in the sheath material. It is not possible to solve all these aspects using a single sheath material. Some proposed solution was the use of combined metals as sheath materials (Fe/Cu, Nb/Ta, Fe/SS, Nb/Cu, etc) but most results indicate that the degradation of $J_c$ due to the reaction of MgB$_2$ with non-ferrous metals is significant. Besides, for technical
applications of high current MgB\textsubscript{2} wires, a multifilamentary composite with small filaments is required. However, it is observed that multifilamentary wires have not as high $J_c$ values as monofilamentary ones [2], [9]. So, careful investigations of the ceramic core microstructure and interface reactions are fundamental for understanding the influence of processing parameters on properties like the critical current density and the irreversibility field.

To explore which are the critical issues of different possible sheath materials a series of samples were prepared using stainless steel, titanium, titanium/copper and silver by different mechanical deformation procedures and treated at different temperatures between 200°C and 900°C. Some of the advantages of using these materials are that SS presents high hardness and chemical compatibility with MgB\textsubscript{2}, Ti has a lightweight and a better malleability performance that expand the spectrum of applications while Ag needs very low temperatures to reduce the stress. It is shown that the positive effect of SiC addition or decrease in the initial particle size may be hindered by the negative effect of high temperature or large intermediate heat treatments (SS and Ti) or the softness of Ag.

2. Experiment Details

2.1. Sample preparation
MgB\textsubscript{2} commercial powder was packed, adding 5at.% Mg powder as extra source of magnesium, into stainless steel (SS), Titanium (Ti) and silver (Ag) tubes (inner and outer diameters ~4.5 and 6.4 mm) and cold-drawn into round wires with external diameter in the range of 1.4-1.5 mm, with intermediate and final annealing treatments at temperatures ranging between 200-900°C. 2.5at.% SiC nanopowder (20-30 nm grain size) was added to the initial mixture and the powders were ball-milled for one hour inside a glove-box before filling the Ti, Ti/Cu and SS tubes. High energy ball milled MgB\textsubscript{2} powder was used for filling Ag tubes in order to decrease the initial particle size and to improve the density of the packed powder [11]. The wires were rolled to obtain MgB\textsubscript{2} tapes or put together with some Cu filaments into new tubes to obtain multifilamentary wires. The different fabrication parameters and characteristic of samples are listed in Table 1. All samples but Ag had a final annealing at 900°C during 30 min.

2.2. Silver sample DTA analysis
It is known that silver may react with Mg degrading the superconducting properties and it also permeates oxygen at high temperatures. Differential thermal analysis (DTA) of a mixture of Ag +MgB\textsubscript{2} was performed to determine the best final temperature to avoid this reaction [11]. According to this study it is necessary to make the heat treatments below ~750°C to avoid the reaction but below ~650°C to avoid the Mg oxidation. Therefore, the final treatment for Ag samples was performed at 615°C for one hour.

2.3. Microstructural characterization
The morphology observations and microanalysis of the samples were done on a Philips 515 SEM microscope fitted with an EDAX 9900 energy dispersive spectrometer (EDS).

The possible reaction between the sheath materials and MgB\textsubscript{2} was analyzed by EDS analysis and electron backscattering images.

2.4. Superconducting characterization
D.C. magnetisation, $M$, of ~ 4-5 mm long pieces of the samples, had also been measured with $H$ parallel to the tape axis, using a Quantum Design SQUID magnetometer. We calculated $J_c$ from magnetisation loops, $M(H)$, using the Bean model and assuming uniform current density. $M(H)$ loops up to 7 T of samples SS2 and Ti1 were performed at the STC-Los Alamos National Laboratory while the others were carried out up to 5 T at Centro Atómico Bariloche.
Table 1. Characteristics of selected MgB$_2$ wires and tapes

| Sample | Sheath      | Type of sample | External Size (mm) | Intermediate treatments quantity (N) and temperature (T) |
|--------|-------------|----------------|--------------------|--------------------------------------------------------|
| SS1    | stainless   | tape           | 0.42 x 2.58        | N = 4+2, T = 900°C                                    |
| SS2    | stainless   | tape           | 0.35 x 2.85        | N = 4+2, T = 600°C                                    |
| Ti1    | titanium    | tape           | 0.35 x 2.5         | N = 4, T = 600°C                                     |
| Ti2    | titanium/copper | tape   | 0.62 x 3.1        | N = 1, T = 600°C                                     |
| Ti3    | titanium/copper | multifilament | 0.75 x 1.86      | N = 4+3, T = 600°C                                   |
| Ag1    | silver      | tape           | 0.45 x 3.7         | N = 8, T = 250 ºC                                    |
| Ag2    | silver      | tape           | 0.75 x 2.7         | N = 8, T = 250 ºC                                    |

3. Results and Discussion

3.1. EDS interface analysis

EDS intensity of the elements that may diffuse across the MgB$_2$/sheath interface (i.e. Mg in SS, Fe from SS in the MgB$_2$) were measured in a polished sample as a function of the distance from the interface to determine the possible formation of an interface reaction layer. The intensity has been normalized to the intensity of the elements measured far away from the interface.

Grivel et al presented a compilation of data on the sintering-temperature dependence of the interface reaction layer thickness for Fe or SS PIT wires [14]. He found out that the thickness of in-situ PIT (samples prepared from Mg and B powder mixtures) increases with the annealing temperature from a few microns at 600°C to 20-30µm at 900°C. In contrast, for ex-situ PIT (samples prepared from pre-reacted MgB$_2$ powders) a few microns thickness layer was observed at 850°C which increases over 5 µm only for temperatures above 950°C [15]. In Fig. 1(a) we can observe that no reaction layer was formed in SS2 sample with only one while there is little diffusion (les than 5 µm) for sample SS1 which has several heat treatments at 900°C in agreement with the reported data. A very slight diffusion of Mg in the Ti layer can be observed in Fig.1(b) while no diffusion was detected for Ag sheaths (see Fig. 1(c)). These results were confirmed by backscattering images in SEM observations (as example see inset of Fig 2(a)). Therefore, the intermediate and final annealing temperatures of our samples were appropriate for avoiding the interface reaction layer in most samples.
3.2. SEM

Figure 2 displays the core microstructures of (a)SS2, (b)Ti1, (c)-(d)Ti3, (e) Ag1, (f)Ag2, samples observed by SEM. The effect of a higher sheath material hardness is apparent in the observed microstructure. Significant differences are found between both extremes: a well connected and compacted MgB$_2$ is present in sample SS2 made with the hardest sheath material (SS) while loose grains and porosity may be seen in samples Ag1 and Ag2 which used a softer material (Ag). Even using smaller particle size in the initial powder and an adequate synthesis temperature, the softness of Ag made impossible to obtain homogeneously dense samples and, as the deformation increases, the inhomogeneities and little cracks at the interface increase.

On the other hand, sample Ti1 also presents a high-density core while the multifilament prepared with the same material Ti3 exhibits porous zones (Fig. 2(c)) as well as dense zones (Fig. 2(d)). The inset of Fig. 2(c) display the cross section of the multifilamentary round wire, before rolling to tape, revealing the position of the six Ti wires (dark) and copper wires (bright) distribution within the Ti tube. No significant sausaging effects have been observed in both round wire or flat tape (see inset of Fig. 2(d)). On the contrary, sample Ti2, fabricated with a copper tube outside the Ti wire presented inhomogeneous core sections in the round wire that worsened when rolling to a tape. These problems formed bad zones, as described in Fig. 3(a) that shows a broken Ti zone where MgB$_2$ is in contact with Cu. The fast diffusion of Mg in Cu could be clearly seen in backscattering electron images of broken zones in this and other samples. Fig. 3(b) also exhibits a backscattered electron image of a broken SS barrier wire inside a multifilamentary SS/Cu wire clearly showing the diffusion of Mg into Cu.

3.3. $J_c$ magnetization

Figure 4 shows the magnetic field dependence of $J_c$ for the samples listed in Table 1. We observed that denser samples have a better performance than the others. In particular, samples SS2 and Ti1 are as good as the HIP wired from Ref. [16], included for comparison. Although sample SS1 was also prepared with SS, the loss of Mg at temperatures higher than 650°C due to the high temperature of the
intermediate treatments (900°C) precludes the re-sinterization of the broken grains during the cold work [10] and also produces a core microstructure similar to Ti3 (not shown here).

**Figure 3.** SEM micrograph of (a) a bad section of sample Ti2 at different magnifications Dark: MgB$_2$ core, bright: copper, intermediate: titanium. (b) Backscattered electron image of a broken SS barrier wire inside a multifilamentary SS/Cu wire.

**Figure 4.** $J_c$ vs. applied field at 5 K as determined from the magnetisation loops $M(H)$ for samples listed in Table 1. A HIP wire sample from Ref [16] has been included for comparison.

Samples SS1 and Ti3 with alike core microstructures have also similar $J_c(H)$ behaviour. While SS1 was degraded by too high intermediate temperature treatments, the multifilament Ti3 underwent to more heat treatments and deformations steps than Ti1. Goldacker et al [17] investigated the effect of filament size reduction and claimed that the degradation of $J_c$ is due to a more and more inhomogeneous microstructure, sausaging effects and a reaction layer between filament and sheath with reduced filament size. We did not observe any reaction between Ti and MgB$_2$ nor a sausaging effect in these samples (see inset of Fig. 2(d)); therefore the microstructure degradation is mainly attributed to heat treatment effects. The connectivity of MgB$_2$ is a first order key parameter for obtaining good superconducting properties. Furthermore, several intermediate heat treatments at high temperatures affect the overall $J_c$ properties degrading the inter-grain critical current more than the possible increase in intra-grain $J_c$ due to SiC addition. Ti1 and Ti3 samples have very good $J_c$
magnetisation values but poor transport results, indicating that some cracks are still present in the samples after the last heat treatments. The good magnetisation $J_c$ data is a promising result for this new material, but some parameters have not yet been optimized when using Ti as sheath material.

Ag1 and Ag2 samples have very poor $J_c$ performance that correlates with the core microstructure. The $M(T)$ dependence in these samples present a very broad transition, typical of inhomogeneous current flowing through the sample due to deterioration in intergrain connectivity.

4. Summary

A study on the effect of different sheath materials and intermediate heat treatments at temperature ranging between 250°C and 900°C in the superconducting properties of MgB$_2$ PIT wires and tapes is presented. No or much reduced interface reaction layers were observed in the samples indicating that the intermediate and final annealing temperatures of our samples were appropriate for the chosen materials. The use of a high hardness sheath material (SS) but with intermediate heat treatments at lower temperatures resulted in very fine and well-connected grain boundaries, while high temperature treatments produced samples with loose grains. SS and Ti monofilamentary tapes with well chosen heat treatments may become as dense as those made by HIPing, with also very high $J_c$ values.

The microstructure degradation in multifilamentary wires is mainly due to heat treatment effects, which should be reduced in time and temperature to obtain high $J_c$ values. Ti is a promising candidate as sheath material for lightweight applications, even when the fabrication parameters may still be further optimised.

The failure in obtaining good material densities due to a soft sheath material like Ag, even using the right heat treatment parameters and small particle size, leads to very poor superconducting properties. Improvements in intragrain $J_c$ due to changes in composition (i.e. SiC doping) may be hindered if other parameters like the heat treatments have not been optimized for achieving a good connectivity between grains.

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