Superconducting properties of the powder-in-tube Cu-Mg-B and Ag-Mg-B wires

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Abstract

The new class of Mg-B superconducting conductors was prepared using the standard in-situ powder-in-tube, PIT, method where Mg+2B mixture was used to fill the copper and silver tubes. Study of the intergranular current, grain connectivity and superconducting phases in wires were conducted by AC susceptibility measurements and direct four point transport measurements. Using SQUID magnetometer, magnetisation versus magnetic field (M-H) curves of the round wires after reactive diffusion were measured at temperatures 5K and magnetic field up to 5T to define the $J_{c,\text{mag}}$. The direct current density measurements of the in-situ Cu-MgB$_2$ performed at 4.2K gave the value of $10^9$A/m$^2$.

Key words: MgB$_2$ superconducting conductors, critical current, processing, critical temperature anomaly.

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1. Introduction

Commercial exploitation of the recently discovered MgB$_2$ superconductors will be severely limited unless mechanically robust, high critical current density, composite conductors can be fabricated with uniform properties over long lengths. There are two different conductor preparation methods: an in situ technique where an Mg+2B or MgB$_2$+(Mg+2B) mixture can be used as a central core of the powder-in-tube, PIT, conductor or an ex-situ technique where fully reacted MgB$_2$ powder which may be doped or chemically modified can be used to fill the metal tube [1-3].

2. Experimental and results

2.1 In-situ Cu/MgB$_2$ wires

All samples were prepared by a mixture of Mg and B powders in stoichiometric amounts and made by PIT method in Cu tubes. Outside diameters of the wires ranged from 1 to 2mm and the cross sectional MgB$_2$ to metal ratio was ~0.3. Wire #1 was sintered at 620°C for 48 hours in vacuum, wire #2 was sintered at 700°C for 1 hour in argon atmosphere (ramp rate of the furnace 300°C/h) and wire #3 was sintered at 800°C for 1 hour in argon atmosphere (ramp rate of the furnace 300°C/h). For ac susceptibility measurements pieces of the samples about 3 mm in length were used. Magnetic field was applied parallel to the axis of the wires. Direct four point current measurements were conducted at 4.2 K in self field.

Wires manufactured by in-situ technique, diffusing Mg to B particles experienced ~25.5% decrease in density from the initial density value after cold deformation, due to the phase transformation from Mg +2(β−B) =>MgB$_2$ (all hexagonal structures).

The internal susceptibility $\chi_{\text{int}}$ is shown in Figure 1 for all wires. The susceptibilities were normalised so as to have $\chi_{\text{int}} = 0$ at 100 K. Wire #1 and wire #2 have a sharp transition with onset $T_c=39$K. In all cases, some anomalous decrease of the susceptibility at T~50 K can be seen. Wire #3 has a broad transition with onset $T_c$~50 K and downset $T_c$~25 K. There is some frequency dependence of the susceptibility due to skin effect in copper. At 50 K the resistivity of Cu is $\rho=4\times10^{-10}$ $\Omega$m [4] and the skin depth $\delta=(\rho/\mu_0\pi f)^{0.5}$ at frequencies $f=333.3$ Hz starts to be comparable with wall thickness of the copper tube of our samples, which is about 0.25 mm. To analyse possible screening effects we grounded the inner core of the wire #2 and wire #3 into a powder and measured ac susceptibilities again. The results still have an anomalous decrease of the susceptibility at $T$~50K [3]. DC SQUID measurements
performed on wire #3 in form of a powder confirmed the anomalous magnetic moment decrease at \( T \approx 50 K \) [3].

Our measurements using a microanalyser with wavelength dispersive spectrometers, MAWDS, conducted on the wire #2 showed that as a result of Cu-Mg-B interaction multiphase conductors have been obtained and there is no interdiffusion between Cu and B, see Fig. 2. X-ray powder pattern conducted on the powdered cores of the conductors shows a mixture of MgB\(_2\) and other phases, namely MgCu\(_2\), MgO, MgB\(_4\) and possibly also higher borides. With increasing temperature more Mg diffused into the copper matrix.

Calculations were performed to investigate the effect, on the X-ray powder data, of Cu substitution into the MgB\(_2\) structure. Several models were considered and the two main ones discussed here: 1) 20% Cu substituted randomly onto Mg sites and 2) 40% Cu on every second Mg layer thus increasing \( c \) from 3.521 to 7.04 Å. Comparing the data calculated from model 1 to that of MgB\(_2\) there was a small variation in the relative intensity of some peaks, the greatest being about 10% for (010) at \( \sim 33.5 - 2\theta \). Model 2 gives two additional peaks: (001) at 12.56 and (011) at 35.94 - 2\( \theta \). The lower peak was never observed in our samples thus this model must be excluded. However, a peak at about 35.9 - 2\( \theta \) was observed and was the reason for considering a doubled cell. This can be indexed as the (022) for Cu\(_2\)Mg as calculated from recent data [5] but not reported in the old PDF data no 1-1226. Thus although model 2 should be excluded, the possibility of low levels of Cu substituted into the MgB\(_2\) structure cannot be ruled out.

Rietveld refinement [6] was carried out on several samples including one where attempts were made to remove some of the metal giving a sample with a higher concentration of black powder. The experimental data were fitted with three crystalline phases: Cu, MgCu\(_2\) and MgB\(_2\) or Mg\(_{0.8}\)Cu\(_{0.2}\)B\(_2\) or the layered model mentioned earlier. In every case the main difficulty was fitting the MgCu\(_2\) phase which could be somewhat disordered or perhaps there is a problem with absorption. The results for MgB\(_2\), Mg\(_{0.8}\)Cu\(_{0.2}\)B\(_2\) and the layered model were: respectively profile (\( R_p \)) 6.05, 6.03 and 6.02 and goodness of fit 101.7, 101.7 and 101.0. Within experimental error these refinements are the same. Thus as stated earlier, the layered model should be excluded because no peak was observed at about 12.5-2\( \theta \) but these data, with considerable overlap of the MgB\(_2\) and MgCu\(_2\) peaks, cannot differentiate between MgB\(_2\) and Mg\(_{0.8}\)Cu\(_{0.2}\)B\(_2\).

Using a SQUID magnetometer, magnetisation versus magnetic field (\( M-H \)) curves of the round \textit{in situ} Cu clad MgB\(_2\) wires after sintering in the range of temperatures and time were measured
at temperature of 5 K and magnetic fields up to 5 T to define the $J_{\text{cmag}}$, see Fig 3. The transport data for the Cu claded wire is incorporated in Fig 3. Use of copper also minimises the overall cost of the tape or round wire, because expensive non magnetic barrier materials (such as Nb or Ta [7]) surrounding the MgB$_2$ phase, giving further room to improve the conductor stabilisation. The reproducibility of the measured transport currents was good and not dependent on the wire diameter.

2.2 Ag-MgB$_2$ conductors
In the case of an in-situ wires made in silver tubes some anomalous decrease of the susceptibility at T~50 K was also observed. It appeared that in-situ wires have a broad transition and almost zero transport current [8]. AC susceptibility measurements of the ex-situ wires additionally sintered also presented anomalous decrease of the susceptibility at T~50 K which disappeared with increasing sintering temperature, Fig.4. Sintering at lower temperatures improved intergrain connectivity of the as drawn ex-situ wire. However further increase of the temperature caused degradation of the superconductor by possible extensive reactive diffusion of Mg to silver matrix. The transport critical current for the ex-situ silver claded wires was considerably lower than that for copper PIT conductors.

3. Conclusions
Cu/(Mg-2B) in-situ conductors present a low cost fully stabilised potential solution for magnet applications. Further systematic investigation of copper and silver possible substitution in Mg borides using STEM with high resolution X-ray diffraction and at Daresbury synchrotrons (UK) are going to be performed in the near future to understand the origin of 50K anomalies.

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Figure captions

Figure 1 The AC susceptibility of in situ Cu/(Mg-2B) wire sintered at different temperatures under protective argon atmosphere, measured at frequency 333.3 Hz in applied magnetic field 10e (rms). The arrow indicates position of the change in susceptibility slope at ~50K common for all samples.

Figure 2 Scanning Electron Micrograph and MAWDS surface analysis of Cu-MgB$_2$ interface region in a in situ Cu/(Mg-2B) conductor sintered at 700°C for 1h.

Figure 3 The transport and magnetic critical current density, $J_{\text{mag}}$, defined from magnetisation, (M-H) curves of the round in situ Mg-2B Cu/(Mg-2B) wires after reactive sintering formation of MgB$_2$; samples were measured at 5K, using a SQUID magnetometer. The measured transport current density $J_{\text{trans}}$ ~10$^5$Acm$^{-2}$ is represented by solid square which was calculated for the whole cross section of the B rich area superconducting core diameter, however it is an underestimated value since only ~70% of the whole cross section can be estimated to be an effective superconductor, see Fig. 2.

Figure 4 The AC susceptibility of in situ Ag-(MgB$_2$) wires sintered at different temperatures under vacuum, measured at frequency 33.3 Hz in applied magnetic field 10e (rms). The arrow indicate position of the change in susceptibility slope at ~50K mostly pronounced for samples sintered at lower temperatures. The origin of curves has been shifted down in steps of 0.033 form a 0 position at 100K to underline the anomalies at 50K.
Fig. 1 B.A. Glowacki et al. ‘Superconducting properties of the powder-in-tube Cu-Mg-B ...’ No. N1.2-07
Fig. 2 B. A. Glowacki et al. ‘Superconducting properties of the powder-in-tube \textit{Cu-Mg-B} ...’ No. N1.2-07
Fig. 3 B.A. Glowacki et al. ‘Superconducting properties of the powder-in-tube Cu-Mg-B ....’ No. N1.2-07
Fig. 4 B.A. Glowacki et al. ‘Superconducting properties of the powder-in-tube Cu-Mg-B ...’ No. N1.2-07