1 Motivation

Superconductivity as a research topic is a fascinating phenomenon, but to use it, economically viable applications are required. The most promising application for superconductivity are magnets, in which case superconductors can be used to obtain higher magnetic fields, lower losses and smaller size than those achievable with conventional methods. A whole range of superconducting elements and materials has been obtained from Hg in 1911 to the Fe-pnictides today, but only from a few of these it is possible to create superconducting wires for magnet applications [Buz01].

One of those materials is magnesium diboride (MgB_2), a material known since 1954 [Jon54], but whose superconducting properties were only discovered in 2001 [Nag01]. MgB_2 is especially interesting for magnet applications such as magnetic resonance imaging (MRI) coils [Kom08]. For this application, the material has two direct competitors: NbTi from which MRI coils are usually built and $YBa_2Cu_3O_{7-\delta}$ which is a high temperature superconductor. NbTi, on the other hand, is a low temperature superconductor with a similar production cost as MgB_2.

The main disadvantage of NbTi is its huge weight and the low critical temperature (T_c = 9 K) which are important parameters in the case of MRI machines. The advantage is the still higher critical current density. NbTi conductors are cooled using liquid helium (LHe, 4.2 K) and hence have only a small temperature margin due to their low critical temperature. This superconductor is ductile deformable which allows long length conductors with many filaments to be produced (figure 1.1). In comparison, MgB_2 is much lighter and has a relatively high critical temperature of 38 K but it is more difficult to deform the conductors (only possible as composite material with metallic sheath).

From the other side, competition with MgB_2 comes from the $YBa_2Cu_3O_{7-\delta}$ superconductor (T_c = 92 K). It has much better critical current density versus magnetic field properties in comparison to MgB_2. The main disadvantage of this superconductor is its high production cost caused by its material properties: due to weak link behaviour $YBa_2Cu_3O_{7-\delta}$ has to be prepared as biaxial textured films (figure 1.2). Another drawback is its large anisotropy. Therefore, it is not possible to produce $YBa_2Cu_3O_{7-\delta}$ wires by the inexpensive powder in tube method, which can easily be used with MgB_2. Almost all commercially available MRI magnets are made with NbTi material but machines with MgB_2 are now entering the market. $YBa_2Cu_3O_{7-\delta}$ cannot yet be reliably produced in long enough lengths to be used for coil production. The main advantages of MgB_2 are its low weight and the application possibility at 20 K which was used to build the first open MRI system [Mod08]. Such a system is very promising since many medical patients have problems with claustrophobia and cannot be examined in closed systems.

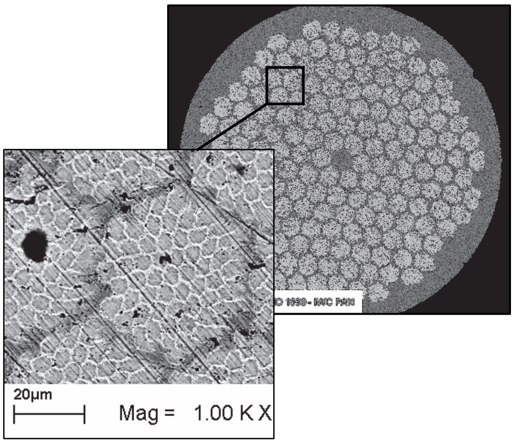

Figure 1.1 Cross section of commercially available NbTi wire.

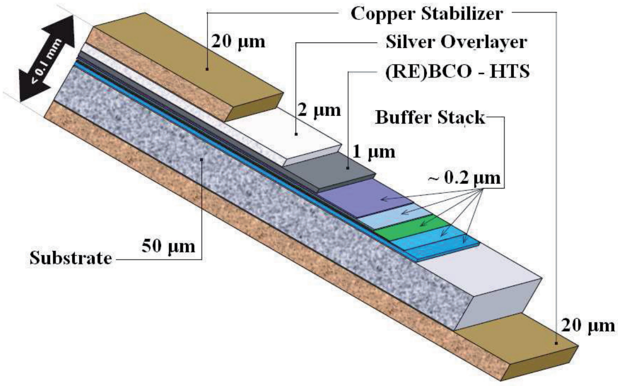

Figure 1.2 Sketch of $YBa_2Cu_3O_{7-\delta}$ tape.

For magnet development, long length conductors are needed with high values of superconducting parameters, such as irreversibility field (H_{irr}), upper critical field (H_{c2}), critical current density (J_c) and engineering current density (J_e). Since 2001, a lot of effort has been done to increase these superconducting properties of MgB_2.

The present research on MgB_2 is focused on production and process up-scaling. On the market there exist two companies, Columbus Superconductors and Hyper Tech, which already offer 1 - 5 km long conductors [Hyp01, Col05] and one which is planning to enter the market - Bruker [Bru10]. However, the J_c has to be improved over these long lengths to reach the levels obtained in short MgB_2 conductors [Her07, Flu09]. Another important feature of a conductor for a magnet application is a flexible architecture so that a coil can be easily wound. The wires for magnet applications need to be multifilamentary to increase the flexibility of the whole conductor, to lower AC losses, and to improve thermal stability. The market of MRI applications needs low cost, flexible and multifilamentary conductor with high J_c values.

There are two powder in tube conductor production strategies currently employed: *in situ* technology which involves filling a tube with Mg + B followed by deformation and final reaction and *ex situ* technology which involves filling a tube with a pre-reacted MgB_2 powder followed by deformation. An interesting approach is also the mechanically alloyed *in situ* technique, where an Mg and B mixture is high energy ball milled. After milling part of the powder is reacted to MgB_2 [Häß06, Häß08, Her07, Her09].

This work is focused on the *ex situ* route of preparation. For MgB_2 conductors a double sheath is used: for instance a Cu-Ni alloy and an Nb chemical barrier. The MgB_2 conductors suffer from work hardening which means that the hardness of the metal sheath is increasing during the deformation and at one point a further deformation is no longer possible. To continue the deformation, the conductor has to be heat treated at a specific temperature to recrystallise the sheath metal. The softening temperature of CuNi30 alloy is around 500 °C at which the *in situ* powder already partially reacts to MgB_2 (figure 1.3). For the mechanically alloyed *in situ* approach this temperature is already the reaction temperature, i.e. the MgB_2 filaments become harder than the outer material. Cracks are created and further deformation is difficult.

The main reason for the *ex situ* material choice is that the reaction in this case is not an issue and the conductor can be annealed during the deformation. The disadvantages of the *ex situ* route are the high sintering temperature which is a problem with the used sheath metals, and the inhomogenity of the powder grain size. Also the *ex situ* powder grains have good superconducting properties inside, but on the surface they contain MgO which blocks sintering and lower the superconducting properties. The idea of this work is to improve the superconducting properties of *ex situ* powder and prepare a deformable precursor powder with similar properties as the *in situ* one.

In the chapter 2 of this thesis, the basic properties of MgB_2 will be shown. The structure and bonding of the compound as well as the phase diagram of magnesium and boron will be described. The superconducting properties as upper critical field, flux pinning and critical current density will be reviewed shortly. The last part will show a literature survey of the *ex situ* approach.

In chapter 3, sample preparation techniques, such as high energy ball milling, bulk preparation and the powder in tube method used for the conductor preparation, are described. Methods of microstructure analysis, such as optical microscopy, electron microscopy, thermal analysis, X-ray diffraction and Rietveld refinements, are detailed.

In addition, electrical measurements of superconducting parameters, both magnetic and transport, are described.

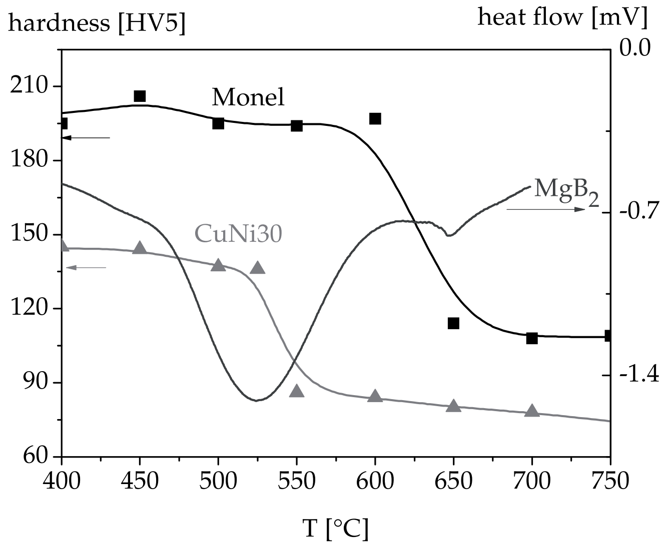

Figure 1.3 Hardness of CuNi30 and Monel sheath correlated with MgB_2 phase formation (from Differential Scanning Calorimetry) as function of temperature.

The representation of the experimental part of this work starts in chapter 4, with a description of an alternative application of the *ex situ* MgB_2 as a chemical barrier for *in situ* filaments in Cu-sheathed conductors. In the beginning, the preparation of the *ex situ* / *in situ* architecture is described. Furthermore, the influence of the sintering temperature and the pressure applied to the conductor during heat treatment on J_c is examined.

In addition to commercial powder, also homemade *ex situ* powder is prepared and its properties are studied (chapter 5). Such powder is made from mechanically alloyed *in situ* powder, for which the synthesis parameters are optimised and from which the conductors are later prepared. The heat treatment conditions for this conductor are also optimised.

In chapter 6, the influence of high energy ball milling on the preparation of *ex situ* powder is shown. From the milled powder, bulk samples are prepared and their superconducting properties are studied. The best powder is chosen for further study and conductors from that precursor are prepared. The influence of the heat treatment on the microstructure and the superconducting properties are studied.

In chapter 7, carbon doping of commercial *ex situ* powder is attempted. Carbon is successfully introduced into the MgB_2 structure during 20 h milling. This powder is further used for a successful monofilament wire preparation.

Finally, chapter 8 is a summary of the whole work comparing different techniques used for powder preparation, properties of the powders and the performance of the conductors prepared from them.