HIPERMAG

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Publishable final activity report

Nano-structure engineering and control.
The objectives for WP1 were to provide the know-how needed for optimized powder processing, i.e. to find methods for the modification of the microstructure of precursor powders and bulk samples to achieve enhanced superconducting properties. This precursor powder was also tested in monofilamentary tapes.

At the beginning of the project work the influence of the *Mg/B ratio* in the precursor powder on the properties of MgB_2 bulk samples was investigated. Excess Mg gives a denser microstructure with bigger grains and excess B enhances the fraction of higher borides. The effect on the superconducting properties is relatively small and superimposed by the influence of boron quality.

In further work it has turned out that the *Boron quality* is an essential parameter for the preparation of high-quality precursor powders. The nominal purity specified by the suppliers considers only metallic impurities and is not sufficient for the characterisation of the boron precursor powder. Oxygen impurities and the grain size of the boron precursor powder were found to affect the reactivity of the powder, the microstructure and the superconducting parameters of bulk samples. Samples showed the highest MgB_2 phase fraction and critical current density if prepared using boron precursor powders with low oxygen content and small grain size.

The investigations show in accordance with the literature the important role of the *grain size* of the powder. The grain size can be reduced by high-energy milling (mechanical alloying) to values lower than a few tens of nanometers. Furthermore, added nanoparticles reduce the grain size and increase the total length of grain boundaries. The grain boundary dislocations are effective pinning centres in MgB_2. We have demonstrated the inverse dependence of critical current density on the mean grain size in dense polycrystalline MgB_2. This dependence points to the grain boundary dislocations as being the dominant pinning centres in the material. The reduction of grain size down to a few tens of nanometres is sufficient to provide high critical current density suitable for most high current applications.

It has been demonstrated that the critical current densities J_c of bulk samples and tapes based on mechanically alloyed nanocrystalline precursor powder are also quite high without doping. For monofilamentary tapes with an Fe-sheath J_c-values of 10^4 A/cm² at 10T and 4.2K could be measured. A further improvement of the critical fields and current densities can be achieved by doping with nanocrystalline powders (carbon in terms of SiC, diamond, nanostructured carbon or carbon nanotubes for instance). *Carbon doping* enhances the upper critical field H_{c2} as shown in the literature. For our bulk samples a very high H_{c2} value of 36T at 4.2K was measured. It should be noted that high transport critical current densities can be realized only if the microstructure is additionally characterized by a good connectivity, i.e. the grain boundaries are clean.
Using nanosized reactive carbon, optimal “doping” results were achieved at relatively low carbon concentrations. The high transport critical current densities of tapes with very dense filaments and a fine grained microstructure could be further enhanced to values of 10^4 Acm^{-2} at 14…16T (4.2K, parallel field).

It seems that collective methods of mechanical alloying and high-pressure ultrasonic cleaning are optimal for producing the best quality starting powder batches of MgB_2 for the fabrication of superconducting wires and tapes. Microstructural investigations show a good

homogeneity of the grain size, together with low reactivity of the powder in relation to the Cu or Fe sheath material. Interesting mechanical properties (good plasticity of the obtained powder) are very promising by the use of the SHS-method (Self propagating High temperature Synthesis) as one of the low cost production methods for commercial powder for wires and tapes of MgB_2.

The results achieved in this workpackage are important for the potential manufacturing of high quality precursor powders. The excellent properties of these carbon doped nanosized precursor powders were demonstrated for bulk samples and monofilamentary tapes (see also WP3).

Micro-structure control

The work in WP2 has led to a strong progress in the understanding of the micro-structure control in MgB_2 wires. All milestones have been achieved, and the conditions for obtaining higher J_c values in "in situ" MgB_2 wires can now be formulated quite precisely:

Powder quality: A very high powder quality is required (> 99.99%), as well for amorphous Boron as for Mg and the additives, e.g. SiC, B4C, Carbon nanopowders or nanotubes. *Oxygen impurities:* The amount of Oxygen impurities has to be minimized, in order to prevent the formation of oxides at the grain boundaries. The main Oxygen sources are: Boron (lowest Oxygen content in Boron particles used in this work: 1.02 wt.%, as B_2O_3), Mg (at least 1 wt.% Oxygen is present at the grain surface, as MgO), and the nanopowder additives. The Oxygen impurities introduced during the manufacture processes have to be minimized. Work with powders must be performed under Ar atmosphere. The ends of the rods and wires must always be closed tightly during deformation by swaging and drawing.

The *powder sizes:* the size of all initial powder particles must be as small as possible. The particle size is of particular importance for the Boron powders. A very narrow particle size distribution is of crucial importance, the very best results having been obtained with Boron sizes well below 0.5 μm. Unfortunately, these powders are not longer available, and most results have been obtained with average powder particles around 1 μm. However, the size distribution reaches values of 10 μm and more, the larger particles being a limiting factor for the critical current density.

The *mixing* procedures used in WP2 also include mechanical alloying, in dry environment under Argon. Wet grinding allows better reduction, but introduces oxide contamination. No exposure to Oxygen is allowed during the mixing and deformation processes.

The *formation kinetics* depends primarily on the powder size, but also on the chemical nature of the additive. SiC additives allow the lowest reaction temperatures. The effect of the Oxygen content on kinetics has still to be investigated. The appropriate set of reaction temperature and time has to be found for each new powder type or additive combination.

The *metallic sheath* has to be chosen in order to avoid too strong a reaction with the powder mixture. The most used sheath material so far is Nb. For special purposes, Ti and Ta may be valuable alternatives. Fe and Ni are used for prototype monofilamentary wires, but show a reaction layer of the order of microns, which limits their use for smaller filament sizes. Monel is used for used for mechanical reinforcement of multifilamentary industrial wires.

A *thermal stabilizer* is necessary for safe operation, and will usually be Cu. Due to the very

different mechanical properties of Cu and Nb or Monel, particular care has to applied to maintain a homogeneous configuration over the wire cross section after deformation.

It was known that *additives or combination of additives* to MgB_2 lead to optimum B_{irr} and J_c values at 4.2 K. In the frame of WP2 and WP4, new additive combinations have been introduced: B_4C + SiC, CaB_6 + SiC, B_4C + LaB_6 (see also WP4). These additives have been added simultaneously (codoping), and have been found to be particularly beneficial for operation at 20K. At present, the maximum J_c value achieved in WP2 for monofilamentary "*in situ*" round wires are the following ones:
At 4.2 K: Wire MgB_2 with 7.5wt.%B_4C + 2.5wt.%SiC: $J_c = 1 \times 10^4$ A/cm^2 at 11.3 T; At 20 K: Wire MgB_2 with 7.5 wt.%B_4C + 2.5 wt.% SiC : $J_c = 1 \times 10^4$ A/cm^2 at ~ 4.7 T

The present works in WP2 show that there is still a considerable margin for improvements, through better powder quality, new additive combinations, higher density after deformation and high temperature reaction under high gas pressures (up to 1 kbar).

Powder processing
The main task of our common investigations was to exploit the know-how generated in WP-1 in order to establish a scalable, cost-effective and reproducible preparation route of MgB_2 precursor powder.

One method of the powder processing was the high energy milling of the Mg and B powder e.g. MA (mechanical alloying). This technology was nicely, consequently developed at IFW-Dresden and was successfully adapted for still higher demand of the better quality pure and doped powder and higher quantity of the material. For a reliable quality control at the starting powders the oxygen concentration and the grain size distribution should be checked. At the milled powders a XRD phase analysis is necessary for quality control.

The group from UBHAM-Birmingham investigated the large kinds of additives possibly for use in powder technology and develop, the nice and highly practical in technology, dependence between the Jc level and the MgB_2 grains and additives sizes. Both result have been used in our powder processing technological aspects, by appropriate using of our new developed high pressure techniques.

The IHPP – Unipress have developed the new high gas medium pressures methods which effectively prevent the oxidation of the milling material, crushed agglomeration, cleaned the nano grains surface before annealing, decreasing the free oxides level and mixing e.g. *US-HP (Ultrasonic High Pressure)* _and *US-VS (Ultrasonic Vacuum Sublimation)* and certain new geometry of *CIP (Cold Isostatic Pressure)* and *HIP (Hot Isostatic Gas Pressure)* all method results by new possibility of cooper using as the sheath material. By applied the patented very effective *"homo- barrier" in composite wire* and *infiltration methods*, as well as lastly applied the *cycling type of HIP*- ing which enable to decreasing the additives level (by increasing the number of the grains boundaries characteristic by the better connectivity of the MgB_2 grains. The connectivity of the fine MgB_2 grains is lastly considered as the main factor for Jc increasing especially in high fields region in which, on the other hands, commonly used nano carbon doping and intragrains additives decrease the connectivity of the grains. It was demonstrated that applied by us, in WP3 investigations; the high pressure *C-HE (cumulative hydro extrusion)* results in highest possible density of CIP-ing of the best quality MA powder from IFW Dresden. The prepared "green body"

wire it selves after the thermal annealing posses high Jc over 10^4 A/cm^2 at (10 T, 4.2K) - see also WP1 section.

All our efforts have been concentrated on the augmenting of the high quality precursor material productions with preserve their best parameters obtained in common WP1 and WP2 efforts.

We found that, as in any material, the superconducting properties of MgB_2 are strongly determined by technology processing involved. The microstructure and composition are the main parameters of the improving of the Jc and Hc_2 parameters.

At last three main material properties are strongly important for high Jc parameters upon high magnetic fields: the *grain size*, the content of the *carbon substituted for boron* place (quantity-closes possible to the solubility limit typical in single crystals or adequate to the solubility limit in the lattice of powder at desired temperature and pressure of annealing) and in our opinion the most important parameter – is the *connectivity of the grains*.

Another important factor is the *intragrains pinning* heavily contributed to the Jc vs. magnetic field dependence.

Tacking in the account another important factor – the influence of the barrier or the sheath material on the total final properties of the wires or tapes the problems getting no solvable by typical individual laboratory.

So the first step in investigation was taken in powder processing for which the best technology of powder preparation, know so far, was to applied MA. Then the preparation process of the conductor was realized by several method. But the main finally remains the *inertness of the superconducting material to the barrier* or sheath material and good thermal and electrical conductivity of the last one.
We found that:
The milling process or/and MA presented by WP1 is a highly beneficial for both *in situ* and *ex situ* powders. It facilitate the sintering, opens the particle surface, introduces the flux pinning centers. In addition the pre-cleaning and mixing methods using by us under high pressure i.e. US-HP and VS-US gives an additional possibility for better quality of the precursor powders preparation.

The milling process is a long time one, and could by shortening or eliminated by the *SHS* (*Self-propagating, High Temperature, Synthesi*s) method, which was lastly introduced by our laboratory, is very effective, and low costs procedure. Additionally applied the US-HP method enabled to very fine homogeneous mixing with pure additives. As we found the carbon doping is the most effective way to increase the Hc_2 and Jc over 10 T limit. The maximum Jc was found for nano grain sized, low temperature annealed samples of wire (tapes) with quite low carbon dopand (on the level of x= 0,04 to 0.06) for the sample measured at 4.2 K. From our experiences for the sample measured at temperature higher than 20 K the carbon doping should not be consider.

It seems to us that for the application at temperature over 20 K or below 7 T, any doping is destructive for high Jc. The most important factor for that kind of material in wires or tapes is the very good connectivity of pure nano grains of MgB_2, i.e. high density of nano material.

For high field operating wire the most important factor is the lowest possible grain size and extremely good connectivity of the sample wire. This can be archived by very high deformation process applied to the wire or tape at the stage of *in situ* or mixed state (*in /ex* – typical for SHS sample). Such deformation of the sample can be attended by rolling or *HE (hydro extrusion)* or final *cycling HIP*-ing methods, lastly discovered and used by IHPP. The occurrence of the liquid state, obtained by the cycling HIP process results in good and long grain border line (surface) working as pining centers. This on the last stage of the HIP process finalize the good connectivity of the grains additionally, by use of the so called *infiltration method* – introduced during WP-3 investigations.

One quite important fact we observe is; that the prior to the milling processes (MA, US-HP, VS-US) the oxidation of *ex situ* material, or remaining the small MgO particles, are not destructive for the final Jc parameters! But the same MgO particles obtained by exposure of the precursor for oxidation, are extremely destructive for final Jc and $Hc_{2.}$
In all cases the high pressure methods are very useful for the first investigation of the wires production and should be or adapted at possibly for industry pressure level, or modified by similar effect by less danger methods in future applications.

Lastly discovered by us very promising SHS applied for the very fine homogeny powder from short time milling process and US-HP showed an enormous practical possibility of this joints technology in the production of large amount high quality precursor for wire and tapes production. The success in that collaboration is still vive and will be continued by very nice collaboration of our laboratories in the frames of students exchange and direct collaborations in our works programs.

Integration
The objectives for WP4 were to bring together the know-how developed in WP2 (Microstructural Control) and WP3 (Powder Processing) to ensure the compatibility between high-performance powders with carefully optimized nano-structure and the mechanical deformation and heat treatment needed for optimal stability.

In the first months very high J_c values could be achieved for undoped and SiC doped monofilamentary wires with Nb/Cu/SS (SS = stainless steel) composite sheath and commercial precursor powders which were among the highest values reported worldwide up to that time. For an undoped wire a transport critical current density of 387 kA/cm^2 in a magnetic field of 3 Tesla was measured. J_c of a SiC doped wire showed better high-field properties and exceeded 10^5 A/cm^2 in a magnetic field of 6 Tesla. The wires for which these high J_c values were achieved, had filament diameters below 65 µm. This excellent result gave hope that it would be possible to manufacture also multifilament wires with similar current carrying capability and with filament diameters of 50 µm and below in a second stage of the HIPERMAG project. Concerning thermal stability, the multifilament design with small filament diameters is superior to a monofilament design with thick filaments, because the heat and current transfer to the sheath in case of a quench is much easier. The availability of multifilament MgB_2 conductors with small filament diameters will therefore be indispensable for future application in MRI-magnets, for example.

The design of these first thin monofilament conductors with Nb barrier to prevent reaction of filament and sheath, with highly conductive Cu component to ensure good thermal stability and with reinforcing stainless steel sheath component seemed to be very promising also for a multifilament conductor design. Therefore, as continuation of this work

multifilament conductors with Nb/Cu/stainless steel composite sheath have been developed. However, in contrast to the good deformation behavior of the monofilament conductors, deformation of the multifilament wires turned out to be much more difficult. Cracks in the Nb barrier occurred and lead to reaction of Mg with Cu from the sheath. As a consequence the current carrying capability was drastically reduced.

It turned out that especially the use of the fine-grained mechanically alloyed precursor powders requires special composites ensuring good deformability of the conductors, because this powder tends to densify strongly during the deformation process. The consequence of the strong densification is an insufficient flow of the powder leading to irregular filament geometries in composites with soft components. It turned out that strong sheath components in close contact to the filament ensure good deformability and preservation of filament geometry during deformation. Good results for multifilamentary tapes with mechanically alloyed precursor powders where achieved for multifilament wires and tapes with Fe sheath. Cu-stabilized multifilament conductors with mechanically alloyed precursor powders could successfully be fabricated when harder barrier materials were used. A good barrier material - titanium - has been found which not only prevents reaction of filament and sheath but which is also hard enough to preserve the filament geometry even when the improved mechanically alloyed powders are used.

Another conductor design which proved to be suitable for introduction of mechanically alloyed precursor powders is a 14-filament tape with Ni sheath and a Cu component with Fe barrier to prevent alloying with Ni. This design is very promising for a scalable process. With C-doped and high-energy ball-milled powders a current densities of 10^4 A/cm^2 in a magnetic field of 13 T has been achieved for short samples. Long length production of conductors > 1km length has already been demonstrated using standard powders.

Even though the precursor powders have been improved continuously throughout the project time, it became more and more clear that further enhancement of current carrying capabilities to values observed in thin films, can only be achieved by improving the connectivity of grains in the filament. Therefore, in a change of the work program basic research tasks with the aim to find ways to optimize the grain connectivity were established in WP4.

In these tasks it could be shown that addition of CaB_6 leads to a field-independent enhancement of the current-carrying capability at 4.2 K. CaB_6 is a commercially available compound which is often used as deoxidizer for production of oxygen free copper. It is assumed that during MgB_2 phase formation CaB_6 binds oxides residing at grain boundaries and increases the effective cross section contributing to the current transport.

By simultaneous addition of carbides (e.g. SiC or B_4C) and borides like CaB_6 and LaB_6 the $J_c(B)$ dependence can be tailored according to the requirements of special applications. C-doping mainly improves the high-field and low-temperature current carrying capability due to improved pinning and enhanced B_{c2} and is therefore the additive of choice for future high-field magnets which will be applied at temperatures at or below 4.2 K. Addition of Ca- or rare-earth-element containing borides like CaB_6 and LaB_6 reduces oxygen contamination at grain boundaries and improves grain connectivity. With this addition conductors that will be applied in low magnetic fields and at elevated temperatures can be optimized. Addition of both types of additives allows optimization of the current carrying capability especially in medium magnetic fields.

The excellent superconducting properties achieved for conductors with quite different sheath composites and geometries show that MgB_2 conductors are indeed multifunctional conductors. In contrast to BiSCCO tapes, for example, which require expensive oxygen-permeable Ag or Ag-alloy sheaths, the possibility to use quite different sheath materials allows tailoring the conductor to the requirements of special applications. Furthermore, the possibility to realize these conductors even in round or quadratic geometry ensures good winding properties for magnet fabrication.

As a result of the investigations performed in the HIPERMAG-project a multifilament conductor optimized with regard to thermal and mechanical stability and ac-losses should have the following design

- A component with high electrical and thermal conductivity, e.g. Cu
- Barriers to prevent interdiffusion of elements between filament and sheath or between different sheath components
    - Nb is suitable for precursor powders with good deformation properties (powders that do not compact too much)
    - Harder barrier materials like Ti or Fe are required in direct contact to fine-grained precursor powders with bad flow properties
- A strong sheath component like Fe, Monel or stainless steel to ensure good compaction of the precursor powders during deformation.
- A strong sheath component with high thermal expansion coefficient to ensure precompression of the filament during cool-down from the temperature of the heat treatment to the temperature of the application.

In the meantime different applications for MgB_2 conductors with quite different designs have been realized in projects in which partners of the HIPERMAG project were involved. Current leads for valves and an ADR magnet on the satellite “Suzaku” were realized as thin monofilament wires with Fe/SS composite sheath. Ultra-thin monofilament wires with stainless-steel sheath serve as liquid-hydrogen level sensors and Cu-stabilized multifilament tapes with Ni sheath were used to build the first MgB_2-MRI magnet worldwide.

Structural analysis

Electron microscopy and spectroscopy techniques as well as high-energy x-ray diffraction were applied in work package 5 for the analysis of superconducting MgB2 ceramics wires and tapes. Electron microscopy and spectroscopy techniques are complimentary to high energy, in-situ x-ray diffraction and the following gives an overview of the concept that was applied in work package 5.

X-ray diffraction is advantageous because it yields a high throughput, only simple sample preparation is necessary, it is fast, and allows the analysis of a large number of samples. X-ray diffraction allows texture analysis particularly important for the anisotropic superconductor MgB2. With the experimental facilities established by the project partners at Risoe it allows in-situ analysis of wires and tapes. X-ray diffraction is not an imaging technique and its lateral resolution is limited. Considering secondary phases in the MgB2 conductors x-ray diffraction is able to detect _MgO but the sensitivity for higher borides is very low, i.e. higher borides cannot be detected.
Extended crystal defects cannot be determined by x-ray diffraction, i.e. no information on pinning active microstructure, dislocations, grain boundaries, precipitates is obtained.

Within the methods available in electron microscopes SEM based and TEM based methods have to be addressed separately. SEM/EPMA yields medium throughput, requires extended sample preparation and yields lateral resolution of 5 nm for imaging and roughly 1 µm for chemical analysis either by EDX or WDX. Secondary phases such as MgO and higher borides can be detected and analysed quantitatively. SEM analysis including EDX spectroscopy and elemental mapping is particularly suitable to study the homogeneity on the µm scale induced by the preparation technology. Analysis of defects is not possible in the SEM and no information on pinning active microstructure, dislocations, grain boundaries, precipitates.

TEM yields medium to small throughput, requires laborous sample preparation, only a small number of samples can be analysed in a given time. TEM allows atomic lateral resolution, strain measurement, determination of the local chemical composition by EDX and EELS spectroscopy and EDX and ESI elemental mapping. Secondary phases like MgO and higher borides can be detected and TEM is unique in obtaining information on pinning active microstructure, dislocations, grain boundaries and precipitates.

Since the above mentioned methods are complimentary a strategy was developed within the project to use the combined strengths of the different techniques and learn most about the samples being analysed. The strengths of in-situ x-ray diffraction are (i) in-situ analysis with access to the time and temperature scale of the sintering, access to metallic Mg, (ii) to study in-situ the MgB2 phase formation, (iii) to analyse the texture, (iv) to correlate texture and jc. The strengths of electron microscopy are (i) to identify and measure the composition of B and higher Mg borides, (ii) to perform phase analysis with SiC additives and C detection, (iii) to determine nm grain sizes and identify pinning centers, (iv) to determine and measure O in MgB2, (v) to establish a jc microstructure correlation model, (vi) to do microstructure analysis on all relevant length scales.

Electron microscopy and spectroscopy methodology concentrated on quantitative analysis of the microstructure and chemical composition of MgB2 wires and tapes. In MgB_2 the correlation of microstructure with superconducting properties, in particular the critical current density requires powerful analytical tools. Critical current densities and electrical resistivities of different MgB_2 superconductors differ by orders of magnitudes and the current limiting mechanisms have not been fully understood. Granularity of MgB_2 is one significant reason for reduced critical current densities and is introduced intrinsically by the anisotropy of B_{c2} but also extrinsically by the microstructure of the material. B_{c2} enhancement by doping is another important challenge for the chemical analysis and at present the doping levels are not well controlled on the sub-µm scale. By quantitative electron microscopy and spectroscopy we mean a combined SEM and TEM analysis that covers various length scales from µm to nm. Contamination free sample preparation, chemical mapping including B and advanced chemical quantification using x-ray microanalysis were essential elements of the applied methodology. The methodology was applied to in-situ and ex-situ MgB_2 wires and tapes with and without SiC additives. Quantitative B analysis by EDX spectroscopy was applied quantitatively in the SEM and TEM, which is a major achievement.

Although MgB_2 is a binary system the thermodynamics of phase formation is complex, the complexity is dramatically increased if additives like SiC are used. The small, sub-µm grain sizes of the matrix and secondary phases requires TEM methods, however, granularity on the µm scale was also identified and underlines the importance of the combined SEM and

TEM studies. Significant differences in the microstructure were observed for in-situ and ex-situ samples. This holds particularly if SiC was added and yielded Mg_2Si for in-situ samples annealed at 600°-650°C and Mg-Si-O phases for ex-situ samples annealed between 900°-1050°C. Four microstructural parameters were identified as relevant for the critical current density of wires and tapes and these were: 1) MgB_2 grain size, 2) colony size, 3) oxygen content and 4) volume fraction of B-rich secondary phases. MgB_2 grain size can only be determined by TEM, colony size, oxygen content and volume fraction of B-rich secondary phases were determined by SEM methods. The formation of oxides was also studied in detail by TEM methods. The importance of electron microscopy methods in the understanding of the thermodynamics of phase formation in MgB_2 as well as in improving the synthesis technology and the superconducting properties of MgB_2 wires and tapes is outlined.
This methodology was applied to MgB2 wires and tapes prepared by various project partners using (i) mechanical alloying technology, (ii) preparing 14 filament long length conductors, (iii) preparing biaxially rolled tapes. Wires were prepared either by ex-situ or in-situ technology with and without SiC additives.

The influence of the quality of boron precursor powder on the microstructure and superconducting properties of MgB_2 bulk samples was investigated and tapes were prepared by IfW Dresden using the mechanical alloying technology. The nominal purity specified by the suppliers considers only metallic impurities and is not sufficient for the characterisation of the boron precursor powder. Oxygen impurities and the grain size of the B precursor powder were found to affect T_c and the microstructure of the MgB_2 tapes. The microstructure was investigated by SEM and TEM. Grains in the boron precursor powders were either nanocrystalline or crystalline with grain sizes varying between 110 and 500 nm. MgB_2 precursor powder was prepared by mechanical alloying which resulted in a small 20-60 nm MgB_2 grain size of bulk samples. Bulk samples showed the highest MgB_2 phase fraction and a critical current density of $4{,}7 \cdot 10^4$ A/cm^2 (at 20K, 1T) if boron precursor powder with small grain size and small fraction of metallic impurities was used. Such powder also yielded compact tapes and required lower annealing temperatures for the MgB_2 phase formation. The typical critical current densities of the tapes were $5{,}0 \cdot 10^4$ A/cm^2 (at 20K, 3T) and were significantly better than that of samples reported recently. These results underline the importance of mechanical alloying for enhancing the critical current density of MgB_2 tapes. Summarising, the phase content, the density and the superconducting properties of MgB_2 bulk and tapes depend on the choice of the boron precursor powder.

Multifilamentary Ni sheathed Cu-stabilised MgB_2 tapes with a critical current density of 2.0 x 10^5 Acm^{-2} (at 20 K and 1 T) were prepared by INFM Genova using a powder in tube technique and pre-reacted (ex-situ) MgB_2 powders. The microstructure and chemical composition of the superconducting core and the MgB_2-Ni interface were studied using SEM, EPMA and TEM. A quick, reliable and standard-less method of B-quantification using SEM-EDX is established for the analysis of MgB_2 wires and tapes. Carbon contamination-free sample preparation was crucial for the analysis of boron. Typical size of MgB_2 colonies, i.e. the arrangement of several well connected grains, in the MgB_2 filaments was between 1 to 6 µm. The colonies are structurally well connected to each other, although sub-micrometer sized voids are present. The B to Mg mole fraction ratio in the MgB_2 colonies was found close to 2 and O mole fraction is less than 1 at.%. Typical size of the MgB_2 grains in the colonies is about 0.5 to 1 µm, however, numerous grains of size 15 to 100 nm are also present. MgO precipitates of the size of 15-70 nm were found in the MgB_2

grains. Long straight dislocations with a density of 1 x 10^{10} cm^{-2} are observed. Non-superconducting layers which appear as oxide layers in SEM and TEM samples were found on the surface of the MgB_2 colonies and yield poor connectivity between the colonies. It is expected that these layers yield a significant reduction of the critical current density J_c. A 10 µm wide intermetallic reaction layer of B, Mg, and Ni is formed at the MgB_2-Ni interface. Reduction of the MgB_2 grain size by milling of starting MgB_2 powder and elimination of non-superconducting layers around MgB_2 colonies could further enhance the critical current density because of improved pinning and connectivity between colonies.

The MgB_2 wires were prepared using the powder-in-tube technique by FZK Karlsruhe using industrial B and MgB_2 powders. The in-situ wires were prepared using a Mg deficient stoichiometry (0.9 Mg + 2B). The deformation was carried out by swaging to a final diameter of 1.1 mm, with intermittent annealing. The final annealing was carried out for 1 hour at 645 °C for in-situ wires and 925 °C for ex-situ wires. The precursor powder, sheath materials and the superconducting properties of these wires were summarised and compared. Density of the MgB_2 core was studied using SE imaging. EDX elemental mapping was used to determine the spatial distribution of B-rich secondary phases, oxygen-rich layers and dense MgB_2 colonies in the MgB_2 matrix. The B, Mg and O mole fractions were determined using quantitative SEM-EDX analysis. Important microstructure results were summarised. The wire with the highest critical current density contained a dense MgB_2 layers along the length of the wire. The intermittent less-dense layers parallel to the length of the wire do not obstruct the flow of transport current. Secondly the B precursor powder in this wire was milled, which is likely to have resulted in small MgB_2 grains. The increased grain boundary pinning would then lead to enhanced Jc. The reduced Jc of an ex-situ wire was limited by the oxide layers in the MgB2 matrix, which resulted in poor connectivity of the superconducting MgB_2 grains.

Stabilized four-filament SiC added *in-situ* MgB_2 wires were prepared by IEE Bratislava using the rectangular wire-in-tube (RWIT) technique, using boron powders of different purity (90% and 99%), SiC powders of different agglomerate size and sheaths of different metals. Critical current density at 10.5 T and 4.2 K improved by 5 times by using boron powder of higher purity, SiC powder of small agglomerate size and mechanically strong Ti sheath. Decrease in T_c and increase in J_c of wires could be explained in terms of carbon doping. Formation of Mg_2Si and B-rich secondary phases, and carbon substitution was studied using EDX chemical mapping in SEM. Addition of SiC yields to the formation of B-rich secondary phases. Our results support the mechanism of carbon doping through the reaction of SiC with Mg to form Mg_2Si and release free carbon. However the extent of effective carbon doping depends on the size of precursor SiC agglomerates, as large SiC agglomerates are unable to react with Mg. B-precursor powder of lower purity and Mg_2Si secondary phase formation led to incomplete phase formation of MgB_2 and consequently to lowered J_c.

MgB_2 wires, tapes and bulk samples have been studied by a combination of X-ray diffraction and electron microscopy. The reaction layers forming at the interface between the ceramic core and Fe or Ni sheaths can be studied with both methods. The complementary techniques enable to study both the microstructure and the formation kinetics of the interface layers. Grain sizes can be determined either by direct observation or by analysis of the shape of X-ray diffraction peaks. Electron microscopy can detect B-rich secondary phases and phases present in small fractions that are not accessible by x-ray

diffraction. On the other hand, synchrotron diffraction provides a fast and non-destructive method for the study of the main phases and their development during *in-situ*, high-temperature investigations. The combination of the two techniques is a very valuable tool for the optimisation of MgB_2-based superconducting materials.

The microstructure analysis was used to establish a **jc microstructure correlation model**. MgB_2 wires and tapes considered in this model were prepared by the powder in tube method using different processing technologies and thoroughly characterised for their superconducting properties. Either pre-reacted MgB_2 (ex-situ) or a mixture of Mg + 2B (in-situ) were used as precursor powders. In some wires the precursor powders were mixed with SiC. The critical current density (J_c) of these wires was found to differ by orders of magnitude, the highest J_c's being 10^4 Acm^{-2} at 10.5 T and 4.2 K. A detailed understanding of the thermodynamics in Mg-B-O and Mg-B-Si-C-O system is necessary to control the phase and microstructure formation in these systems. Ex-situ wires show oxygen-poor MgB_2 colonies (a colony is a dense arrangement of several MgB_2 grains) embedded in a porous matrix introducing structural granularity. In-situ wires are generally more dense, but show inhibited MgB_2 phase formation with significantly higher fraction of B-rich secondary phases in comparison to the ex-situ wires. SiC in the in-situ wires results in the formation of Mg_2Si secondary phases. The size of the MgB_2 grains varied between 20 –1000 nm among the wires and tapes. A microstructure- critical current density model was established to explain the large, order of magnitude, differences in the J_c's of MgB_2 wires and tapes. The model contains the following microstructure parameters: 1) MgB_2 grain size, 2) colony size, 3) oxygen mole fraction and 4). volume fraction of B-rich secondary phases. Jc vs. B curves at 4.2 K are to a good approximation straight lines and were parameterized. These parameters were correlated with the parameters of the microstructure yielding e.g. a quantitative relationship between the grain size and the slope of the logarithmic jc(B) curve.

The role of partner 10 (RISO) was to perform non-destructive microstructural analyses by means of hard x-ray diffraction. The samples, which were provided by several other partners of the consortium, were investigated at the synchrotron beamline BW5 in DESY/HASYLAB, Hamburg, Germany. Some samples (wires, tapes as well as pellets) were investigated at room temperature, while others were studied *in-situ* during high-temperature treatments performed in a furnace flushed with Ar gas.

The metal sheath results in very strong diffraction. As a result, the acquisition time was limited in order to avoid damages to the detector plate. Under such conditions, it was often difficult to distinguish contributions from weakly diffracting phases, like higher-borides, from the background noise. In order to avoid this problem, absorber screens have been used to decrease the signal coming from the metal sheath. These screens consist of a Pb ring and/or a hollow Al/Pb plate positioned at suitable positions to occult the strongest diffraction intensities of the metal sheath. Thanks to these absorbers and a few modifications of the furnace itself, the signal from the powder core of the samples was much more visible. This resulted in many otherwise impossible studies, which can be summarised as follows.

The phase analysis could encompass not only compounds containing relatively "heavy" elements, like Mg_2Si, Fe_2B, etc. but borides and even boron as well.

The formation of an interface reaction layer consisting of Fe_2B in Fe-sheath samples was followed in-situ. Its kinetics was found to depend strongly on the powder pre-treatment. Mechanically alloyed nano-powders result in a significantly more reactive mixture towards

the formation of Fe_2B. It was estimated that the Fe_2B reaction layer could be detected as soon as its thickness was in excess of about 100nm.

Characterisation of the grain size and strain fields proved difficult, owing mostly to the characteristics of the detector. Nevertheless, the grain size values commonly found by means of an analysis of the shape of selected Bragg reflections were in close agreement with the results of TEM investigations.

In-situ studies of SiC-doped samples revealed that the Mg_2Si phase starts forming, like the MgB_2 compound, well below the melting point of Mg, indicating that a solid-state reaction is taking place. The phase formation scheme appears identical for all the doping levels under study. A similar scenario was observed in samples prepared with Mg or MgH_2 reagents. In the latter case, MgH_2 decomposes to Mg.

Studies performed on wires in which the powder precursor mixture was in contact with metals other than Fe showed that no reaction occurs with Ta and Nb. In contrast, $MgNi_{2.5}B_2$ is formed at the interface between the powder and a Ni sheath. In this last case, a thin Nb barrier is efficient for avoiding spurious reactions.

During in-situ investigations, it was observed that the intensity of the Mg signal slowly decreases already at low temperatures. This effect is partly attributable to the enhanced vibrations of the Mg atoms and can be accounted for by the Debye-Waller factor. The partially amorphous boron present in some of the studied precursor powder mixtures was found to loose its crystallinity during the temperature increase around 600°C, while a small amount of MgB_2 is formed. One reason might be that a solid phase reaction takes place between the boron and the surface of the Mg crystallites, whereby the boron is rearranged and is creating a MgB_2 surface layer. This surface layer may prohibit or slow down further reaction until the Mg is melted thereby increasing the atomic diffusion. The kinetics of MgB_2 formation is much faster when Mg is in the molten state.

Investigations involving various kinds of boron powders revealed that crystalline boron is extremely difficult to convert into MgB_2, even when Mg is molten. In contrast, the MgB_2 phase readily forms in the solid state when amorphous boron is used.

Below the melting temperature of Mg, the kinetics of MgB_2 formation using semi-amorphous boron can be described by a power law with a slope of 0.77.

Performing diffraction studies with various angles between the incident beam and the plane of tapes, it was possible to determine the degree of preferential orientation of the MgB_2 crystallites. The starting Mg powder present in the tapes prior to the reaction appears to have a significant deformation texture and this texture is quite similar to that of the MgB_2 phase formed during the conversion heat-treatment. While the texture provides a sound basis for understanding the large critical current anisotropy of the tapes, the similarity of the degrees of preferential orientation of the Mg and MgB_2 phases is puzzling. This might be caused for example by nucleation at the interface between the precursor powder and the Fe sheath or by growth from a small amount of MgB_2 nuclei formed during the precursor powder preparation and that is textured during tape deformation.

It was also observed that the degree of preferential orientation is broadly independent of the amount of carbon doped into the MgB_2 phase. The differences in critical current anisotropy resulting from this type of doping are therefore due to other factors.

Physical analysis.

Fundamental Aspects ICL's activities were first aimed at characterising the changes in the key fundamental parameters as the MgB2 was modified in various ways. The techniques utilised were measurement of the heat capacity in magnetic field, which provides a reliable evaluation of the H_{c2} , and point contact spectroscopy (PCS) in magnetic field, which gives a direct measure of the two superconducting energy gaps and how they shrink with applied field. Both techniques were able to give information on another key aspect of the processed material – its homogeneity or lack of it: the micro-calorimetry utilises samples of mass ~ micrograms, or about 100 microns in size, and PCS gathers information on the scale of microns.

Thermal Stability and Quench Propagation (UT, IOC and ICMA) The quench development of metal sheathed MgB_2 conductors has been analysed. Cu-stabilized and non-stabilized conductors have been studied. Experimentally, energy pulses were deposited to the conductor by passing rectangular current pulses through a graphite-based-epoxy heater. The temperature and the electric field profiles around the point heat disturbance that gives rise to a quench, as well as their time evolution, were measured from multiple voltage taps and thermocouples along the conductor. The experimental results are in qualitative agreement with the simulated ones, obtained by solving the one-dimensional heat balance equation of the system. The temperature and current dependences of the minimum quench energy (MQE) and the quench propagation velocity (v) are presented. Our results show that the Cu-stabilization of MgB_2 wires leads to enhanced stability with a higher MQE and a larger MPZ, hence significantly reduces the possibility of local burn-out as seen in standard Fe-sheathed wires. It was also found that the non-linear power-law current sharing in the normal zone has significant influence on the onset of the quench process and results in a marked deviation from the classical quench theory based on the critical state model. The unexpected increase of MPZ size with transport current for finite n-values, contradictory to the prediction of the standard current-share model for CSM, has been explained on the basis of a non-linear current-share model based on power-law superconducting $E(J)$ with a finite power exponent.

The Temperature dependence of the normal zone propagation velocity (v_{NZP}) is measured on a mono-core (Monel/Nb/MgB_2) wire and a Cu-stabilised multi-core (Ni/Fe/MgB_2) tape at different current levels. As expected, v_{NZP} increases with increasing current and decreases with increasing temperature. As first general observation, both conductors display v_{NZP} values that lie in the range 1-10 cm/s, i.e. ~ 100 times lower than typical values for Nb_3Sn or NbTi conductors. This confirms earlier measurements by partner 13 and implies that quench detection in MgB_2 based devices will have to be carefully designed.

A second and on first sight somewhat surprising observation is the similarity between both conductors, with v_{NZP} changing by only a factor ~ 2 going from the poorly stabilized conductor to the Cu-stabilized tape. This similarity turns out to be coincidental. A simple model of normal zone propagation states that

$$v_{NZP} = \frac{J_m}{C}\sqrt{\frac{\kappa\rho}{(T_{cs}-T_0)}},$$

with C the heat capacity, ρ the electrical resistivity and κ the thermal conductivity of the matrix; J_m the current density in the matrix; T_{cs} the current sharing temperature (defined by $I_c(T_{cs}) = I$) and T_0 the base temperature. The stabilizing Cu layer in conductor D4.3 strongly

reduces ρ but also increases κ, so that its overall effect on v_{NZP} is relatively small. It is also shown that the T-dependence of v_{NZP} is in first order mainly determined by the T-dependence of the heat capacity C and thermal conductivity k (and to a lesser extend ρ).

IOC made comprehensive characterisations of thermal-electrical properties of various benchmark and optimised conductors. The data were used by several partners for further conductor optimisation and stability analysis.

In addition to adiabatic stability described above, conductor stability under non-adiabatic conditions was studied by IOC in the context of over-current stability in liquid neon and quench propagation in conductors cooled by neon vapour. It was shown that with appropriate boiling heat transfer activation, the stabilised conductors can operate safely at 2-3 times of the nominal critical current in dissipative mode. Furthermore, nucleate boiling conditioned can be maintained in the over-current mode hence allow rapid recovery to superconducting state once the current is reduced to below the critical value. Therefore a critical requirement for superconducting fault current limier (SFCL) is satisfied. The quench initiation of conductors cooled in Neon vapour showed similar characteristics as those in adiabatic condition. The natural convective cooling of Neon vapour can be estimated satisfactorily using standard correlations and increases the minimum quench energy by about 100%. However, the quench temperature and size of minimum propagation zone is almost unchanged.

Pinning properties (ICL and ICMA) ICMA have analysed the critical currents of bulk materials processed by resistive sintering (RS) and hot isostatic pressing (HIP) (UBir, IFW). Various starting powders were used, including *in situ* and *ex situ*, mechanically alloyed and nanoparticles added (SiC, TiO_2, $SrTiO_3$, $BaTiO_3$, Al_2O_3). The effects of grain connectivity, flux-creep phenomena, grain size and the added nanoparticles on the critical current density have been studied. A correlation between J_c and grain size, D has been obtained. At fixed temperature and field value (T= 20 K and B= 2 T), J_c decreases with $1/D$. Among the anaysed doping particles, it has been concluded that the reaction Mg+2B+SiC using HIP process is the most efficient to increase J_c at high fields. Moreover, the temperature and magnetic field dependence of the power-law n-values characterising the $E(J)$ curves of MgB_2 superconducting samples has been analysed. This is done by means of magnetic relaxation measurements, using the normalized relaxation rate of irreversible magnetization M_{irr}, S=-dlnM_{irr}/dln$t$, which directly relates to the E-J curve $E \propto J^n$, with the n-exponent approximately equal to 1+1/S. The study has been done at temperatures and fields ranging from (T=5 K, B=1 T) and up to (T,B) near the irreversibility line. Different undoped and SiC-doped bulk samples have been analysed. We have observed a strong decrease in the n-values when increasing temperature and magnetic field with some differences among the analysed samples. We found correlation between critical current density (J_c) and n-values, with high n-values (n>30) always related to high critical current densities ($J_c > 10^8$ A/m^2).

ICMA compared the magnetic field decay of the critical current at different temperatures, $I_c(B,T)$, obtained by transport and magnetic measurements for Cu-stabilized multifilament conductors. A good agreement between the I_c field dependence obtained for transport and magnetic measurements is observed. At high fields there are small discrepancies, being the measured transport values lower than those obtained from magnetic hysteresis loops. This could be due to low n-value at these fields, since magnetic criterion to determine J_c is more restrictive than the 1 V/cm-criterion used for transport measurements.

Integrating the (modified) MgB_2 into an optimised conductor requires that not only are these

intrinsic attributes retained during the conductor processing, but that also the contacts between the MgB_2 particles are clean and do not block the flow of supercurrent. Here, another specialised technique from ICL, scanning Hall probe imaging, allows the pattern of current flow to be imaged on a scale of order 10 microns. By the end of the project, the conductors being fabricated by other Partners were showing not only high performance (high critical currents maintained to high fields), but also excellent homogeneity. The latter point is of great importance, because it indicates that there is no serious impediment to scale-up to industrial production.

Mechanical Properties and AC Losses (UT and IOC) In terms of mechanical and AC loss properties, all benchmark conductors show a reversible and linear variation of the critical current with axial strain up to a critical limit, followed with an irreversible degradation. The critical strain limit is independent of temperature and magnetic field. Its value can be engineered by proper sheath design. The amplitude of the beneficial reversible strain variation is strongly temperature- and field dependent, but obeys a simple scaling relation. From a fundamental viewpoint, such scaling indicates an intrinsic origin of the reversible strain effects, which might provide clues towards further improvement of the superconducting properties. Preliminary AC loss measurements show hysteretic losses in ferromagnetic sheath and in filaments to dominate. Detailed measurement and analysis have carried out by IOC leading to the identification of different loss mechanisms including ferromagnetic hysteresis modulated by eddy/super-currents, coupling current, flux pinning hysteresis.