Magnesium diboride films on metallic and ceramic substrates

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Abstract. A boron suspension in terpineol was applied to iron, titanium as well as to polycrystalline aluminium oxide, titanium dioxide and yttria doped zirconium dioxide substrates by screen printing. The samples were dried at 125 °C. The specimens were placed into a covered aluminium oxide crucible together with metallic magnesium. Conversion to magnesium diboride was carried out in an argon - hydrogen (6.5 vol-%) atmosphere under ambient pressure. Sintering temperature depended on the substrate chosen and varied between 750 °C and 950 °C. Dense and uniform MgB$_2$ layers were obtained, showing transition temperatures of up to 38 K. Characterisation of the films was performed by X-ray diffraction, by scanning electron microscopy as well as by temperature - resistance measurements. Furthermore, technological applications of this technique will be discussed.

1. Introduction
With the discovery of the superconductivity in magnesium diboride in the year 2001 [1], a new generation of superconductors was discovered. The relatively cheap raw material and the isotropic behaviour of the critical current density in the superconducting state initiated vast research efforts on this compound. Although MgB$_2$ was first synthesized a long time ago [2], problems in manufacturing this compound in pure, MgO free form, are still present [3]. Strict exclusion of oxygen and water vapour during synthesis is mandatory. Currently, the powder in tube (PIT) technique [4] is the most effective way in the fabrication of superconducting wires and tapes [5, 6].

Thin film devices and Josephson junctions e.g. for SQUID applications are usually prepared by rather expensive physical and physico-chemical vacuum deposition techniques such as molecular beam epitaxy (MBE) [7], hybrid physico - chemical vapour deposition (HPCVD) [8] or reactive evaporation (RE) [9]. However, these techniques can only be used for the production of small devices in non-continuous processes.

Very little research has been carried out on wet-deposition of thin films for the electrical conductors. In previous publications, we described the deposition of boron films via screen printing onto various single-crystalline substrates such as yttria stabilized zirconia [10], alumina [11], magnesia [12] but also on buffered iron [13] and its further conversion into the superconducting material by magnesium vapour transport. In this paper, we report on the possibilities in producing superconducting films on various polycrystalline ceramic and metallic substrates in view of a possible method to produce MgB$_2$ based superconducting coated conductors in a cheap and continuous process.
2. Experimental details

2.1. Sample Fabrication

Conventional iron as well as high-purity titanium (ASTM B 265) sheets were cold-rolled to flat tapes in more than 70 steps to a final thickness of approximately 0.2 mm. After cutting the tapes into pieces of 15 mm by 5 mm, the surface was mechanically polished with grinding papers number 800 and 1 200 in order to remove oxidic impurities.

The polycrystalline ceramic substrates: alumina (Al$_2$O$_3$ für Chromatographie, Merck), yttria stabilized zirconia (TZ-3YS B, TOSOH Zirconia, Japan) and titanium dioxide (zur Synthese, Merck) were prepared from the respective powders. The powders were compacted at 0.5 GPa into discs with a diameter of 10 mm and then sintered, using the individual temperature programs in air listed in table 1.

| Substrate material | Sintering Temperature / °C | Sintering Time / h |
|--------------------|-----------------------------|-------------------|
| Al$_2$O$_3$        | 850                         | 3                 |
| ZrO$_2$ doped with 3 mol % Y$_2$O$_3$ | 850 | 3     |
| TiO$_2$            | 850                         | 3                 |

Amorphous boron powder (95 - 97 %, Zeller, Austria) was first wet-milled in a mixture of acetone (50 ml acetone per gram boron) and terpineol in a zirconia ball mill. The suspension was then heated on a hot plate to evaporate acetone and parts of the terpineol until a highly viscous paste for screen-printing was obtained. The paste was then printed through a sieve onto the various substrates mentioned above and dried at 125 °C. After drying, the boron films had a thickness of approximately 20 µm.

The specimens were put into a sealed aluminium oxide crucible together with pure magnesium as source material. Conversion to MgB$_2$ was carried out in argon - hydrogen (6.5 %, v/v) atmosphere under ambient pressure at temperatures given in table 2. Both, heating and cooling rates were kept constant at 5 °C min$^{-1}$.

| Substrate Material | Sintering Temperature / °C | Sintering Time / h |
|--------------------|-----------------------------|-------------------|
| Al$_2$O$_3$        | 850                         | 3                 |
| ZrO$_2$ (3 mol % Y$_2$O$_3$) | 850 | 3     |
| TiO$_2$            | 850                         | 3                 |
| Fe                 | 800                         | 3                 |
| Ti                 | 900                         | 5                 |
2.2. Characterisation
The grain size of the boron precursor was analyzed by a laser particle sizer (Coulter LS230, Beckmann Coulter, U. S. A.). The superconducting films were characterized by X-ray diffraction (Rigaku Geigerflex Dmax II, Japan, Fe-filtered Co Kα-radiation and X’Pert Pro, Panalytical, Ni-filtered Cu Kα-radiation) and by scanning electron microscopy (Zeiss Gemini 1540 XB, Germany) in combination with energy dispersive X-ray fluorescence spectroscopy (Oxford Instruments, Great Britain). The thickness of the films was analyzed by a profilometer (Perthometer C5D, Fa. Mahr, Germany). The superconducting properties were characterised by the temperature dependence of the electrical resistance.

3. Results

3.1. Paste for Screen Printing
Optimal screen printing behaviour was obtained with a paste, containing equal mass of boron and terpineol. The overall boron grain size on a number fraction scale was below 0.1 µm. This enables a fast conversion into the superconducting material, due to the large surface of the boron particles.

3.2. MgB$_2$ films on metallic substrates
The XRD patterns for MgB$_2$ on iron clearly indicated the formation of metal borides, decreasing the superconducting properties, such as critical temperature of the MgB$_2$ film (figure 1). In case of titanium as substrate material, also some small amounts of titanium dioxide were observed. Magnesium vapour, unfortunately, alloys with titanium at high temperatures during the formation process. This results in the formation of a very brittle substrate and poor conversion of the boron film into the superconducting material.

In case of iron substrates, the major drop of the resistance occurs at temperatures of about 38 K with some tailing to 30 K, whereas the superconducting film on pure titanium shows a much stronger tailing but no sudden jump in the resistance.

![Figure 1. Electrical resistance versus temperature of MgB$_2$ on iron (○) and titanium (△)](image-url)
3.3. MgB$_2$ films on polycrystalline ceramic substrates

The MgB$_2$ films on alumina and yttria stabilised zirconia were uniform, possessing a homogeneous dark brown colour. The titanium dioxide started to react with magnesium and boron, forming very brittle specimens with poor electrical properties, as seen in figure 3.

![X-Ray diffraction pattern](image1)

**Figure 2.** X-Ray diffraction pattern of MgB$_2$ on poly-crystalline Al$_2$O$_3$ (nickel filtered Cu K$_\alpha$ radiation), sintered at 850 °C for 3 h. The MgB$_2$ peaks are indexed.

Whereas the electrical resistance of the superconducting film on titanium dioxide is still not zero at low temperatures, both alumina and yttria stabilized zirconia show very narrow transition ranges of only 2 K (figure 3).

![Electrical resistance](image2)

**Figure 3.** Electrical resistance versus temperature of MgB$_2$ on Al$_2$O$_3$ (○), ZrO$_2$ (stabilized with 3 mol % Y$_2$O$_3$) (△) and TiO$_2$ (◇)
4. Discussion and summary
Boron films on iron, titanium, on polycrystalline alumina, yttria stabilized zirconia and titanium dioxide were applied via screen-printing. Conversion into the superconducting material by magnesium vapour transport was achieved. Titanium and titanium dioxide substrates turned out to be bad candidates since both titanium and titanium dioxide react with magnesium and boron, forming very brittle compounds.

Poly-crystalline alumina and poly-crystalline zirconia, stabilized with 3 mol % yttria, proved to be good substrate materials. In both cases, homogenous films, containing only little amounts of oxidic impurities have been achieved. Transition temperatures of up to 38 K with a very narrow transition range of only 2 K were realized.

An interesting model for the technical fabrication of flexible superconducting ribbons could be a combination of iron as substrate material, buffered with a thin layer of alumina or yttria stabilized zirconia [13]. This combination would combine the excellent properties of the ceramic material for the formation of magnesium diboride films with the flexibility of a thin metallic tape. Further investigations on this procedure are under way.

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