Al-alloyed MgB$_2$: correlation of superconducting properties, microstructure and chemical composition

B Birajdar$^1$, T Wenzel$^2$, P Manfrinetti$^3$, A Palenzona$^3$, M Putti$^4$, and O Eibl$^1$

$^1$ Institute of Applied Physics, University of Tübingen, Auf der Morgenstelle 10, D-72076 Tübingen, Germany

$^2$ Institute of Geosciences, Mineralogy and Geodynamics, University of Tübingen, Wilhelmstraße 56, D-72074 Tübingen, Germany

$^3$ INFM-LAMIA, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 33, 16146 Genova, Italy

$^4$ INFM-LAMIA, Dipartimento di Fisica, Universita` di Genova, Via Dodecaneso 33, 16146 Genova, Italy

Abstract. Al-alloyed MgB$_2$ was prepared by solid state reaction of Mg$_{1-x}$Al$_x$ alloy and crystalline B powder particles. The nominal composition of the samples was Mg$_{1-x}$Al$_x$B$_2$ , with $x = 0, 0.1, 0.2, 0.3$. Residual resistivity ($\rho_0$) of the samples measured by four-probe technique is comparable to the single crystals, indicating the excellent quality of these samples. The lattice parameters $c$ and $a$ decrease at a rate of 1.15 pm and 0.17 pm per at.% Al, respectively. Superconducting transition temperature ($T_c$) determined by measuring the resistive superconducting transition, decreases with increasing Al alloying at a rate of 1.56 K/at.% Al. Microstructure and chemical composition have been investigated by scanning electron microscopy (SEM), electron probe microanalysis (EPMA), and transmission electron microscopy (TEM). Al is incorporated into MgB$_2$ grains of $\sim$1 $\mu$m size by substitution of Mg lattice sites with Al. Al was found to be distributed inhomogenously which partially explains the broadening of the superconducting transition width ($\Delta T_c$) with increasing Al mole fraction. Al alloyed samples contain large ($\sim$15 $\mu$m) and small ($\sim$ 2 $\mu$m) secondary phases embedded in the (Mg,Al)B$_2$ matrix. The composition of large secondary phases is found to be (Mg,Al)$_{B_{16-\delta}}$ , with the mole fraction of excess boron ($\delta$) increasing from 0.99 at.% in pure sample to 4.14 at.% in highest alloyed sample. The Al to Mg mole fraction ratio in these large secondary phases is about half of that in the matrix. The size and density of the large secondary phases increased with increase in Al mole fraction. The secondary phases constitute less than 4% of the total sample volume and are thus not likely to affect the bulk superconductivity.

1. Introduction
The electronic structure of MgB$_2$ can be modified by substituting B or Mg atoms in the MgB$_2$. Al-alloyed MgB$_2$ was prepared by solid state reaction of Mg$_{1-x}$Al$_x$ alloy and crystalline B powder particles. The changes in the microstructure due to Al-alloying might also influence the superconducting properties. Therefore the microstructure of Al-alloyed MgB2 ceramics was studied.
on the micrometer scale using EPMA and on the nanometer scale using TEM. Specially the homogeneity of Al-alloying and the formation of secondary phases with Al-alloying are studied.

2. Experimental

Al-alloyed MgB$_2$ was prepared in a two step process. In the first step Mg-Al alloys are prepared with aluminium mole fractions of 0, 3.33, 6.66 and 10 at.% for samples 1 to 4 respectively. In the second step cylindrical piece of Mg-Al alloy and crystalline B powder (325 mesh) are put in Ta crucibles, welded in argon and closed in quartz tubes. The quartz tube is then placed in a vertical furnace which is at 850-900°C; after one hour the temperature is raised and maintained at 1000°C for 100 hours.

EPMA by wavelength-dispersive x-ray spectroscopy (WDX) was performed with a JEOL Superprobe 8900 RL operated at 15 keV primary energy with a probe current of 15 nA. Sample surfaces had to be polished very well and the so called “area intensity mode of measurement” had to be used to obtain precise quantitative analysis [1] for boron, which suffers from strong absorption and chemical shift of B-K$_\alpha$ x-ray peak.

For TEM analysis a small piece of sample 3 (Mg$_{0.8}$Al$_{0.2}$B$_2$) was crushed in a silica mortar, dispersed in ethanol and then placed onto a carbon foil supported by a copper grid. Thin electron transparent grains on these foils were investigated by a LEO 912 TEM, operated at 120 kV. An Energy dispersive x-ray (EDX) detector equipped with an ultra-thin window was used to acquire EDX spectra which were analysed using INCA 4.01 software package [2] from Oxford Instruments.

3. Results and discussion:

3.1. Superconducting and normal state properties

Behaviour of superconducting properties namely, $T_c$, superconducting transition width ($\Delta T_c$), and normal state properties ($\rho_0$, $a$, $c$) of Al-alloyed MgB$_2$ have been recently investigated by Putti et.al. [3,4] and summarised in table 1. $T_c$ was defined as $(T_{90\%}+T_{10\%})/2$ and $\Delta T_c$ defined as $T_{90\%}-T_{10\%}$, where $T_{90\%}$ and $T_{10\%}$ are temperatures corresponding to 90% and 10% of the resistive transition. $T_c$ decreases while $\Delta T_c$ increases with increasing Al concentration as shown in figure 1(a). The variation of $\rho_0$ (Figure 1(a)) with Al mole fraction is linear until aluminium concentration in sample 3, thereby obeying the Nordheim rule [5]. $\rho_0$ of sample 4 however is higher than expected. Lattice parameter $c$ which is the distance between the adjacent B-planes decreases at the rate of 1.15 pm/at.% Al with increasing Al mole fraction (Figure 1(b)). In contrast the in-plane lattice parameter $a$ decreases only by 1.3 pm for an Al mole fraction of 7.62 at.%.

![Figure 1.(a) Variation of $T_c$, $\Delta T_c$, and $\rho_0$ at 40 K with Al at. % determined by EPMA. (b) Variation of lattice parameters $a$ and $c$ with Al at. % determined by EPMA.](image-url)
Figure 2. Left half: (a) SE images for samples 1 to 4. (b) Magnified image of the area marked in (a). Arrows and arrowheads respectively indicate the large secondary phases inside dark regions and the small secondary phases. Right half: Correlation diagram of B-Mg (▲), B-Al (△) and B-O (◆) mole fractions from EPMA of (a) the matrix and (b) the large secondary phases of sample 3. The ideal position of MgB₂, MgB₈ and MgB₁₂ are also indicated for reference.

Figure 3. Left half: TEM-dark field (a) and bright field (b) image of MgB₂ grain of sample 3 under two beam conditions. Right half: (a) Correlation diagram of Al-Mg mole fractions determined using TEM-EDX spectra (△) and EPMA quantification of matrix (●) of sample 3.
### Table 1. Superconducting properties of pure and Al alloyed MgB$_2$.

| Sample No. | Nominal Composition | $T_c$ (K) | $\Delta T_c$ (K) | $\rho_0$ (μΩcm) | a (pm) | c (pm) | Al at.% EPMA | Al at.% Nominal |
|------------|---------------------|-----------|------------------|-----------------|--------|--------|--------------|----------------|
| 1          | MgB$_2$             | 39.19     | 0.2              | 2.5             | 308.5  | 352.5  | 0            | 0              |
| 2          | Mg$_{0.9}$Al$_{0.1}$B$_2$ | 35.06     | 3.26             | 7.95            | 307.7  | 348.3  | 3.27         | 3.33           |
| 3          | Mg$_{0.8}$Al$_{0.2}$B$_2$ | 33.27     | 3.56             | 11.69           | 307.7  | 345.3  | 5.4          | 6.67           |
| 4          | Mg$_{0.7}$Al$_{0.3}$B$_2$ | 27.27     | 6.32             | 24.47           | 307.2  | 343.7  | 7.62         | 10.0           |

3.2. Microstructural analysis

Figure 2 shows ~15 μm sized secondary phases embedded in the matrix of (Mg,Al)B$_2$. The size and number of the large secondary phases increases with increasing Al alloying. Their composition is determined using EPMA to be (Mg,Al)B$_{7+\delta}$, the mole fraction of excess boron being 0.99, 2.95, 3.73, and 4.14 at.% for samples 1 to 4 respectively.

3.3. Correlation of microstructure and superconducting properties

The fraction of the secondary phases is small, and the normal and superconducting properties presented by the samples can be attributed to the matrix. The $T_c$ versus Al mole fraction curve is in agreement with the calculations of Kortus et al.[6] which considered both, the decrease in density of states and increase in interband scattering with increasing Al-alloying. $\Delta T_c$ increases with increasing Al mole fraction and is related to the inhomogeneities in the Al-distribution. The $\Delta T_c$ for sample 3 for example is 3.56 K. The EPMA and TEM-EDX measurements (Figure 3) on sample 3 show that maximum variation in the Al mole fractions is 0.77 at.% This predicts a $\Delta T_c$ of 1.21 K which is less than the experimentally observed value of 3.56 K. It should however be noted that the inhomogeneities determined by EPMA and TEM-EDX suffer from poor statistics as measurement from only ~ 10 grains are considered [7]. The residual resistivity $\rho_0$ increases linearly with the Al mole fraction at the rate of about 2 μΩcm /at.% Al until sample 3. The residual resistivity $\rho_0$ of sample 4 is higher than the value expected by the Nordheim rule. Partly this is because of the unusually large density of voids observed in this sample. But it might be due to the reduction of the density of states plus the increase of scattering centres both being introduced by Al alloying.

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