Heat treatment influence on microstructure and properties of MgB$_2$ superconductor

I Abdyukhanov, A Tsapleva, P Lukyanov, P Konovalov, E Kotova
SC A A Bochvar High-Technology Research Institute of Inorganic Materials, Moscow, 5A Rogova Street, Russia
E-mail ASTsapleva@bochvar.ru

Abstract. Study results of 1 mm diameter MgB$_2$ superconductors fabricated by “powder in tube” method are presented. Ti and Nb were used as diffuse barriers materials. The mixture of magnesium and boron, powder of MgB$_2$, and also mixture of magnesium, boron and MgB$_2$ were used to form superconducting compound. Heat treatments in temperature range of 650-700 °C and 750-900 °C for 1h were conducted. It is established that 1 h heat treatment at 700 °C or 1 h at 900 °C heat treatment are sufficient for formation of MgB$_2$ superconducting phase ($T_c$=38 K) in superconductors with titanium barrier and powder mixture of magnesium and boron or magnesium, boron and magnesium diboride. The $T_c$ of in-situ process Nb - sheated superconductors was 37.6 K, the same $T_c$ were measured for ex-situ superconductors heat treated at 900 °C for 1 h. The critical current measurement results of fabricated superconductors were presented, optimal heat treatment modes were determined for fabricated superconductors.

1. Introduction

It’s more than 15 years passed since the discovery of superconducting properties of magnesium diboride in 2001 [1]. The technical superconductors based on this compound are produced by “powder in tube” method [2]. The main point of this method is metal tube filling with MgB$_2$ powder (ex-situ variant) or with magnesium and boron powder mixture (in-situ variant) [3,4].

The in-situ superconductors are known to have higher critical current capacities than ex-situ superconductors. On the other hand critical current degradation of in-situ wires in high magnetic fields are more remarkable as compared with ex-situ ones. This degradation is due to the smaller grain boundary density of synthesized magnesium diboride and their high electromagnetic connectivity in comparison with magnesium diboride in ex-situ powder core with less grain size and weak-links between particles. Porosity formation by MgB$_2$ synthesis from magnesium and boron mixture within wire can be a reason to critical current decrease by 24% from theoretical possible values.

It should be noted [5] that in-situ superconductors are characterized by thermomagnetic instability in the temperature range up to 20 K. For this reason scientists of different countries had investigated the properties and structure of the superconductors made of powder mixture of magnesium, boron and magnesium diboride with various components ratio [5-7]. The increase of x to 0.3 in (Mg+2B)$_{1-x}$ (MgB$_2$)$_{3x}$ mixture for superconductors with inner sheath made of iron leads to improvement of critical current. The further x increase doesn’t lead to critical current capacity improvement [5].

The goal of the studies is electrophysical properties (critical current density and critical temperature) and microstructure investigation of superconductors with Cu/Nb and Ti sheath produced by “powder in tube” method.
2. Materials and investigation methods

$\text{MgB}_2$ based superconductor specimens were produced by “powder in tube” method. To fabricate \textit{in-situ} superconductors Ti and Cu/Nb tubes were filled with mixture of magnesium powder (99 % purity, 60-100 $\mu$m particle size) and amorphous boron (99 % purity, 2-3 $\mu$m particle size). For \textit{ex-situ} superconductor №3 Cu/Nb tube was filled with MgB$_2$ powder (95 % purity, 1 $\mu$m particle size). Experimental №4 superconductor in titanium sheath contained powder mixture with the ratio (MgB$_2$)$_{0.7}$(Mg+2B)$_{0.3}$. Each composite was subjected to deformation to 1 mm diameter followed by 1 h heat treatment. Superconductors characteristics and heat treatment regimes are presented in Table 1.

| Superconductor name | №1 | №2 | №3 | №4 |
|---------------------|-----|-----|-----|-----|
| Sheath material     | Cu/Nb | Ti | Cu/Nb | Ti |
| Mixture characteristics | Mg:B=1.1:2 | Mg:B=1.1:2 | MgB$_2$ | (MgB$_2$)$_{0.7}$(Mg+2B)$_{0.3}$ |
| Powder fill factor, % | 27 | 30 | 35 | 30 |
| Anneal temperature, °C | 650 | 650 | 900 | 900 |
|                     | 700 | 700 | 1000 | 1000 |

The critical temperature ($T_c$) of samples was detected by voltage-temperature characteristics (VTC) to using Sniper-Researches SR – SC – 05 measurement system in accordance with IEC-61788-10 standard. The measurement of VTCs were conducted on 60-70 mm long samples that were soldered to current and voltage probe’s wafer contacts and equipped with Cernox CX-1030-SD-4B thermal sensor. The total temperature measurement error (sensor accuracy and thermal fluctuations taken into account) was ~ 30 mK for 20-40 K range.

The magnetization curve measurement based method was used to estimate critical current density capacity. The measurement of magnetization was carried out with PPMS-9 measuring unit in magnetic fields of up to 9 T.

3. Experimental data and discussion of the results

The longitudinal and transversal direction microstructures were investigated after the superconductors production. The longitudinal section of \textit{ex-situ} №1 superconductor is characterized by uniform powder core along the length, absence of “sausaging” and porosity. The superconductor №1 has uniform and equal width niobium diffuse barrier along the length (Fig 1). The powder core of superconductor №4 is composed of MgB$_2$ particles, Mg and B. It’s also known that magnesium particles stretch themselves during deformation process whereas hard magnesium diboride particles reduce themselves in size and redistribute across the cross-section as well as boron particles [8].

![Fig. 1 Longitudinal section of №1 superconductor](200\mu m)

The magnesium particles in \textit{in-situ} superconductors also stretch themselves along deformation axis whereas boron particles distribute themselves between them. The heat treatment results in
superconducting compound formation. The powder cores in №1 and №2 superconductors are bulk dense regions with voids in both longitudinal and cross-sections (Fig.2). The typical MgB$_2$ particles size for №1 and №2 superconductors is 1.1±0.3 µm.

![Fig. 2 Cross and longitudinal sections of superconductors №1 (a, b) after heat treatment 650°C, 1h and №2 (c, d) after heat treatment 700°C, 1h](image)

By the use of fractographic analysis of fracture surface of samples (№3 and №4) it was found that powder core after 900 °C heat treatment during 1 h consists of magnesium diboride particles (Fig.3) with 375±130 nm and 305±74 nm particle size, respectively. It’s shown that the particle size is almost 3 times smaller as compared to the initial size (1 µm). Moreover the particles of №3 superconductor are more uniform in size, particle size range is 140-460 µm as compared to the №4 superconductor particle size (180-720 µm). They have various form: all round form particles in №3 superconductor, both round and square-shaped form in №4 superconductor.

![Fig. 3 SEM image of powder core wires №3 (a) and №4 (b) after annealing 900 °C, 1 h](image)
VTC plots were drawn after various regimes heat treatment and critical transition temperature was detected. The critical temperature ($T_c$) of superconductor №1 after 650 °C heat treatment during 1 h is 37.26 K. $T_c$ of superconductor №2 after 650 °C heat treatment during 1 h is higher (37.65 K). The rise of anneal temperature from 650 to 700 °C leads to increase of $T_c$ for superconductor №2 to 38.43 K and VTC dispersion up to 0.6 K. VTC of superconductor №1 annealed at 700 °C for 1 h has 0.76 K dispersion and $T_c$=38.1 K. These values are close to the critical temperature of MgB$_2$ compound that indicates the complete reaction synthesis within the superconductor core.

VTC of superconductors №3 and №4 are presented in the figures 4 and 5, respectively.

Fig. 4 VTCs of wire №3 after heat treatment: 850°C, 1h, 900 °C, 1h, 1000 °C, 1h

It was found that superconductor №3 after annealing at 900 °C has critical transition temperature of 37.5 K. The increase of anneal temperature for superconductor №3 from 900 to 1000 °C results in 0.5 K $T_c$ drop and substantial dispersion of VTC transition. This in turn indicates the degradation of superconductive compound and the formation of non-superconductive borides that correlates well with some work results [9].

The superconductivity transition is sharp for superconductor №4 only after heat treatment at 900 °C for 1 h, critical temperature is 38.11 K (Fig.5). The temperature increase to 1000 °C results in $T_c$ rise to 39 K that is the theoretical transition temperature of MgB$_2$ compound and proves stoichiometric MgB$_2$ formation. The lower anneal temperature (e.g. 750 °C or 850 °C) is found to lead to the lack of superconductivity transition despite the presence of fully stoichiometric magnesium diboride by the X-ray data analysis.

It is related to the presence of magnesium oxide on the surface of magnesium diboride’s particles and it leads to the weakening of electromagnetic links between particles that in turn considerably limits the critical current in superconductors. The heat treatment at high enough temperatures (e.g. higher than 900 °C) results in particles’ surface melting that favours sintering of the powder. The duration of the heat treatment should be carefully defined to avoid the process of magnesium diboride dissolution.
The critical current density by magnetization loops analysis for superconductors №3 and 4 was estimated. Magnetization measurements were carried out in the 4.2-20 K temperature range in the magnetic fields from 0 to 2.5 T. It was shown that using niobium as a diffuse barrier material results in sharp increase of critical current density in self field at 5.5 K. This is due to the significant contribution of the currents passing in niobium that is superconductive under these conditions to the total superconductor current capacity [10]. This means that it is possible to estimate the critical current density for MgB2 superconductor №3 only in the magnetic fields higher than 0.25 T.

Critical current density (J_c) estimation results for superconductor №3 at 5.5 K, 10 K, 15 K, 20 K are presented in the Table 2 and for superconductor №4 – in the Table 3.

**Table 2** J_c of superconductor №3, after heat treatment 1000 °C, 1h (A/mm²)

| Magnetic field, T | Measurement temperature, K |
|------------------|---------------------------|
|                  | 5.5 | 10 | 15 | 20 |
| 0                | 2031* | 830 | 665 | 503 |
| 0.5              | 383  | 317 | 241 | 170 |
| 1                | 200  | 172 | 135 | 91  |
| 1.5              | 128  | 110 | 83  | 51  |
| 2                | 86.5 | 72.5| 51  | 25  |
| 2.5              | 58   | 46  | 27.3| 8   |

* - with Nb barrier contribution

It is found that critical current density of superconductor №4 is increased by ~ 2.5-2.7 times when anneal temperature rose from 900 to 1000 °C. It should be noted that J_c of superconductor №4 is higher in the whole temperature range ~ 10 % compared to the superconductor №3 under the same heat treatment regimes conditions. This reflects the particle connectivity of the magnesium diboride particles during the magnesium and boron synthesis process in the powder core and also the presence of impurity phases in the powder core which are the flux pinning centers of magnetic vortices that in turn are beneficial in critical current density increase.
Table 3 Jc of superconductor № 4 after heat treatment (A/mm²)

| Magnetic field, T | Heat treatment 900 °C, 1 h | Heat treatment 1000 °C, 1 h |
|------------------|-----------------------------|-----------------------------|
|                  | 4.2 | 10 | 15 | 20 | 4.2 | 10 | 15 | 20 |
| 0                | 431 | 353 | 272 | 197.5 | 1061 | 900.3 | 722.3 | 561.4 |
| 0.5              | 142 | 111 | 92 | 56 | 385 | 310 | 237 | 169.4 |
| 1                | 76  | 62  | 46 | 30.5 | 265  | 170 | 133.5 | 93.4 |
| 1.5              | 50  | 40  | 30 | 18.1 | 131  | 110.6 | 86.6 | 57 |
| 2                | 35  | 28  | 19.5 | 9.5 | 92.4 | 77 | 57.5 | 33 |
| 2.5              | 25  | 19  | 12 | 4  | 66.4 | 53.4 | 36 | 16.5 |

Conclusions

Electrophysical properties (critical current density and critical temperature) and microstructure of MgB₂ superconductors produced by “powder in tube” with Cu/Nb and titanium sheath are investigated. It was found that in-situ superconductors microstructure is characterized by numerous voids presence surrounded by magnesium diboride regions. Average grain size of magnesium diboride is 1.1±0.3 μm. Ex-situ powder core is defined by the lack of porosity, the average MgB₂ particles size is 375±130 nm and 305±74 nm for Cu/Nb sheathed and Ti sheathed conductors, respectively.

It was found that critical temperature of in-situ superconductors increases from 38.1 K to 38.4 K with the anneal temperature rise from 650 °C to 700 °C for Cu/Nb and Ti sheathed superconductors, respectively. The increase of anneal temperature from 900 °C to 1000 °C is found to lead to the rise of the critical temperature up to 39 K for titanium sheathed superconductors and 37 K (0.5 K drop) for Cu/Nb sheathed samples. It was defined that critical current density Jc of ex-situ made superconductors with titanium sheath is higher in whole temperature range ~10 % than for Cu/Nb sheathed superconductors with the same heat treatment regime.

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