Microstructure and properties MgB$_2$ superconductors after heat treatment

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Abstract. The power-in-tube method is used to produce MgB$_2$ wires. In this technology initial powders of B and Mg (as powder or stick) (in-situ technology) or MgB$_2$ powder (ex-situ technology) are put inside the metal sheaths, then the resulting powder-filling sheaths have been drawn up to requirement size. The important aspect is the choice of the optimum final heat treatment for each kind of wire. Heat treatments of MgB$_2$ superconductors, fabricated by in-situ method, are necessary for the formation superconducting compound. In wire, produced by ex-situ method, heat treatment is carried out for sintering the particles of magnesium diboride and, as a consequence, reducing the effect of weak - links between them and increasing of the critical current density. In the work the results of MgB$_2$ superconductors research of 1 mm in dia produced by in-situ and ex-situ methods are presented. The series of heat treatments of superconductors sample produced by in-situ method have been carried out at temperatures from 650 to 700 °C and duration from 0.25 to 0.5h. The heat treatment of samples produced by ex-situ method has been carried out at temperatures from 750 to 900 °C and duration 1h. It was shown that powder core of in-situ superconductors has been characterized by the high level of porosity and by areas of superconducting compounds of high density. The microstructure of powder core of ex-situ superconductors is characterized by a lot of nanometric size particles, are united in conglomerates. It was established that a critical temperature of superconductors, produced by different methods, was 36,4 К and 37,5 К for in-situ and ex-situ superconductors, respectively. On the basis of the data obtained, the recommendations have been formulated to choose the optimal heat treatment regime for superconductors of both types.

1. Introduction
Since its discovery in 2001 superconducting material of MgB$_2$ more than 15 years have already passed. [1]. Now the main method of industrial manufacturing of MgB$_2$ superconductors is “powder in tube” [2]. For example, one of the companies, the Columbus Superconductor, fabricates superconductors by the filling the metal tubes with finished superconducting compound (ex-situ method) [3], other company, HyperTech, uses as an initial powder a mixture of magnesium and boron (in-situ method) [4]. The main problem of the ex-situ method is the complexity of producing a finely dispersed, high-purity magnesium diboride powder. The critical current of such conductors will be determined by the current characteristics of the particles of magnesium diboride, the connectivity of the grains, the size of the regions of bound grains, the total number of them. Electro-physical characteristics of individual magnesium diboride particles are determined by the process of preparation of the original powder, the connectivity between them from the quality of the surface of each of the particles. The presence of various impurities in the initial MgB$_2$ powder leads to a substantial decrease in the grain connectivity and, as a consequence, to a degradation in the superconducting characteristics of the superconductor [5,6]. Typically, a superconductor is produced by drawing or rolling a powder-filled metal sheath. The wire of the final size is subjected to heat treatment to sinter the particles of magnesium diboride with each other and reduce the negative effect of the problem of weak – links [7].

A distinctive feature of the in-situ method of the production of MgB$_2$ superconductors is that the formation of a superconducting compound takes place inside a wire of the final size after heat treatment. The literature data on the investigation of in-situ conductors indicate that the synthesis of
magnesium diboride begins at a temperature of 550-570 °C and takes a very long time, and with increasing temperature to 650 °C it proceeds quite intensively for several minutes [7]. On the other hand, it is known that the optimum temperature for the formation of magnesium diboride from a mixture of magnesium and boron powders is 800 °C [8]. For the sintering of magnesium diboride particles in the preparation of superconductors by the ex-situ method, heat treatments are usually used at temperatures close to 900 °C [6], and it is indicated in the work that when the heating temperature increases to 800 °C [9], the superconducting compound and the formation of higher borides, for example MgB$_2$, MgB$_6$, MgB$_{12}$, for this reason the key factor here is the time of heat treatment.

In connection with this, the purpose of this work was to study the processes taking place in conductors of both types after different heat treatment regimes.

2. Materials and methods of research

The samples of MgB$_2$ superconductors were fabricated by «powder in tube» method. In the manufacture of a superconductor in an in-situ method, a bimetallic Cu/Nb tube, one of the ends of which was welded, was filled with a mixture of magnesium powders (99% purity, particle size 60-160 μm) and amorphous boron (99% purity, particle size 2-3 μm). The initial powders were mixed in the stoichiometric ratio.

The ex-situ superconductor was fabricated similarly. But it was used the MgB$_2$ powder (95% purity, particle size 1-0.5 μm) as initial powder. The end of the tube sheaths was crimped afterwards. The entire filling procedure was carried out in an argon atmosphere. We have drawn the powder-filling sheaths up to 1 mm in dia. The images of MgB$_2$ wires cross-section are shown in figure 1. The dimensions of the structural components of the investigated superconductors are presented in table 1.

Then the samples of in-situ superconductors were heat treated at 650 °C, 0.25h, 650 °C, 0.5h and ex-situ ones were heat treated at 750, 850 and 900 °C at duration 1h for each temperature and 0.5h at 900 °C. A high purity argon gas flow was maintained throughout of the heat treatment process.

The critical temperature ($T_c$) was determined from the volt-temperature curve (VTC) of the samples in accordance with the recommendations of the IEC-61788-10 standard on the SR-SC-05 installation made by Sniper-Researches. VTC were measured on samples of 60-70 mm in length, which were soldered to current and potential contacts on a probe substrate equipped with a temperature sensor Cernox CX-1030-SD-4B. The overall error of measurement of the temperature (taking in account the error of the sensor and temperature fluctuations) for the range 20-40 K was ~ 30 mK. The measuring current did not exceed 100 mA.

The microstructure of the conductors after annealing was investigated using scanning electron microscope Carl Zeiss Nvision 40 with the prefix Oxford X-Max.

The phase analysis was carried out on a D8 Advance (Bruker) X-ray diffractometer in Co Ka-radiation when the spectrum was taken in the range of diffraction angles 20 = 30-130 °.

Figure 1. Cross-sections of MgB$_2$ wires produced by «powder in tube» method: ex-situ (a) and in-situ (b).
Table 1. Characteristics of the structural components of superconductors of 1 mm in dia

| Characteristics          | 1 (in-situ) | 2 (ex-situ) |
|--------------------------|-------------|-------------|
| Sheath material          | Cu/Nb       | Cu/Nb       |
| Powder core fraction, %  | 27          | 32          |

3. Results and discussion
Before carrying out the heat treatment, the powder core of conductors of both types was investigated. The fractures of MgB$_2$ superconductors are shown in figure 2. It is shown, that powder core of in-situ superconductors consisted of magnesium particles, surrounded by a lot of boron particles (figure 2a). Microstructure powder core of ex-situ superconductors was characterized a plurality of MgB$_2$ particles (figure 2b).

![Figure 2](image_url)

Figure 2. SEM image of powder core MgB$_2$ wires ex–situ (a) and in-situ (b) before heat treatment

After heat treatment microstructure of powder core has changed. Microstructure of wire produced in-situ method was characterized by high level of porosity and regions of dens MgB$_2$ even after annealing at 650°C, 0.25h (figure 3 a). We have observed a lot of particles of MgB$_2$ and no pores in wire 2 after all heat treatments (figure 3 b).

![Figure 3](image_url)

Figure 3. SEM image of powder core MgB$_2$ wire 1 after annealing 650°C, 0.25h (a) and SEM image of powder core MgB$_2$ wire 2 after annealing 900°C, 1h (b).
Investigations of the microstructure of the powder core, depending on the duration of the heat treatment at 650 °C for conductor 1 or the increase in temperature from 750 to 900 °C for conductor 2, did not reveal significant changes by means of scanning microscopy. Changes in the phase composition of the powder core and the crystal lattice of magnesium diboride were detected X-ray phase analysis. The results are shown in table 2 and table 3.

Analysis of the obtained data shows that the parameter a, which is determined by the distance between the Mg atoms in the basal plane (0001), does not change within the measurement error with increasing heat treatment time. The parameter c, i.e. the distance between the basal planes in which the planes filled with Mg and B atoms alternate, the more then more the amount of this phase. This indicates that the increase of the duration of heat treatment at a temperature of 650 °C increases the amount of MgB₂, under this process the phase composition tends to stoichiometric. It was found that the heat treatment duration of 0.5 h at the temperature 650 °C was not sufficient to complete synthesize magnesium and boron into magnesium diboride.

| Heat treatment | Share of phases, % | The parameters of the crystal lattice MgB₂ |
|----------------|--------------------|------------------------------------------|
|                | Cu     Nb MgB₂ Mg  | a, Å  c, Å  c/a  β₁₁₀°  β₁₀₂° |
| 650 °C, 0.25h  | 60 15  20 5       | 3.084 3.498 1.134 0.38 0.63 |
| 650 °C, 0.5h   | 59 11  27 3       | 3.083 3.500 1.135 0.33 0.45 |

Table 2. Results of quantitative X-ray analysis of wire 1 after heat treatment.

| Heat treatment | Share of phases, % | The parameters of the crystal lattice MgB₂ |
|----------------|--------------------|------------------------------------------|
|                | Cu     Nb MgB₂ MgO | a, Å  c, Å  c/a  β₁₁₀°  β₁₀₂° |
| Before         | 55 12  33 -       | 3.086 3.525 1.142 0.33 0.41 |
| 750 °C, 1 h    | 50 8  42 -       | 3.081 3.520 1.142 0.35 0.28 |
| 850 °C, 1 h    | 53 10 37 -       | 3.085 3.514 1.139 0.36 0.38 |
| 900 °C, 0.5 h  | 53 8  32 7       | 3.083 3.500 1.135 0.33 0.45 |

Table 3. Results of quantitative X-ray analysis of conductor 1 after heat treatment.

Analysis of the values of the parameters of the magnesium diboride lattice in wire 2 (table 3) shows that the ideal stoichiometric ratio of magnesium and boron atoms is observed only in the initial state, before heat treatment, and after heat treatment at 750 °C, when the phase has a ratio with c/a = 1.142. As the heat treatment temperature increases, the parameter c of the crystal lattice decreases, which may indicate the beginning of the decay of the superconducting compound. The integral broadening of the maximum (110), whose interplanar distance depends only on the parameter a, is also practically independent of the heat treatment of the trend, but the broadening of the peak (102), whose interplanar distance depends both on a and c, increases with decreasing phase number. This result can be explained by the inhomogeneity of the B distribution in the crystal lattice of the MgB₂ phase. Together with this, we observed the formation of magnesium oxide, and with an increase in the duration of heat treatment at a temperature of 900 °C, the formation of higher borides was possible.

Another integral characteristic showing the presence of a superconducting compound in the manufactured superconductor is the critical temperature. VTC of superconductor 1 were previously presented in [8]. An increase in the stoichiometry of magnesium diboride was shown with an increase in the duration of heat treatment. The maximum value of the critical temperature of the wire 1 after different heat treatments was 36.4 K, which is lower than the theoretical temperature of magnesium diboride. This is explained by the presence of residual magnesium (table 2) and the possible formation of the finest layers of magnesium oxide, the presence of which is not determined by X-ray analysis methods.
Volt-temperature curves of conductor 2 are shown in Fig. 4, depending on the heat treatment regime. A superconducting transition at a temperature of 37.5 K is observed only after heat treatment at a temperature of 900 °C. After heat treatment at lower temperatures, there is practically no transition to the superconducting state (there is a residual resistance), despite the fact that the X-ray analysis data show the presence of completely stoichiometric magnesium diboride. The discrepancy observed can be explained by the effect of weak - links in conductors produced by ex-situ method. Magnesium oxide on the surface of the initial particles of magnesium diboride can lead to the appearance of weak - links. It is known that weak intergranular bonds substantially limit the critical current in ceramic high-temperature superconductors. Intergranular resistance was also observed in magnesium diboride. For example, it was found in the work by the TEM method that in polycrystalline bulk MgB$_2$ there is an amorphous non-superconducting layer of 5-20 nm thick on the granule boundaries [5]. Heat treatment of the wire at sufficiently high temperatures up to 900 °C leads to a reduction of the negative effect of weak bonds, but when this is necessary it is essential to limit its duration in order to avoid the intensive process of decomposition of magnesium diboride.

![VTC of wire 2 after different heat treatments.](image)

Figure 4. VTC of wire 2 after different heat treatments.

4. Conclusion

In this work, a study was made of the ceramic core of magnesium diboride conductors by the methods of scanning microscopy and X-ray phase analysis, and their critical temperature was measured. X-ray phase analysis showed that the maximum amount of MgB$_2$ compound is observed in a superconductor annealed at 750 °C.

It is shown that the parameter a of the crystal lattice of the MgB$_2$ phase does not depend on the thermal treatment regime of the superconductor, while the c parameter increases with the amount of magnesium diboride formed, with the ratio c / a tending to its ideal value of 1.142.

It has been established that the integral broadening of the peak (110) does not depend on the thermal treatment regime, while the peak width (102) has a minimum value at the maximum amount of MgB$_2$ phase in the conductor (750 °C).

It has been established that the conductors obtained by different methods have a critical temperature of 36.4 K and 37.5 K after different annealing modes: 650 °C, 1 h for in-situ conductors, 900 °C, 1 hour for ex-situ conductors.

On the basis of the data obtained, it was shown that the optimal mode of heat treatment of a superconductor made by the in-situ method is 650 °C with a duration of at least 1 h, and for a conductor made by the ex-situ method 900 °C for a duration of not more than 1 h.

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5. References

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