Microstructure and critical current of bulk MgB$_2$ superconductor

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Abstract. The structure of bulk MgB$_2$ specimens after cold deformation in Bridgeman anvils and “Toroid” chamber and following recovery annealings has been studied by scanning and transmission electron microscopy. It is demonstrated that in spite of the matrix phase grain coarsening by 5-7 times under annealing compared to the as-deformed state, the critical current density increases by a factor of 3 ($6.7 \times 10^4$ A/cm$^2$ at 30 K after deformation in the “Toroid” chamber and recovery annealing).

1. Introduction
The MgB$_2$ superconductor has some considerable advantages compared to other superconducting materials [1]: critical temperature of 39 K, high charge carriers density $1.7-2.8 \times 10^{23}$ A/cm$^3$, high critical current density $j_c$ of about $10^7$ A/cm$^2$ (4.2 K, 0 T), as well as high coherency lengths $\xi_{ab}(0) = 37-120$ Å and $\xi_c(0) = 16-36$ Å and no weak links between grains. Due to these features and relatively cheap manufacturing, MgB$_2$ is a promising material for fabrication of superconductors operating at liquid nitrogen temperature.

Bulk specimens of MgB$_2$ are obtained by pressing tablets of Mg and B powders with following annealing or by hot pressing under pressure. The MgB$_2$-based ribbons and wires are produced by in situ (metal tubes are filled with Mg and B powders with following deformation and annealing) and ex-situ (the ready-made MgB$_2$ powder is used instead of Mg and B) methods [2]. According to the X-ray data, there are always lines of both MgB$_2$ and MgO in the MgB$_2$ compound spectra independently on the fabrication method [3]. The presence of MgO particles can deteriorate inter-grain contacts, thus decreasing the $j_c$. On the other hand, grain and subgrain refinement, the presence of dislocations and fine MgO particles, which can serve as additional pinning centers [4], result in high superconducting properties.

The investigations of structure can contribute to better understanding of processes occurring at all the stages of MgB$_2$ superconductor fabrication, and thus working out optimal synthesis conditions and regimes of cold and hot deformation with following annealings. Understanding of structure will open opportunities for obtaining superconductors with high density of ceramics and with the structure containing great amount of pinning centers ensuring high critical current density $j_c$ [5].

2. Experimental
Tablets with composition Mg:B = 1:2 pressed under 600, 800 and 1000 MPa were annealed at 900, 1000 and 1100°C for 1 and 2 h in argon with hydrogen atmosphere the pressure of 0.165 MPa. The as-
synthesized tablets were subjected to quasi-hydrostatic reduction in the “Toroid” chamber under the pressure of $P = 4.1$ GPa or to deformation in Bridgeman anvils under the pressure of $P = 1.3$ GPa with anvils turn angles of 0, 20 and 45°. The recovery annealings were carried out at 800 and 950°C for 30 min or 1 h in argon atmosphere the pressure of 1 MPa.

The structure was studied by X-ray method in DRON-3M diffractometer, in Cr$\text{K}_\alpha$ radiation, and by scanning electron microscopy in Quanta-200 microscope with EDAX device for microanalysis and transmission electron microscopy in JEM-200CX microscope. Magnetization was measured by vibration magnetometer VSM-7407, and critical current density was determined from magnetization curves by Bin formula.

3. Results and discussion

Figure 1 demonstrates micrographs of synthesized ceramics dependently on preliminary compacting pressure by single-axis pressing and on temperature and time of synthesis. Without the preliminary compacting or under low compacting pressure, as well as at increased sintering temperatures, especially at longer sintering times, the ceramics structure is very porous, with considerable deviation of chemical composition both in Mg and B and high content of oxygen in porous areas (figure 1a). The higher is the compacting pressure, the more dense areas are formed in the ceramics structure (figure 1b), with composition of Mg:B = 1:2 according to the microanalysis data. Besides, the sintering temperature must not be higher than 900-950°C to avoid considerable grain growth.

As it is practically impossible to synthesize oxygen-free ceramics based on MgB$_2$, even if the initial components of high purity are used and synthesis is carried out in protective atmosphere, one must control the number, sizes and size distribution of MgO impurities. An excess amount of MgO with large particle sizes weakens the inter-grain linkages and decreases the superconducting properties of MgB$_2$ ceramics. Coarse (the sizes of up to 0.5 µm) precipitates of MgO on the surface of MgB$_2$ grains are formed in the ceramics synthesized without preliminary compacting (figure 2a) or at temperature higher than 900°C. In the ceramics preliminary compacted under 1000 MPa and synthesized at 900°C, even in porous areas the oxygen content is low and good stoichiometric ratio of Mg and B is observed (figure 2b). It is confirmed by X-ray analysis data, according to which the main phase is MgB$_2$ and only small amount of MgO is present.
Figure 2. SEM-images of the structure of MgB$_2$ ceramics and EDAX data after synthesis at 900°C, 1 h without preliminary compacting, the ratio of elements is Mg:B:O = 18:67:15 (a) and after compacting under 1000 MPa and synthesis at 900°C, 1 h, the ratio is Mg:B:O = 33:63:4 (b).

The treatment of synthesized ceramics by shift deformation in Bridgeman anvils under the pressure of 1.3 GPa increases its density, especially at larger turn angles (figure 3), from 1.44 g/cm$^3$ to about 2.2 g/cm$^3$.

Figure 3. SEM-images of structure of MgB$_2$ ceramics after synthesis and shift under the pressure of 1.3 GPa: $\alpha = 20^\circ$ (a), $\alpha = 45^\circ$ (b).

More detailed information on the evolution of structure of MgB$_2$ ceramics under various regimes of deformation and annealing was obtained by transmission electron microscopy.
According to TEM data, deformation results in considerable fragmentation of the ceramics accompanied by the formation of great amount of defects.

Figure 4a demonstrates TEM structure of the MgB$_2$ ceramics subjected to shift under pressure with the anvil turn angle of 20°. It should be noted that practically the same structure was observed when the angle was increased to 45°.

Figure 4. Bright-field images of structure of MgB$_2$ ceramics after shift under the pressure of 1.3 GPa, $\alpha = 20^\circ$ (a) and after shift under 1.3 GPa, $\alpha = 20^\circ$ and annealing at 950°C for 30 min (b).

The structure of the as-deformed specimens is highly defective, and especially defective are crystallite boundaries. Along with areas with high dislocation density, there are areas with crystallites which have sharp and nearly straight boundaries. In such areas the average size of structural fragments is 50-100 nm. In case of higher strain degree (the anvil turn angle of 45°) there are areas in which crystallite sizes are only 10-20 nm. It can be suggested that such highly defective structure is responsible for the critical current density decreasing by a factor of 20 compared to the initial state.

Under the recovery annealing relaxation processes are developed, which result in redistribution of defects, healing of cracks and grain growth (figure 4b). In spite of some grain coarsening, the critical current density after such treatment is $5.5 \times 10^4$ A/cm$^2$.

After the shift in Bridgeman anvils under the pressure of 1.3 GPa with anvil turn of 45° and following recovery annealing at 950°C for 30 min, the nanoscale structure was obtained in the ceramics, containing MgO particles comparable in sizes with the matrix phase grains (figure 5a). This structure resulted in higher critical current density, $j_c = 5.8 \times 10^4$ A/cm$^2$ [6].

The most uniform in sizes (of about 100 nm) structure of the MgB$_2$ ceramics with dispersed (10-70 nm) inclusions of magnesium oxide and higher magnesium borides was obtained in case of uniform reduction in “Toroid” chamber (quasi-hydrostatic pressing) with the following recovery annealing (figure 5b). As a result of the latter treatment the ceramics density was 2.4 g/cm$^3$, and the critical current density $6.7 \times 10^4$ A/cm$^2$ (at 30 K).

Dispersed structure with the sizes of 10 nm was obtained by the treatment including double deformation process and annealing at lower temperature (800°C) to limit the grain growth.

Figure 6 demonstrates a dark-field image of the as-treated ceramics in coinciding reflections 101$_{\text{MgB}_2}$ and 200$_{\text{MgO}}$. The paler light-grey areas belong to the MgB$_2$ phase, and bright white spots correspond to the MgO. It is seen that the MgO particles are uniformly distributed in the specimen bulk and their sizes are 10-30 nm.
Figure 5. TEM images of the MgB$_2$ ceramics structure: dark-field image after the shift under pressure 1.3 GPa, $\alpha = 45^\circ$ and annealing at 950°C, 30 min (a); bright-field image after reduction in the “Toroid” chamber under 4.1 GPa and annealing at 950°C, 30 min (b).

Figure 6. Dark-field image of the MgB$_2$ ceramics after the deformation under 1 GPa and annealing at 800°C, 1 h + deformation under 0.5 GPa and annealing at 800°C, 1 h: the reflections in the insert are 1 – 100$_{\text{MgB}_2}$, 2 – a ring of 101$_{\text{MgB}_2} + 200_{\text{MgO}}$, 3 – 002$_{\text{MgB}_2}$, 4 – 110$_{\text{MgB}_2}$, 5 – 111$_{\text{MgO}}$, 6 and 7 – higher boride reflections.

It should be noted that in all the specimens under study there is some amount of MgO after heat treatments. If the oxygen atoms replace the boron atoms in the MgB$_2$ lattice and occupy their positions, the MgO particles are formed uniformly distributed all over the volume of the MgB$_2$ phase [7]. As stated in a number of publications [8-12], the MgO inclusions can positively affect the superconducting properties if there is a good linkage between the MgO particles and MgB$_2$ grains. If the oxygen reacts with the residual magnesium under the post deformation heat treatment, the forming MgO particles are coarse and locally distributed. Consequently, the MgO particles generated from the decomposition of MgB$_2$ compound are more effective pinning centers than those formed by the residual magnesium oxidation.

4. Summary
Microstructure of MgB$_2$ superconductor has been studied by TEM after deformation-thermal treatments, and the factors responsible for an improvement of critical current density have been revealed.

It is demonstrated that deformation of MgB$_2$ both in the toroidal chamber and in Bridgeman anvils results in the formation of nanocrystalline structure with crystallite sizes of 10-20 nm, but cracks are generated as well, which results in dramatic decrease of the critical current density.

Under the following recovery annealing the MgB$_2$ grain sizes increase to 50-150 nm, and dense conglomerates of grains are formed.
After the recovery annealing magnesium oxide and higher borides are present in the structure in form of dispersed inclusions the sizes of 10-70 nm, and they can serve as additional pinning centers.

In spite of some grain growth, annealing of the deformed MgB$_2$ specimens results in an increase of critical current density by about a factor of 3 compared to that in the initial state (up to $j_c = 6.7 \times 10^4$ A/cm$^2$ at 30 K), which is due to the healing of cracks formed under the deformation and to the strengthening of linkages between MgB$_2$ grains.

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