Transmission EBSD (t-EBSD) to determine grain and grain boundary properties on nanostructured superconductor samples

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Abstract. The knowledge of the properties of the grains and their grain boundaries is essential for the further optimization of sample performance of various high-$T_c$ samples (YBa$_2$Cu$_3$O$_y$ (YBCO), Bi-based cuprates, MgB$_2$, iron-based materials). In these materials either the grains are of nanometer dimensions or the various additions of secondary phase(s) to improve the flux pinning are required to be of nanometer dimensions, so a high achievable resolution and better imaging properties are important to obtain reasonably high image quality of the recorded Kikuchi patterns to enable automated orientation mapping using the EBSD technique. Therefore, the newly developed transmission-EBSD (t-EBSD) technique is the method of choice to analyze the grain and the grain boundary properties in such nanostructured superconducting materials. Several results obtained on MgB$_2$, melt-textured, infiltration-growth processed YBCO and electrospun Bi$_2$Sr$_2$CaCu$_2$O$_8$ nanowires are presented.

1. Introduction

A proper knowledge of the microstructure of superconducting samples is essential to interpret data of the common integral measurement techniques like AC or DC magnetization or electric transport data (resistance, $I/V$-measurements). The electron backscatter diffraction (EBSD) technique was demonstrated in the literature by several authors to be a very useful tool on metallic and ceramic samples [1–4]. In the case of YBa$_2$Cu$_3$O$_y$ (YBCO or Y-123) superconductors, the introduction of flux pinning sites in the nanometer range demands a high-resolution microstructure analysis for melt-textured bulks as well as for tapes (coated conductors or powder-in-tube), whereas polycrystalline materials like MgB$_2$ or iron-based superconductors exhibit grain sizes in the nanometer range, which is also difficult to be analyzed for the standard EBSD technique. The transmission EBSD (t-EBSD) technique was very recently developed by several authors [5–8] with the goal to improve the spatial resolution of EBSD on materials with nanometer-sized grains. The samples investigated require to be transparent for the electron beam, so the sample fabrication as for transmission electron microscopy (TEM) has to be applied. As result, the spatial resolution could be improved from several tens of nanometers to \(\sim 5-10\) nm, depending on the material to be studied [9, 10]. Additionally, the effects of charging in non-conducting samples are considerably reduced, which is very important for non-conducting,
semiconducting or even biomaterials [11]. Therefore, the t-EBSD technique is optimally suited for the analysis of crystallographic orientations of the grains or inclusions also in the various superconducting materials, especially those intended for applications [12,13]. Up to now, the use of t-EBSD in the literature focused mainly on MgB$_2$, where the nanometer-sized grains and carbon additions as flux pinning sites play an important role [14,15]. In the case of sintered MgB$_2$ samples prepared using various reaction temperatures, t-EBSD was found to be the only way to obtain EBSD mappings on all the samples [15]. Furthermore, the crystallographic orientations of crystallites within electrospun Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi-2212) nanowire fabric samples could only be investigated by employing the t-EBSD technique [16].

In this contribution, we present results of grain and grain boundary (GB) properties like the boundary density, GB misorientation and the grain size aspect ratio for spark-plasma sintered (SPS) MgB$_2$, melt-textured, infiltration-growth (IG)-processed YBCO and electrospun Bi-2212 nanowires. To enable a direct comparison of the results obtained, we give the same mappings and plots for each sample type, wherever possible.

2. Experimental procedures

The materials investigated comprise spark-plasma sintered (SPS) MgB$_2$ [17,18], melt-textured YBCO bulk samples prepared by the infiltration growth (IG) technique [19] and Bi-2212 nanowires [20]. Details about sample preparation can be found in the references mentioned.

In a first step, all sample surfaces were subjected to mechanical polishing using SiO$_2$ papers, diamond pastes (3 µm, 1 µm and 0.25 µm) and Struers SiO$_2$ OP-S suspension (colloidal silica, particle size ≈ 40 nm) to a total roughness of several nanometers. Details of the polishing procedure are described in previous publications [4,21]. The polished sample surfaces were then analyzed in the scanning electron microscope (SEM) to select the best-suited sites for the subsequent TEM slice fabrication.

In a second step, the TEM slices for the t-EBSD measurements were fabricated using a dual-beam focused-ion beam (FIB) workstation (FEI Strata DB 235) with a routine allowing
for reduced surface damage. After lifting-off the TEM slice from the sample with the micromanipulator, the surface is ion-polished in a separate step by 2 KeV Ga-ions to a thickness of about 80 nm. This step serves to further reduce the preparation damage of the surface area and for a further thinning of the sample to be transparent to the electron beam. Here, it should be noted that, in general, polycrystalline samples are difficult to be handled in this process. The breaking out using the micromanipulator may lead to irregular-shaped bottom sides of the slice; in the worst case, the slice can break into several pieces. To further improve the imaging quality, the TEM slices were treated by additional low-angle argon ion-polishing (5 KeV, 5 min) to increase the image quality (IQ) of the resulting Kikuchi patterns as described in [22] for the investigation of ferrite samples.

Figure 1 (a) gives a schematic drawing of the configuration for operating EBSD in the transmission mode (t-EBSD). The t-EBSD works with a transmitted electron beam in contrast to the conventional mode of EBSD. Therefore, an electron-transparent sample is required for t-EBSD. Such samples can be straightforwardly prepared using FIB milling. The TEM-slices were mounted in the SEM on a specially fabricated sample holder allowing for the correct 70° inclination of the sample required for EBSD. The stage with the sample holder is inclined to an angle of −20°, which enables, together with the sample mounting, the same detector position to be used for the EBSD detector as in the standard configuration. This is shown in Fig. 1 (b). Here, the electron beam is passing through the sample (transmission mode) and an electron cone emanating from the sample is formed on its backside [23]. When this cone is intercepted by the phosphor screen, the Kikuchi patterns can be observed. Figure 1 (c) presents the final TEM slice and its cross section (d), ready for investigation.

The EBSD analysis was performed in a JEOL 7000F SEM microscope equipped with an orientation imaging analysis unit (EDAX Inc., OIM Analysis™) [24]. The Kikuchi patterns were generated at an acceleration voltage of 15 kV (standard configuration), and at 30 kV in t-EBSD mode. The patterns were recorded by means of a DigiView camera system. For t-EBSD, the working distance is set to 5 mm. The stepsize was chosen to be 5 nm. More details of the t-EBSD measurements are described in Refs. [11,15].

3. Results and discussion

Figure 2 presents EBSD measurements and analysis on the SPS-MgB$_2$ sample. The original bulk sample (diameter 30 mm, thickness 15 mm) was cut twice in perpendicular direction in the center, producing a slice of 2 mm thickness. This slice was cut in several $2 \times 2 \times 2$ mm$^3$ cubes for various measurements. The sample surface of the TEM slice was selected to be a horizontal plane with respect to the original bulk. The uniaxial pressure (50 MPa) was applied parallel to the bulk height [17,18], i.e., perpendicular to the selected sample surface.

Figure 2 (a) presents the EBSD image quality (IQ) mapping. We notice that there are elongated, large MgB$_2$ grains with high IQ values, but also may tiny grains with lower IQs, filling the spaces between the bigger ones. In some large grains, there are embedded small grains to be seen. In Fig. 2 (b) an orientation mapping in the ND-direction (i.e., normal to the sample surface) is given. The color code for the orientation is shown in the stereographic triangle below the map. We see here that the grains in SPS-sample are not fully randomly oriented, but do show a preferred texture as indicated by the dominant magenta color. Figure 2 (c) gives the corresponding pole figure. Figure 2 (d) is an IQ-map with the EBSD-detected GBs highlighted in color. The minimum GB misorientation detectable by EBSD is 2°. The colors are distributed as follows: 2° – 15° using blue lines, 20° – 55° using green lines, 60° – 75° using yellow lines, 80° – 125° using orange lines and 130° and above using red lines. The largest amount of the GBs is found in the range 20° – 55° (green), with some small angle GBs (blue) found within the large MgB$_2$ grains. This is further illustrated in the plot of Fig. 2 (g), giving the statistical distribution of the GB misorientation. The total length of all GBs detected in the analyzed area.
Figure 2. EBSD measurement and analysis on a SPS-MgB$_2$ sample. (a) IQ map, (b) orientation mapping giving the orientations normal to the sample surface (ND), (c) corresponding pole figure, (d) IQ map with the grain boundaries marked in color ($2^\circ$ – 15$^\circ$, 20$^\circ$ – 55$^\circ$, 60$^\circ$ – 75$^\circ$, 80$^\circ$ – 125$^\circ$ and 130$^\circ$ and above), (e) map of the grain shape aspect ratio, (f) plot of the boundary density, (g) plot of the GB misorientation and (h) plot of the grain shape aspect ratio.

is 440.36 $\mu$m (25424 boundaries with misorientation > $2^\circ$). In Fig. 2 (e), a map of the grain shape aspect ratio, $\gamma_{ar}$, is presented. This ratio ranges from 0.1 (blue) to 0.9 (red), defined as the length of the minor axis divided by the length of the major axis. Therefore, round grains have $\gamma_{ar} \approx 1$ [24]. The plot of Fig. 2 (f) gives the GB density (boundary line length/area) as function of the misorientation; extracted from Fig. 2 (d). The high number of GBs in the investigated area is due to the MgB$_2$ grain size in the 100 nm range, and thus, a strong GB pinning can be provided. The plot of Fig. 2 (g) presents the statistics of the GB misorientation angles, showing a maximum at 50$^\circ$. This is a consequence of the texture induced by the SPS process [15]. Finally, Fig. 2 (h) gives the distribution of the grain shape aspect ratio for all grains in the map, corresponding to the map of Fig. 2 (e). The maximum of ~0.6 indicates that the MgB$_2$ grains have dominantly an elliptic shape, whereas the small grains have a circular shape. This analysis yields important information about the sample studied. The GBs with misorientation angles of approx. 50$^\circ$ can be indeed effective flux pinning sites. A dominating pinning at GBs is also what is observed in magnetic measurements of this sample type. However, the presence
Figure 3. EBSD measurement and analysis on an IG-processed YBCO sample. (a) IQ map, (b) orientation mapping giving the orientations normal to the sample surface (ND), (c) corresponding pole figures, (left) YBCO and (right) 211, (d) IQ map with the grain boundaries marked in color ($\pm 2^\circ$–$15^\circ$, $20^\circ$–$55^\circ$, $60^\circ$–$75^\circ$, $80^\circ$–$125^\circ$, and $130^\circ$ and above), (e) map of the grain shape aspect ratio, (f) plot of the boundary density, (g) plot of the GB misorientation and (h) plot of the grain shape aspect ratio.

of the numerous small grains along the GBs provides a larger resistance to the current flow as could be expected from a sample without additional flux pinning sites. These results, therefore, corroborate the results of the resistance measurements discussed in [25].

Figure 3 shows a t-EBSD analysis on an IG-processed, YBCO bulk sample [19]. The unique properties of the IG-processed samples (i.e., extremely high irreversibility fields) are due to the presence of very small $\text{Y}_2\text{BaCuO}_5$ (211) particles, being useful flux pinning sites as their size is comparable to 2 times the coherence length, $\xi$, especially at elevated temperatures. As result, these particles provide good flux pinning [26–28]. The sample selected for the investigation stems from the $c$-axis growth sector of the bulk (diameter 20 mm, height 8 mm), $\sim$5 mm apart and 3 mm below the seed crystal. The sample surface is a typical $(a,b)$-plane of a melt-textured YBCO sample. To investigate the properties of these tiny 211 particles and their interaction with the YBCO matrix, the location for milling out the TEM slice was carefully chosen between the large 211 particles. In EBSD configuration (tilted to $70^\circ$), the SEM image clearly reveals these particles (Fig. 3 (a)) as dark spots. Figure 3 (b) gives an orientation map in ND direction for both phases, YBCO and 211. The color code for this map is given in the stereographic triangles below the map. The unit cells of YBCO and 211 are both orthorhombic, but the $c$-axis
of 211 is much longer as that of YBCO, so the distinction between the two cells is simple, but some problems prevail as discussed in detail in Ref. [29]. Due to the increased IQ values of the t-EBSD images, it is possible to resolve the tiny 211 particles embedded within the YBCO matrix, which have sizes between 18 and 45 nm. From this mapping, we can learn that the larger 211 grains cause an alteration of the surrounding YBCO matrix like the big 211 grains measured in Refs. [30,31]. Only the extremely small 211 grains do not affect the homogeneous growth of the YBCO matrix. This is a very important result for the fabrication of chemical flux pinning sites using secondary phases. In Fig. 3 (c), the corresponding pole figures are given for YBCO (left) and 211 (right). This figure reveals the strong texture of YBCO and the random-like orientation of the 211 particles. Figure 3 (d) presents an IQ map with the highlighted GBs. The total length of the GBs in the investigated section is 104.48 µm (4524 boundaries with misorientation > 2°).

Fig. 3 (e) shows the grain aspect ratio mapping, revealing a large number of small, round grains embedded in a big, one-grain matrix, which is typical for melt-textured YBCO. The plot of Fig. 3 (f) gives the GB density in the investigated area. Here, we show the data for the two phases separately. The GB density for YBCO is nearly constant, with a sharp increase towards 90°, whereas the 211 phase exhibits an increasing GB density. Fig. 3 (g) shows the distribution of the GB misorientations, where YBCO shows a majority of low-angle GBs. The 211 phase has in contrast some GBs with angles between 40 and 60°, and a maximum at 70°. Fig. 3 (h) presents a plot of the grain boundary aspect ratio of both phases. YBCO exhibits several large, elongated grains, while the 211 phase has a peak at ~0.6. For both phases, the small grains have a grain size aspect ratio of 0.8. These phase-resolution analysis of the GB and grain properties corroborates the earlier results obtained on melt-textured bulk samples [30,31].

Finally, Fig. 4 presents t-EBSD results obtained on an individual piece of a nanowire from an electrospun, Bi-2212 nanowire network sample [20]. The dimensions of the nanowires enable t-EBSD measurements without additional sample preparation as discussed in Ref. [16]. Figure 4 (a) presents a SEM image of Bi-2212 nanowires mounted on a TEM grid. The yellow rectangle marks the analyzed area. In Fig. 4 (b), the result of the grain orientation mapping in normal orientation is presented. The color code is given in the stereographic triangle below the map. We observe that the Bi-2212 grains have a dominant orientation in [100]-direction (dominating green color in the map), which is due to the previous arrangement of the precursor material within the original polymer nanowire. In Fig. 4 (c), the corresponding pole figures in ND (left) and RD (right) directions are shown, which manifest the grain orientation along the former polymer nanowire. Figure 4 (d) presents an IQ map with the highlighted GBs. A large number of small-angle GBs is observed, but also a large number of GBs with 30 – 90° misorientation. The total length of the GBs in the investigated section is 71.85 µm (2489 boundaries with misorientation > 2°). On such a sample with strongly anisotropic, mostly elongated grains which is typical for the Bi-2212 or Bi-2223 compounds [32,33], an analysis of the grain shape aspect ratio is very informative. Figure 4 (e) gives the grain shape aspect ratio mapping. The map reveals that a medium ratio of 0.6 is dominating in the selected area. This information describes the grain growth depending, e.g., on the reaction temperature and the holding time. Therefore, such EBSD analysis enables an optimization of the grain shape aspects of such an anisotropic material. Figure 4 (f) presents the GB density in the measured area, which is here monotonously increasing with increasing misorientation. Fig. 4 (g) shows the distribution of the GB misorientations, revealing a high amount of small-angle GBs and a large number of GBs in the range 40 – 90°. The plot of Fig. 4 (h) gives the distribution of the grain shape aspect ratio. The Bi-2212 grains have a compact shape, which is due to the reduced reaction temperature (800 °C) necessary to maintain the nanowire shape. The more elongated grains being typical for the Bi-2212 compound require obviously reaction temperatures around 830 °C as common for the tape fabrication [34].
Figure 4. EBSD measurement and analysis on an IG-processed YBCO sample. (a) SEM image of a piece of a Bi-2212 nanowire network fabric sample, (b) orientation mapping giving the orientations normal to the sample surface (ND), (c) corresponding pole figures in ND and RD directions, (d) IQ map with the grain boundaries marked in color ($2^\circ$ – $15^\circ$, $20^\circ$ – $55^\circ$, $60^\circ$ – $75^\circ$, $80^\circ$ – $125^\circ$ and $130^\circ$ and above), (e) map of the grain shape aspect ratio, (f) plot of the boundary density, (g) plot of the GB misorientation and (h) plot of the grain shape aspect ratio.

4. Conclusions
The t-EBSD technique is demonstrated to be a very useful instrument to analyze the microstructures of various superconducting materials, especially when grains in the nanometer range or nanometer-sized particles as flux pinning sites embedded in the superconducting matrix are to be analyzed. The use of FIB-prepared TEM-slices allows proper areas for analysis to be selected, which is very important regarding inhomogeneously distributed flux pinning sites. Furthermore, t-EBSD enables automated multi-phase EBSD scans to be performed due to the increased image quality of the Kikuchi patterns obtained on ceramic samples or on samples with nanometer-sized grains. In general, the EBSD data collected on various superconducting samples provide essential input to develop specifically tailored growth techniques for superconducting materials.

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