TEM and electron backscatter diffraction analysis (EBSD) on superconducting nanowires

A. Koblischka-Veneva, M. R. Koblischka, X. L. Zeng, J. Schmauch, U. Hartmann
Experimental Physics, Saarland University, Campus C 6 3, 66123 Saarbrücken, Germany
E-mail: a.koblischka-veneva@mx.uni-saarland.de

Abstract. Electrospun, superconducting nanowires are characterized concerning the grain orientation, their texture and the respective grain boundary misorientations by means of electron backscatter diffraction (EBSD) analysis. The individual nanowires in such electrospun, nonwoven nanowire networks of Bi$_2$Sr$_2$CaCu$_2$O$_x$ (Bi-2212) are polycrystalline, have average diameters up to 250 nm and their grains are in the 20-50 nm range. This requires a high spatial resolution for the analysis in the scanning electron microscope. However, the small diameter of the nanowires enables the application of the newly developed transmission EBSD (t-EBSD) technique without the preparation of TEM slices. Here, we present TEM images of individual nanowires and several EBSD mappings on Bi-2212 nanowires and compare their microstructure to those of filaments of the first generation tapes.

1. Introduction
Electrospinning is a versatile technique to fabricate long, polycrystalline nanowires of ceramic materials, including high-$T_c$ superconductors [1]. In the literature, this enabled already the growth of (La,Sr)CuO$_4$ [2,3], YBa$_2$Cu$_3$O$_x$ [4,5] and Bi$_2$Sr$_2$CaCu$_2$O$_x$ (Bi-2212) [6–9] nanowires. The resulting nanowires are polycrystalline with grain sizes of about 40-60 nm, but are up to several hundreds of micrometers long. After the electrospinning process, a fabric-like material consisting of polymer nanowires containing the ceramic precursor is created. After the heat treatment, the polymer is burned off and grains of the superconducting material are formed. By means of focused ion-beam milling, individual nanowires can be cut out from the fabric-like sheets. These nanowires can now serve as objects for further studies of physical properties concerning superconductivity in reduced dimensions. Therefore, a detailed understanding of the resulting microstructure within an individual nanowire is strongly required. For this purpose, we employ here the electron backscatter diffraction (EBSD) analysis on such nanowires in order to obtain information on the crystallographic grain orientation and the resulting texture. Due to the small sizes of the Bi-2212 grains within the nanowires, we employ the recently developed transmission EBSD (t-EBSD) technique [10–12] on our samples. As only a small amount of nanowire pieces is transparent to the electron beam, we used a modified approach by using the sample holder as for t-EBSD, but working in reflection mode. This enables the study of nanowire pieces without any further surface preparation.

In the present contribution, we describe the transmission electron microscopy (TEM) investigation and the approach to perform EBSD analysis on pieces of Bi-2212 nanowires.
2. Experimental procedures

Bi-2212 nanowire networks were grown by the electrospinning technique, employing acetate powders of all constituents and PVP (polyvinyl pyrrolidone, M.W.1,300,000) dissolved in propionic acid. After the electrospinning process, a heat treatment is required to remove all organic material from the as-prepared nanowire networks and to form the superconducting phase. Finally, an oxygenation step in pure $O_2$ is required. X-ray analysis confirmed that the samples are pure Bi-2212 phase with some residing carbon. Details of the nanowire fabrication procedure are given elsewhere [2,3]. Samples for TEM/t-EBSD were prepared by ultrasonication of nanowire network pieces in ethanol for 5 s. Then, a drop of this liquid was placed on a carbon-coated TEM grid and dried. Such a Bi-2212 piece can now serve for TEM and t-EBSD. An image is presented in Fig. 2.

The TEM analysis was performed by JEOL JSM-7000 F transmission electron microscope operating at 200 kV with a LaB$_6$ cathode. For TEM investigations, several nanowire pieces separated from the nanowire fabric by ultrasound treatment were placed on a carbon-coated TEM copper grid. This enabled to search nanowire regions which were thin enough to enable the transmission mode. No additional treatment of the sample surface was carried out.

For EBSD measurements, the TEM-grids were mounted in the scanning electron microscope (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. Here, the electron beam is passing through the sample (transmission mode) and the electron cone is formed on the backside of the sample. The holder further enables a second way of operation of EBSD like for standard EBSD in reflection mode together with the TEM-prepared sample. This second operation mode was chosen for the
Figure 2. SEM image of a sectioned Bi-2212 nanowire fabric on the TEM grid. The inset shows a SEM image of a complete nanowire fabric.

present nanowire samples not to be limited to only electron-beam transparent sections. The electron beam operates at 30 kV, and the working distance is set to 5 mm. The EBSD stepsize was chosen to be 5 nm. An image of our sample holder and the entire arrangement within the SEM chamber is presented in Fig. 1.

This approach enables here for the first time a proper analysis of nanowire samples with nanometer-sized grains. However, as the nanowire samples were mostly too thick to operate EBSD in transmission, we operated EBSD also in reflection mode but using the custom-built sample holder for TEM grids.

3. Results and discussion
In previous publications, SEM images of the entire nanowire fabrics were presented [7, 8], see also the inset to Fig. 2. Here, we now focus on the microstructure of individual nanowire pieces. Firstly, Fig. 2 shows an SEM image of a nanowire fabric piece on the TEM grid, ready for further investigations. One can clearly see the Bi-2212 grains with their specific elongated shape. Some crystallites are even pointing away from the main nanowire. This image further demonstrates that for t-EBSD in either mode a high SEM magnification is required; in our case up to 70000×.

Figure 3 presents TEM images of Bi-2212 nanowires showing sections with interconnects between two nanowires (a,b). These interconnects of the nanowires, which are formed during the processing due to shrinking effects, are essential for the current flow through a nanowire fabric sample. This was discussed in detail in Ref. [13] together with a modelling approach. The
Figure 3. TEM images of Bi-2212 nanowires showing sections with an interconnect between two nanowires (a,b). Images (c) and (d) present sections of individual nanowires. In (d), one can see that the nanowire consists only of one single Bi-2212 grain.

Figure 4 (a) – (d) give more details about the grain boundaries (GBs) between the grains within a nanowire. Here, it is important to note that a large number of the interconnects and many connections between the grains have survived the ultrasonic treatment. This indicates that the grains stick closely together, thus providing good electric contacts for the current flow. Transport measurements on such individual nanowire pieces will enable the study of the magnetic properties of the interconnects determine the overall field dependence of the critical currents, so it is important to understand how these interconnects are built up. Images (c) and (d) present sections of individual, thin nanowires. In Fig. 3(d), one can see that the nanowire consists in the center only of one single Bi-2212 grain, which is about 200 nm long, but only \( \sim 100 \) nm wide.
Figure 4. TEM images of individual Bi-2212 nanowire sections. Images (a), (b) and (c) present several thin nanowire sections, and (d) shows a grain boundary within the nanowire in high magnification. Note also that the edges of the grains are transparent to the electron beam.

GB influence on the current flow. It is further remarkable that in (a) the nanowire exhibits connections between elongated Bi-2212 grains, whereas images (c) and (d) show a small grain quasi as contact element between two bigger ones. The TEM image suggests that this small grain is misoriented by a high angle which can be up to 90°.

Now, we will turn to the EBSD measurements on such nanowire sections. As already stated before, the t-EBSD can be carried out in reflection mode in order to enable the investigation of samples which have a thickness larger than one single grain. EBSD measurements using the t-EBSD technique were already done in the literature on superconductors like MgB$_2$ [14–16], but now yet on ceramic high-$T_c$ superconductors.

Figure 5 presents an EBSD-mapping on a nanowire section. Here, we selected a large piece
Figure 5. EBSD mapping on a nanowire section. The map (a) is an image quality (IQ) map resembling a SEM image. Additionally, the map is overlaid with the EBSD-detected grain boundaries (yellow). The map (b) shows an inverse pole figure map giving the crystallographic orientations. The color code is given in the stereographic triangle below the map. (c) is a SEM image of the investigated nanowire section. (d) shows the inverse pole figure in [001]-direction. Only some specific grain orientations are obtained.

Figure 6. EBSD results for the grain size (a) and the misorientation angles (b).
allowing an EBSD mapping. The selected area spans \(2000 \times 1600\) nm; the EBSD step size for this measurement was 40 nm. Fig. 5 (a) shows an image quality (IQ) map, together with the EBSD detected GBs marked in yellow. The resulting IQ of the Kikuchi patterns obtained was quite high despite that there was no surface preparation. The strong variation of the IQ values stems from the height differences in the nanowire piece, see the inset to Fig. 5 (a). Fig. 5 (b) is an inverse pole figure (IPF) map, giving the crystallographic orientation of the grains. The color code for this map is given in the stereographic triangle below the map. The distribution of the colors suggests directly that there are only some orientations; the grains in the nanowire are far from being randomly oriented. This is manifested in the inverse pole figure in [001]-direction presented in (c). Here only 8 spots are found. The highest peak is obtained close to the [100]-direction, which says that most of the grains have their \(c\)-axis in the nanowire plane. Here, we can state that the electrospun Bi-2212 nanowires are similar to tiny filaments extracted from multifilamentary wires or tapes [17–19]. As the as-spun nanowires are formed as polymer nanowires containing the precursor material, there is still the information of the main wire direction at the beginning of the Bi-2212 formation, so the growth direction of the Bi-2212 grains takes place in the direction of the former polymer nanowire. This explains why we find so many elongated Bi-2212 grains with only some orientations.

In Fig. 6, more results of the EBSD analysis are presented. (a) shows the EBSD-detected grain size. Grains can be as small as 40 nm, but also big grains with size up to 450 nm can be found. Image (b) shows the misorientation angles. The largest number fraction are orientations of up to \(10^\circ\), but then there are many misorientations in the range from 20° to 90° (c). As expected, the misorientation distribution does not correspond to the result which would be obtained in a fully random situation, which demonstrates again that the grains in the nanowire are oriented along the nanowire direction, however, also high misorientations of the Bi-2212 grains exist as seen in the TEM-images (Figs. 4 (c,d)).

Further EBSD analysis of different types of nanowire sections found in the TEM images will enable to construct a complete picture of the building principles of such nanowires. This knowledge will help to prepare nanowire networks with improved properties for certain applications in the future.

4. Conclusions

To conclude, we presented a TEM investigation on individual Bi-2212 nanowire pieces stemming from electrospun nanowire fabrics. We further have investigated the crystallographic orientation of Bi-2212 grains within individual nanowire pieces in detail using the t-EBSD technique in reflection mode. The analysis demonstrates that the Bi-2212 grains within a nanowire are mainly oriented with their \(c\)-axis parallel to the nanowire direction.

Acknowledgments

This work is subsidized by the DFG project Ko2323/8, which is gratefully acknowledged.

References

[1] Wu H, Pan W, Lin D and Li H 2012 J. Adv. Ceramics 1 2
[2] Li J-M, Zeng X L, Moa A D and Xu Z-A 20111 CrystEngComm 13 6964
[3] Zeng X L, Koblischka M R and Hartmann U 2015 Mat. Res. Express 2 095022
[4] Duarte E A, Rudawski N G, Quintero P A, Meisel M W and Nino J C 2015 Supercond. Sci. Technol. 28 015006
[5] Rotta M, Zadorosny L, Carvalho C L, Malmonge J A, Malmonge L F and Zadorosny R 2016 Ceram. Int. 42 16230
[6] Duarte E A, Quintero P A, Meisel M W and Nino J C 2013 Physica C 496 109
[7] Koblischka M R, Zeng X L, Karwoth T, Hauet T and Hartmann U 2016 AIP Adv. 6 035115
[8] Koblischka M R, Zeng X L, Karwoth T, Hauet T and Hartmann U 2016 IEEE Trans. Appl. Supercond. 26 1800605
[9] Zeng X L, Koblischka M R, Karwoth T, Hauet T and Hartmann U 2017 Supercond. Sci. Technol. 30 035014
[10] Trimby P W 2012 Ultramicroscopy 120 16
[11] Keller R and Geiss R 2012 J. Microsc. 245 245
[12] Sneddon G C, Trimby P W and Cairney J M 2016 Materials Science and Engineering R 110 1
[13] Zeng X L, Karwoth T, Koblischka M R, Hartmann U, Gokhfeld D, Chang C and Hauet T 2017 Phys. Rev. Mater. 1 044802
[14] Yeoh W K, Cui X Y, Gault B, De Silva K S B, Xu X, Liu H W, Yen H-W, Wong D, Bao P, Larson D J, Martin I, Li W X, Zheng R K, Wang X L, Dou S X and Ringer S Pl 2014 Nanoscale 6 6166
[15] Wong D C K, Yeoh WK, Trimby P W, De Silva K S B, Bao P, Li W X, Xu X, Dou S X, Ringer S P and Zheng R K 2015 Scripta Mater. 101 36
[16] Koblischka-Veneva A, Koblischka M R, Schmauch J, Inoue K, Muralidhar M, Berger K and Noudem J 2016 Supercond. Sci. Technol. 29 044007
[17] Kametani F, Jiang J, Matras M, Abraimov D, Hellstrom E E and Larbalestier D C 2015 Sci. Rep. 5 8285
[18] Koblischka-Veneva A, Koblischka M R, Qu T, Han Z and Mücklich F 2008 Physica C 468 174
[19] Skov-Hansen P, Koblischka M R, Vase P, Kovac P and Marti F 2001 IEEE Trans. Appl. Supercond. 11 3740