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Hata, Satoshi
Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Harini, Sosiati
The Research Laboratory for High Voltade Electron Microscopy

Yoshidome, Takeshi
Department of Applied Science for Electronics and Materials, Kyushu University

Kuwano, Noriyuki
Art, Science and Technology Center for Cooperative Research, Kyushu University

他

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Transmission Electron Microscopy Observation of MgB_2 Superconducting Materials with Inhomogeneous Microstructure: Influences of Specimen Preparation Methods

Satoshi HATA [*1,†] Harini SOSIATI [*2] Takeshi YOSHIDOME [*3]
Noriyuki KUWANO [*4] Akiyoshi MATSUMOTO [*5] Hitoshi KITAGUCHI [*5]
and Hiroaki KUMAKURA [*5]
[†]E-mail of corresponding author: *hata@mm.kyushu-u.ac.jp*

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Transmission electron microscopy (TEM) observation of microstructure in MgB_2 superconducting materials was carried out using different TEM specimen preparation methods. When a focused ion beam microsampling (FIB-MS) technique was applied to prepare thin foil specimens, TEM observation revealed inhomogeneous microstructure in MgB_2 tapes fabricated by an *in situ* powder-in-tube (PIT) process: the microstructure composed of a densely crystallized MgB_2 area, a partially crystallized area containing amorphous phases, μm-sized holes, etc. It was also revealed that doping with SiC in the PIT process makes distribution of the crystallized and partially crystallized areas uniform. On the other hand, when a conventional TEM specimen preparation, pulverizing the specimen into powders and thinning the powders with an Ar ion mill was performed, the microstructural characters of the MgB_2 tapes described above were hardly recognized.

Key words: *MgB_2, Superconducting material, Focused ion beam (FIB), Microsampling, Transmission electron microscopy (TEM)*

1. Introduction

The MgB_2 superconductor discovered in 2001[1] is considered as a new superconducting material. For practical applications of MgB_2, the critical current density (J_c) under magnetic fields should be increased. In the research for increasing J_c in MgB_2 materials, microstructure characterization by transmission electron microscopy (TEM) is effective, because J_c closely depends on the microstructure. Here, we focus on microstructural inhomogeneity in MgB_2 materials. It is known that fabrication of MgB_2 materials with uniform quality is not easy. This is due to a large difference in melting temperature between Mg and B, high volatility of Mg, high reactivity of Mg with oxygen, etc. Because of the facts, resultant MgB_2 materials often have inhomogeneous microstructure. In this case, preparation of thin foil specimens as well as TEM observation should be carefully performed for a correct microstructure characterization.

This paper reports influences of TEM specimen preparation methods on observed microstructure in MgB_2 superconducting materials. Thin foil specimens for TEM observation are prepared from MgB_2 tapes using two methods: one is a modern method with a focused ion beam microsampling (FIB-MS) technique[2] and another is a conventional method with an Ar ion mill. The former method clearly reveals inhomogeneous microstructure in the MgB_2 tapes. On the other hand, the latter method makes the original inhomogeneous microstructure invisible. In addition, the former FIB-MS method is also

*1 Department of Molecular and Materials Sciences
*2 The Research Laboratory for High Voltage Electron Microscopy
*3 Department of Applied Science for Electronics and Materials, Graduate student
*4 Art, Science and Technology Center for Cooperative Research
*5 National Institute for Materials Science, Ibaraki 305-0047, Japan

applied to observe inhomogeneous microstructure in an as-rolled tape before the reaction of MgB_2 formation. An effectiveness of using the FIB-MS technique for MgB_2 tapes has been reported in a previous paper.[3)] However, a comparison in TEM data between FIB milled and Ar ion milled specimens of the same MgB_2 tapes is not published as far as the authors know. This is the originality of the present paper.

2. Experimental

MgB_2 tapes were fabricated by an *in situ* powder-in-tube (PIT) process.[3-5)] MgH_2, amorphous B and SiC powders were mixed together, where the molar ratio, MgH_2:B, was 1:2 and the SiC contents were 0, 5 and 10 mol% of the resultant MgB_2 content. The mixed powders were densely packed in Fe tubes and then cold-rolled into tapes with the final sizes about 4 mm width and 0.5 mm thickness. These 'as-rolled' tapes were heat treated at 873 K for 3.6 ks under a high-purity Ar atmosphere and then cooled in the furnace. By the heat treatment, MgB_2 superconducting tapes were obtained. Hereinafter, the MgB_2 tapes with the different SiC contents were designated as SiC-0, SiC-5 and SiC-10, respectively. J_c values in the MgB_2 tapes were evaluated by transport critical current measurements.[3-5)] At 4.2 K under a magnetic field of 12 T, the evaluated J_c values were 650, 5000 and 6500 A cm^{-2} for SiC-0, SiC-5 and SiC-10, respectively. This indicates that the addition of SiC significantly increases J_c under the magnetic field.[3-8)]

A FIB mill (Hitachi FB-2000K) equipped with a MS unit was used for preparing thin foil specimens. The accelerating voltage was 30 kV during the entire FIB milling process. By using the FIB-MS technique,[2)] microsamples with dimensions of 15 μm (width) × 3 μm (thickness) × 15 μm (depth) were picked up from middle and edge parts of MgB_2 cores in the tape specimens. The picked-up microsamples were finally thinned down to 150-200 nm by the FIB milling. For comparison, thin foil specimens were also prepared by a conventional method: pulverizing the MgB_2 core into a powder and subsequently thinning the powder with an Ar ion mill (Gatan PIPS Model 691). TEM observation and energy-dispersive x-ray spectroscopy (EDX) analysis were performed with an FEI TECNAI-F20 microscope operated at 200 kV.

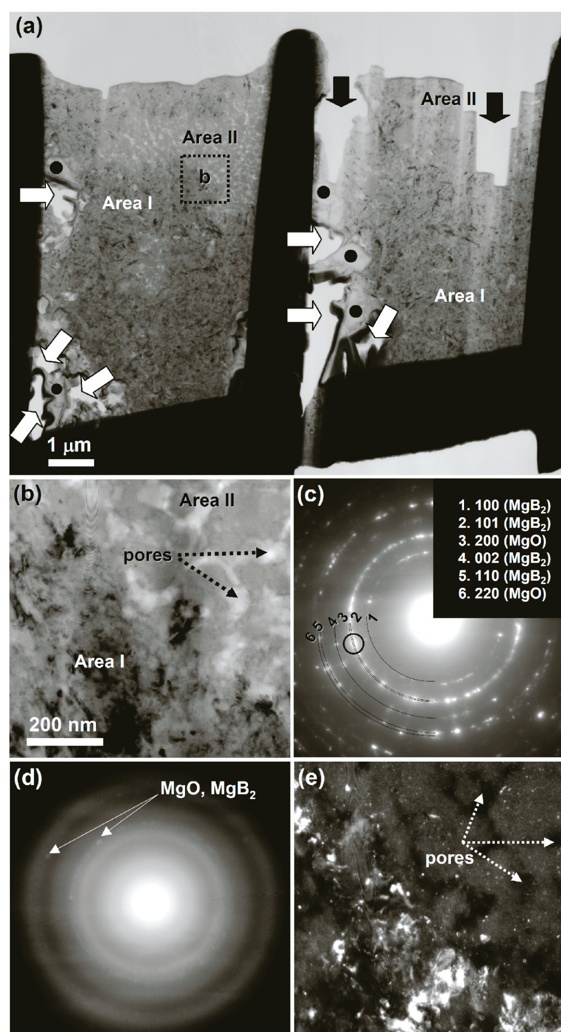

Fig. 1 (a) Bright-field TEM image of a FIB microsample of SiC-0. (b) Magnified image of area b indicated with an open square in (a). (c) and (d) Electron diffraction patterns obtained from areas I and II in (b), respectively. (e) Dark-field TEM image taken with Bragg reflections, $\boldsymbol{g}(hkl)$ = 101_{MgB2} and 200_{MgO}, marked with a small circle in (c).

3. Results and Discussion

Figure 1(a) shows a typical bright-field (BF) TEM image of a FIB microsample of SiC-0 that was picked up from the middle part of the MgB_2 core. Very dark areas correspond to thick areas remaining after the FIB milling. Thin FIB milled area shows a variety of microstructure at a μm scale as follows: area I with dark diffraction contrast of fine crystals; area II with porous microstructure; μm-sized holes (white arrowheads) that are differentiated from defects introduced by the FIB milling (black arrowheads); and an amorphous area (black dots) near the μm-sized holes. The

amorphous area corresponds to non-reacted B powders, being supported by EDX analysis. The μm-sized holes may be formed during the heat treatment, because the reaction, Mg + 2B → MgB_2, brings about notable volume contractions in the tape specimens.[9)]

Figure 1(b) shows a magnified image of area b indicated with an open square in Fig. 1(a). Area I has a compact microstructure consisting of fine crystals. An electron diffraction pattern (EDP) in Fig. 1(c) obtained from area I indicates that the fine crystals are those of MgB_2 and MgO. On the other hand, area II shows many pores with bright contrast. An EDP in Fig. 1(d) obtained from area II shows blurry intensity distribution as well as weak diffraction spots attributed to MgO or MgB_2. Figure 1(e) shows a dark-field (DF) TEM image taken with Bragg reflections, $\boldsymbol{g}(hkl)$ = 101_{MgB2} and 200_{MgO}, marked with the small circle in Fig. 1(c). Crystal sizes of MgB_2 and/or MgO are 10-100 nm in area I and 5-10 nm in area II respectively, and the amount of the crystals is much smaller in area II than in area I. These results indicate that area II predominantly contains amorphous phases. Hereinafter, areas I and II are called 'crystallized' and 'partially crystallized' areas, respectively. The partially crystallized areas may be caused by Mg deficiency due to vaporization and oxidation of Mg or shortage of the heat treatment for MgB_2 formation. The crystallized and partially crystallized areas and μm-sized holes were similarly recognized in SiC-5 and SiC-10. It was also clarified that the microstructural features described above are almost the same between the middle and edge parts of the MgB_2 core, suggesting no reaction between the MgB_2 core and the Fe tube.

Figure 2 shows EDPs and DFTEM images ($\boldsymbol{g}$ = 101_{MgB2} and 200_{MgO}) obtained from the FIB microsamples of SiC-0 (Fig. 2(a)), SiC-5 (Fig. 2(b)) and SiC-10 (Fig. 2(c)). The crystallized and partially crystallized areas become small in size and uniform in distribution with the increase of SiC content. Such different sizes and distribution of the crystallized and partially crystallized areas may give different connectivities between MgB_2 crystals.[10)] The diffraction from MgB_2 tends to decrease in intensity and exhibit ring-shaped intensity distribution with SiC doping. This correlates with the decrease of coarse grains of MgB_2, as recognized in the DFTEM images. The decrease of MgB_2 grain sizes enhances J_c under magnetic fields because grain boundaries act as magnetic flux pinning centers.[11-13)]

Figure 3 shows BFTEM images and EDPs of

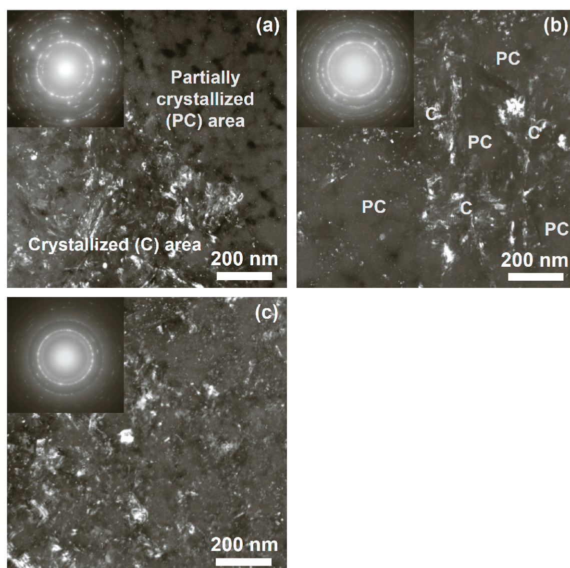

Fig. 2 Electron diffraction patterns and dark-field TEM images ($\boldsymbol{g}$ = 101_{MgB2} and 200_{MgO}) obtained from FIB microsamples. (a) SiC-0, (b) SiC-5, and (c) SiC-10.

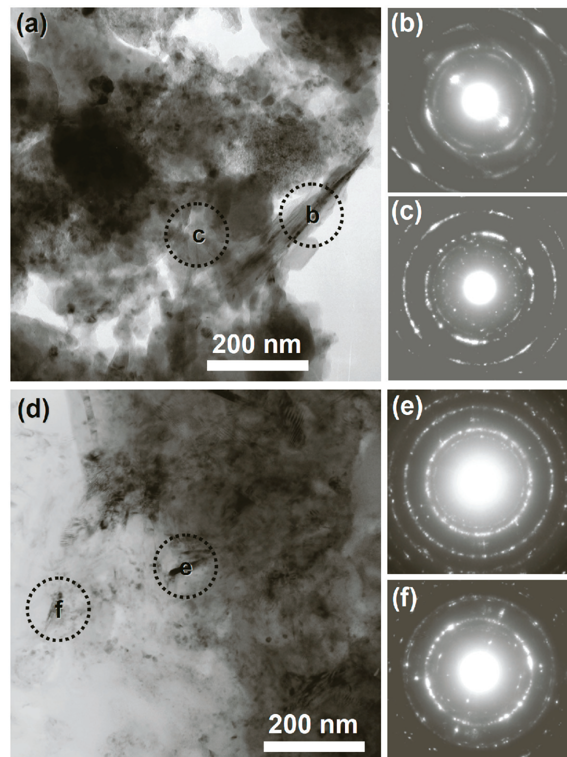

Fig. 3 TEM results of SiC-5 obtained by a conventional specimen preparation method: pulverizing the specimen into powders and subsequently thinning the powders with an Ar ion mill. (a) and (d) Bright-field TEM images. (b), (c), (e) and (f) Electron diffraction patterns taken from encircled areas b, c, e and f, respectively.

SiC-5 using the conventional TEM specimen preparation method. MgB_2 crystals with granular and needle-like shapes[4] are observed. However, one cannot recognize porous microstructure containing amorphous phases and μm-sized holes. In fact, all the EDPs in Fig. 3 show polycrystalline features. This is a difference in the observed microstructure between the TEM specimens prepared with the FIB-MS method and those with the conventional method. Here, we discuss the difference depending on the specimen preparation methods. In the case of the TEM specimen prepared by the FIB-MS method, one has to take into account of FIB damage on the specimen surface induced by bombardment of accelerated Ga ions.[15, 16] However, the typical thickness of the FIB damage layer is about 5-30 nm[15-17] which is thinner than the final specimen thickness in the present study (150-200 nm). In addition, it is hard to interpret that the uniform scanning of the focused Ga ion beam during the FIB milling would form the inhomogeneous microstructure at the μm scale as shown in Figs. 1 and 2. On the other hand, when the TEM specimen is prepared by the conventional method, the non-crystalline region with low density shown in Figs. 1 and 2 could be preferentially removed or thinned down during the pulverizing process and/or the Ar ion milling process. The non-uniform specimen thickness in Fig. 3 seems to support the preferential removal or thinning down of the non-crystallized region. Based on these interpretations, we believe that one can observe the original inhomogeneous microstructure in MgB_2 tapes using the FIB-MS method rather than the conventional method if the FIB-milled specimen is thick enough to avoid artifacts due to the Ga ion beam radiation damage.

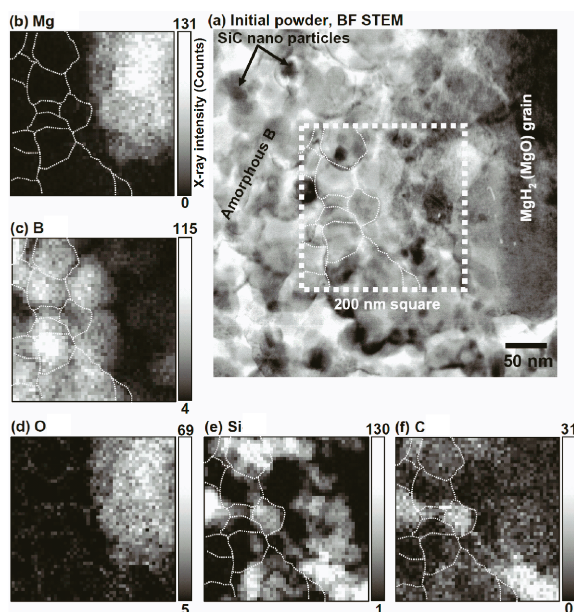

Fig. 4 EDX elemental mapping in an as-rolled tape specimen (SiC-10) before the heat treatment, being composed of MgH_2, amorphous B and SiC powders. (a) Bright-field scanning TEM image, where the open square drawn by straight broken lines indicates the EDX mapping region. (b) Mg map, (c) B map, (d) O map, (e) Si map and (f) C map. Curved broken lines in (a), (b), (c), (e) and (f) denote O-rich regions located at peripheries of the B and SiC powders. The O map in (d) suggests that the MgH_2 powder was transformed to MgO during the TEM specimen preparation process.

A FIB-milled specimen tends to have uniform thickness in a wide area even if the specimen consists of different phases. This is advantageous for preserving the inhomogeneous microstructure in MgB_2 tapes. Figure 4 demonstrates the advantage: microstructure observation in an as-rolled tape (SiC-10) before the heat treatment (details are described in the figure caption). The FIB milled specimen clearly shows sizes and distribution of MgH_2, amorphous B and SiC powders. EDX elemental maps directly indicate incorporation of oxygen with the MgH_2, B and SiC powders.[18] These microstructural features in the as-rolled state are informative to understand the formation process of the inhomogeneous microstructure in MgB_2 tapes.

4. Conclusions

TEM specimen preparation using the FIB-MS technique is suitable for studying microstructure of MgB_2 superconducting materials when the microstructure contain inhomogeneous features at μm to sub-μm scales. As a demonstration, the microstructure of MgB_2 tapes fabricated by the *in situ* PIT process has been characterized as follows: (i) the microstructure composed of densely crystallized MgB_2 areas, partially crystallized areas containing amorphous phases, and μm-sized holes; (ii) changes in size and distribution of the crystallized and partially crystallized areas with SiC doping. These findings are hardly obtained by a conventional TEM specimen preparation: pulverizing the specimen into a powder and thinning the powder with an Ar ion mill, because the inhomogeneous microstructure containing non-crystalline areas

may be lost during the specimen preparation. The inhomogeneity and porosity in the microstructure that degrade superconducting properties are important issues for the development of MgB_2 materials.[10] Thus, the appropriate TEM specimen preparation method is indispensable for a correct microstructure characterization of MgB_2 materials.

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