Development of Method for Analyzing Sintering Reaction of Bi-Based Oxide Superconducting Wires Using SPring-8

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Bi-based oxide superconducting wires that operate at temperatures higher than liquid nitrogen temperature are currently being studied to achieve the practical use as electric power transmission wires, electromagnets, and so on. In order to realize larger power transmission and smaller size, the increase of superconducting current is required. To achieve this goal, the authors are optimizing the sintering process for superconductors so that the formation of hetero-phases that block superconducting current can be suppressed. The authors have developed a system for observing the changes in crystal phases during the sintering process in order to fully understand the mechanism of reaction.

1. Introduction

Practical use of superconducting wires that use liquid nitrogen refrigerant is presently under way. One potential candidate of such superconducting wires is Bi-based oxide superconducting wire. The potential of this type of superconducting wire was demonstrated successfully when Sumitomo Electric's Bi-based oxide superconducting wire was used in the transmission line to supply electricity to about 70,000 households in Albany, New York for nine months in 2007. Due to this success, practical applications of this Bi-based oxide superconducting wires are expected to expand in the future. However, for Bi-based oxide superconducting wires to become commonplace, higher critical current must be achieved in order to obtain improved power transmission capability and enable the downsizing of electromagnets and motors. To improve the critical current of wires, crystal orientation must be enhanced and hetero-phase must be reduced. **Figure 1** shows the cross-section of the microstructure of Bi-based oxide superconducting wire. Hetero-phases such as Sr-Ca-Cu-O and Ca-Pb-O are shown in **Fig. 1** as the black areas in the grain boundaries of superconducting domains. The authors hypothesized that these hetero-phases disturb superconducting current flows and give lower critical current. **Figure 2** shows the manufacturing process of this wire. In the first sintering process, Bi-2223 [$(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$] is generated from the precursor powder whose main content is Bi-2212 [$(Bi,Pb)_2Sr_2CaCu_2O_x$]. In this study, the authors aim to clarify the reactions that occur during the first sintering process, and to develop a new process for reducing hetero-phases. In previous studies, powder diffraction measurement methods like high-temperature powder X-ray diffraction and high-temperature powder neutron diffraction were used to understand the reaction mechanism in the first sintering process. An important step in the sintering process of the wire is the diffusion of atmosphere gas through silver sheath. Therefore, the manufacturing process cannot be reproduced when performing high-temperature X-ray diffraction measurement on powder specimen. Both E. Giannini [1] and H. F. Poulsen [2] used powder-filled silver sheaths as specimens in the neutron diffraction and X-ray diffraction measurements. They used single-filament specimens that have only one type of precursor powder enclosed in a silver sheath. However, practical wires must have a multi-filament structure. In conventional studies, the sintering reactions of practical-use wires cannot be analyzed using the conditions that reproduce the manufacturing process. In this study, using highly-brilliant synchrotron radiation of the SPring-8, the authors developed a mea-

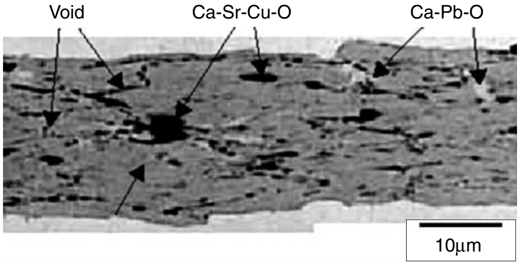

Fig. 1. Cross-sectional microstructure of Bi-based oxide superconducting wire

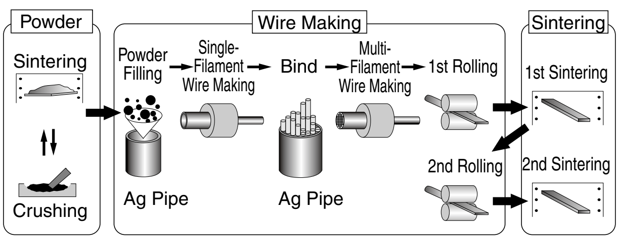

Fig. 2. Manufacturing process of Bi-based oxide superconducting wire

surement technique for examining crystal phase changes during the sintering process.

2. Experimental Methods

2-1 Heating Furnaces

Figure 2 shows the process used for manufacturing the wire. First, a silver pipe was filled with a precursor powder. Then the pipe were bound, rolled flat and sintered repeatedly to be formed into a tape-like shape. This study focuses on the first sintering process in which Bi-2223 is generated from the precursor powder whose main content is Bi-2212. In the process, sintering is conducted at temperatures in excess of 800˚C under a controlled atmosphere. Therefore, in order to perform in-situ analysis of sintering reactions, it is necessary that (A) atmosphere control is possible, (B) temperature is controlled at an accuracy of plus or minus 1˚C at 800˚C or higher, and (C) X-ray diffraction measurement is available under conditions (A) and (B). Because heating furnace must satisfy all these conditions, a small heating furnace owned by the SPring-8 BL02B1 was used in this study. This furnace was designed for X-ray diffraction measurement of plate-shaped samples at a maximum temperature of 1,200˚C and under a controlled atmosphere [**Fig. 3(a)**]. To maintain temperature uniformity, insulators were installed at the opening of the horseshoe-shaped heater [**Fig. 3(b)**]. Later, the authors manufactured a hollow-square shaped heater to stabilize the sample setting angle and to enable the measurement of two samples at a same time (**Fig. 4**).

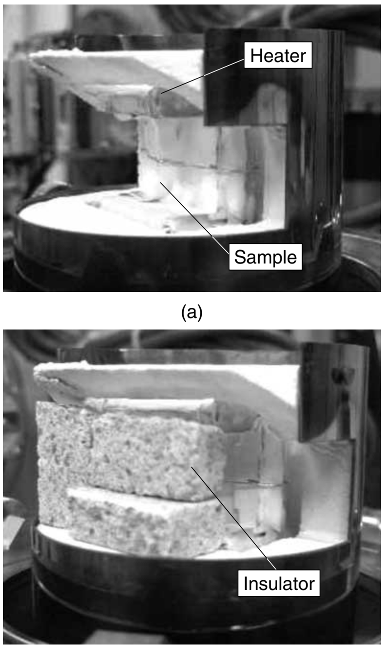

Fig. 3. Inner structure of furnace in SPring-8 BL02B1
(a) Standard condition with sample wire
(b) With heat insulators set at heater opening

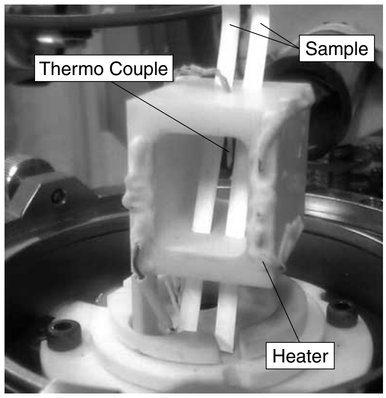

Fig. 4. Newly constructed hollow-square shaped heater with sample wires

2-2 Measurement Conditions

The wire surface was covered with silver about 20 μm thick, as shown in **Fig. 5**. Hence, X-rays that can be transmitted through silver need to be used in measuring the X-ray diffraction pattern of the superconductor. Silver has almost the same X-ray mass absorption coefficients at 25 keV and 50 keV. Therefore, the 25 keV X-ray of higher brilliance was used.

When measuring the X-ray diffraction using a 25 keV X-ray, diffraction angles from 5 degrees to 20 degrees need to be measured in order to detect the peaks of the expected compounds. Moreover, it was necessary to measure more than ten points per peak in order to calculate the quantity of the compounds from the peak areas. Hence, judging from the peak width, each peak was measured every 0.01 degrees.

During the sintering process, X-ray diffraction needs to be measured at least every 30 minutes. Therefore, conditions under which one measurement can be performed within 10 minutes were investigated. X-ray diffraction measurement methods can be classified roughly into two methods: the photographic method and the counter method. The authors selected the photographic method because short measurement time and high S/N are needed. An imaging plate that was superior in area and dynamic range was used as the X-ray detection device. In order to acquire sufficient resolution, the distance between the sample and the imaging plate (i.e. camera length) was determined so that a pixel (50 μm sq.) of the imaging plate was equivalent to the 0.01 degrees diffraction angle.

The X-ray incident angle must be set to less than five degrees in the Bragg case (reflection case). However, there are concerns that an X-ray incident at low angle may cause the increase of the X-ray absorp-

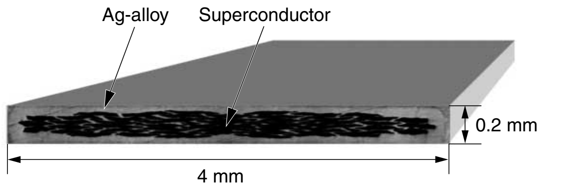

Fig. 5. Cross-sectional image of Bi-based oxide superconducting wire

tion by silver and also cause the lowering of resolving power due to the X-rays expansion at the sample surface. To avoid these problems, the authors carried out the X-ray diffraction measurement in the Laue case (transmission case). Furthermore, because the wire is of a tape shape that has a c-axis crystal orientation in the thickness direction, the sample was set at about 20 degrees from the incident X-ray so that numerous measurable diffraction lines can be obtained.

2-3 Sintering Atmosphere

When sintering the wire, it is necessary that the gas atmosphere is controlled through the silver sheath. Therefore, the atmosphere in the furnace was controlled by supplying a composition-adjusted gas from a cylinder. The gas was supplied from the top of the furnace and exhausted from the lower part in order to control the atmosphere near the wire. The quantity of the gas supplied and the composition of the atmosphere were monitored using the exhausted gas. In the case where the sample length is short, the reaction observed may be different from that in the production furnace because of gas diffusion from the end of the wire. Therefore, the minimum wire length was assumed to be 10 cm, and the authors confirmed that the sintering conditions in this furnace were equal to those in the production furnace by observing the wire's microstructure, identifying the compound with X-ray diffraction measurements, and studying superconducting characteristics.

2-4 Synchrotron Radiation Measurement

The X-ray diffraction measurements were carried out in the BL19B2 and BL16XU at SPring-8. **Figure 6** shows the layout of the measurement setup in the BL16XU. The incident X-ray size was set to 1 mm^W for determining the average structure information and to 0.1 mm^V for the purpose of ensuring the resolving power. Because the highly-brilliant X-rays scattered from the slits cause the background to increase, lead boards were attached to reduce the background. The diffraction patterns of the two samples were exposed on an imaging plate, thus shortening the read time.

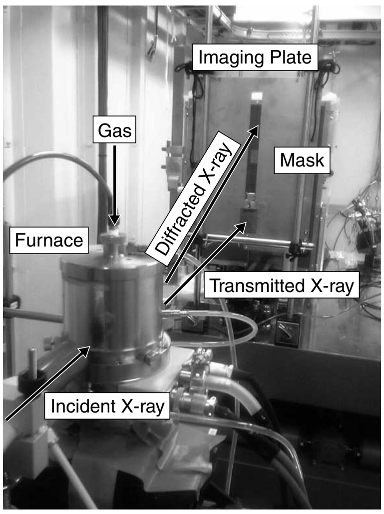

Fig. 6. Experimental layout at SPring-8 BL16XU

2-5 Analyses

The X-ray diffraction pattern recorded on the imaging plate was read by FUJIFILM Corporation's BAS2500. The silver diffraction line was used as an internal standard for compensating the camera length and the imaging plate tilt angle. Fit2D was used to correct and convert the diffraction pattern to the diffraction intensity against diffraction angle [(3)-(7)].

3. Results and Discussion

Figure 7 shows examples of X-ray diffraction patterns. Diffraction rings from several compounds can be clearly observed in each sample. **Figure 8** shows an example of the X-ray diffraction chart obtained from the diffraction pattern. There are a lot of small peaks as well as a few large peaks, which are due to the heterophases and the main phase, respectively. To verify the measurement quality of the photographic method, the authors made a comparison of the photographic and

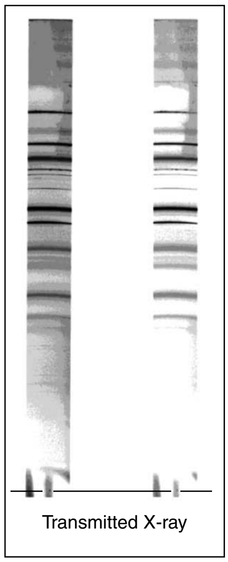

Fig. 7. X-ray diffraction pattern of Bi-based oxide superconducting wire

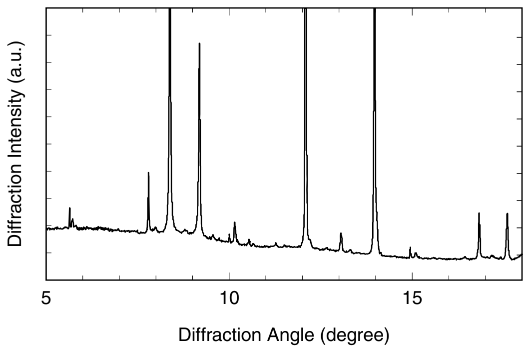

Fig. 8. X-ray diffraction intensity against diffraction angle of Bi-based oxide superconducting wire obtained from X-ray diffraction pattern

counter methods in measuring the diffraction peak of Bi-2223 115. The measurement conditions of the counter method was the incident X-ray beam size of 1 mm x 1 mm, a resolution of 0.02 degrees by double-slit geometry, and the measurement time per point of one second with a scintillation detector (OKEN SP-10) in the BL16XU. **Figure 9** shows the Bi-2223 115 diffraction peaks obtained by the photographic method and the counter method. The diffraction peak variation by the photographic method was much smaller than that by a counter method, but there was no clear difference in resolution between the two methods. These results indicate that high-quality diffraction patterns of wires can be obtained in less time by the photographic method than by the counter method.

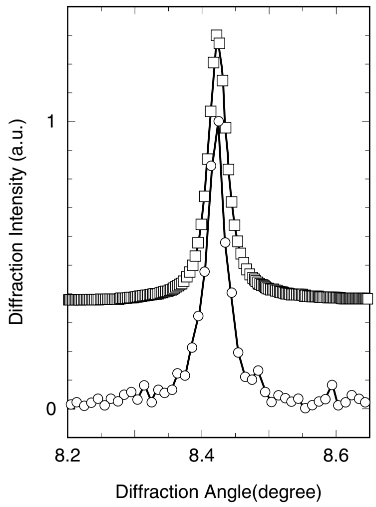

Fig. 9. X-ray diffraction pattern of Bi-based oxide superconducting wire by counter method and photographic method (○: counter method, □: photographic method)

Figure 10 shows the diffraction charts after the sintering process. The passage of process time is from the bottom to the top of the chart. The peaks indicated by open squares are the peaks of Bi-2212 and the peaks indicated by open circles are the peaks of Bi-2223. It is clearly shown that Bi2223 grew with the passage of process time. As an example of representative reactions, **Fig. 11** shows the quantitative changes of Bi-2212 and Bi-2223. Here, each peak area was calculated, and the total peak area of Bi-2212 and Bi-2223 was assumed 1 in each chart and the proportion of each diffraction peak area was plotted against process time. The cooling start time was defined as 0 h. **Figure 11** clearly demonstrates that Bi-2223 increases with sintering time, and Bi-2212 increases and Bi-2223 decreases with cooling time. Although these reactions had been pointed out in the past, they were unable to be observed by ex situ analysis because sintering needed to be terminated and the wires must be cooled in order to observe diffraction pattern. Hence, this is the first time the direct in situ observation of the reactions in a wire was made during the sintering process.

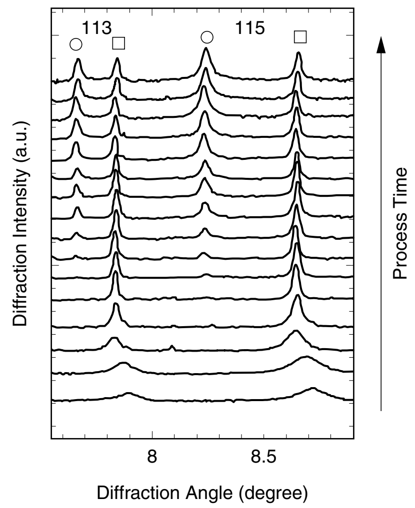

Fig. 10. Changes in X-ray diffraction pattern during sintering of Bi-based oxide superconducting wire

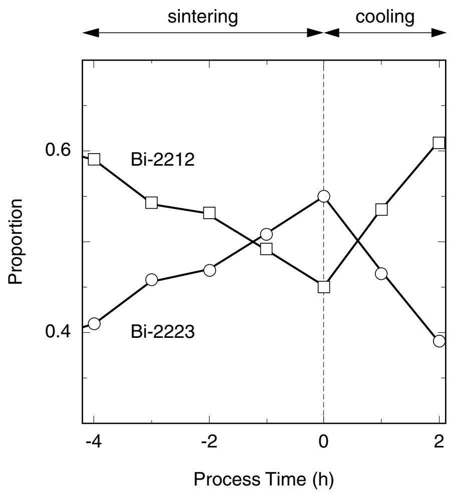

Fig. 11. Change of proportion between Bi-2212 and Bi-2223 during sintering and cooling

Further improvements of this technique will enable the analysis of reactions under various conditions, which leads to further improvement of the sintering process.

4. Conclusion

The authors successfully designed a system for observing the reaction that occurs during the sintering process of a Bi-based oxide superconducting wire by using the highly-brilliant synchrotron radiation of SPring-8. This system allows the changes from Bi-2212 to Bi-2223 in the sintering process and from Bi-2223 to Bi-2212 in the cooling process to be directly observed in situ.

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