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# The microstructure changes of Bi-2212/Ag composite tapes processed under a temperature gradient

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## Abstract

The microstructure changes of Bi-2212/Ag tapes during melt-solidification under a temperature gradient have been investigated by using an oil-quenching technique. The cross-sections and oxide layers at the oxide/silver interfaces of the tapes quenched from several temperatures were examined by using SEM observation and X-ray diffraction analysis. At maximum processing temperature  $T_{\max}$ , impurity phases such as Bi-free and Cu-free solid phases exist in the liquid. When the solidification of the Bi-2212 phase started at the low-temperature region, most of the Bi-free and Cu-free phases at the region near the oxide/silver interface disappeared. A large grain size of Bi-2212 near the oxide/silver interface was obtained by the heat treatment under the temperature gradient. Large in-plane textured domains were obtained by the growth of Bi-2212 grains whose *a*- and/or *b*-axes were aligned. This in-plane texturing can basically be explained by the unidirectional solidification.

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*Keywords:* Temperature gradient; Oil-quench; Melt-solidification; In-plane texture

Bi-2212/Ag composite tapes are one of the most promising high- $T_c$  superconducting materials for applications at low temperatures and high fields.  $J_c$  values of  $\sim 3.5 \times 10^5$  A/cm<sup>2</sup> at 4.2 K in 10 T were obtained for Bi-2212 tapes prepared by the dip-coating method [1]. Recently, we fabricated Bi-2212/Ag tapes with in-plane texturing, which have a higher  $J_c$  value of  $4.8 \times 10^5$  A/cm<sup>2</sup> by the heat treatment under the temperature gradient [2]. The high  $J_c$  value of these tapes is due to the high *c*-axis alignment, in-plane texturing on the *ab*-plane, and large grain size. The oil-quenching technique is one

of the most effective experiments to investigate the growth mechanism of the Bi-2212 phase [3–6]. In this report, we investigated the growth mechanism of the Bi-2212 phase under a temperature gradient.

Samples were prepared by the dip-coating technique [7]. A vertical tube furnace with a temperature gradient of 2.0 °C/cm was constructed for oil-quenching. The oxide layers of these samples were partially melted at maximum processing temperature ( $T_{\max}$ ) and then slowly cooled at the rate of 2 °C/h in flowing oxygen. The temperature gradient of this furnace was fixed at 2.0 °C/cm during the heat treatment. The temperature gradient direction is the longitudinal direction of the tape. This  $T_{\max}$  was the temperature at the higher-temperature region of the tape with a temperature gradient. The samples were oil-quenched from

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various temperatures during solidification. After the oil-quenching, we removed the silver substrates by using a solution of  $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 4:4:5$ . The microstructure changes of the oxide layer were examined by using SEM observation and X-ray diffraction (XRD) analysis, and the elemental composition was estimated using energy dispersive X-ray spectroscopy.

Fig. 1 shows the XRD patterns of oxide at the oxide/silver interface at the higher-temperature region quenched from various temperatures. First, we measured the XRD patterns of both the low- and high-temperature regions of the tapes. However, we could not observe the difference in the formation mechanism of the Bi-2212 phase at the low-temperature region and the high-temperature region. At  $T_{\text{max}} = 893^\circ\text{C}$ , Bi-free and Cu-free impurity phases existed in the oxide layer. Although the Bi-2201 and Bi-2212 phases formed around  $880^\circ\text{C}$ , the intensity of the XRD peaks of the Bi-2201 phase was much stronger than that of the Bi-2212 phase. Around  $870^\circ\text{C}$ , the Bi-2201 phase disappeared as the Bi-2212 phase grew. This formation mechanism of the Bi-2212 phase was almost the same as that of normally heat-treated tape.

Fig. 2 shows SEM images of longitudinal sections of the tapes quenched from each tempera-

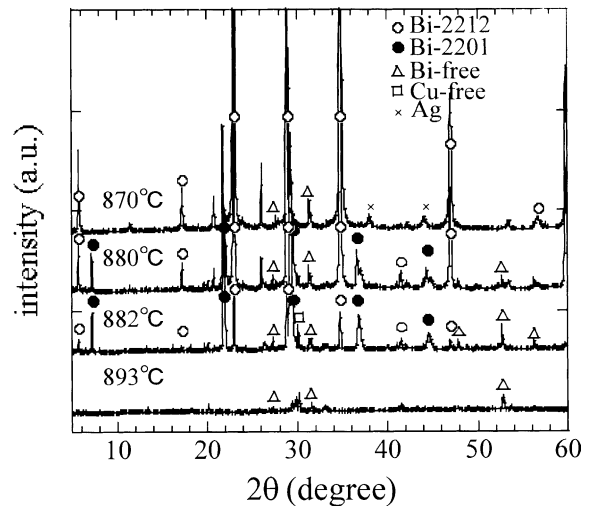


Fig. 1. XRD patterns of an oxide layer near the oxide/silver interface at the higher-temperature region quenched from several temperatures.

ture. At  $893^\circ\text{C}$  (at the high-temperature region), Cu-free and Bi-free phases existed in molten oxide. The grain size of the impurity phases at the high-temperature region was larger than that at the low-temperature region. While the Bi-2212 phase nucleated at the low-temperature region of the tape around  $882^\circ\text{C}$ , solidification had not yet started at the high-temperature region. At  $874^\circ\text{C}$ ,

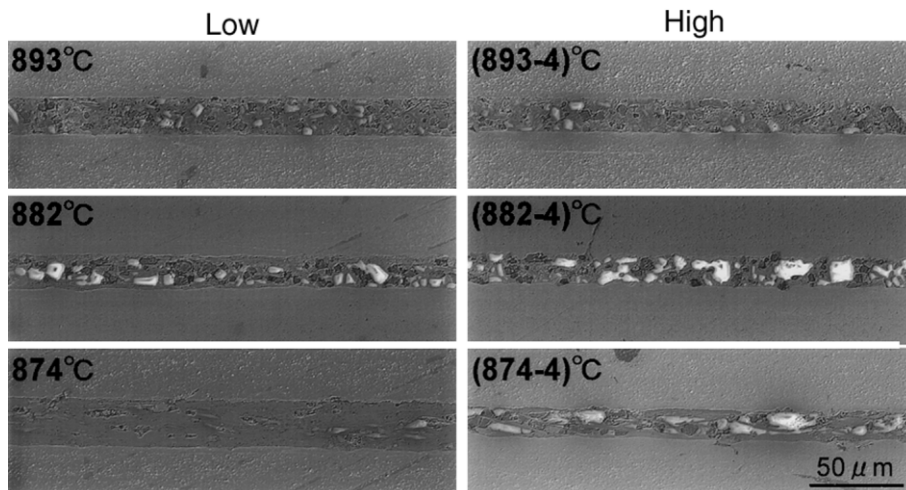


Fig. 2. SEM images of cross-sections of the tapes quenched from several temperatures. Left figures: high-temperature region; right figures: low-temperature region. The dark-gray precipitates are the Bi-free phase; the white ones are the Cu-free phase; and the bright-gray ones are Bi-2212 grains.

the solidification of the Bi-2212 phase had almost finished at both the low- and high-temperature regions. Well-aligned Bi-2212 grains were formed at the low-temperature region, and there were a small number of them in the impurity phases. On the other hand, large grains of the impurity phases existed at the high-temperature region. These large grains of the impurity phases existed at the high temperature of 893 °C and remained through the final stage of solidification.

Fig. 3 shows SEM images of oxides at the oxide/silver interface of the tape quenched from 878 °C.

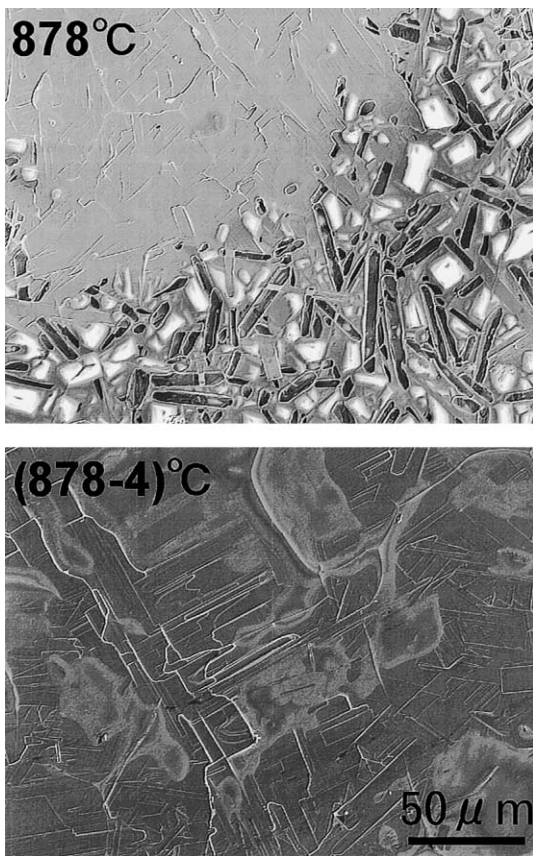


Fig. 3. SEM images of the oxide layer at the oxide/silver interface of the tape quenched from 878 °C. The upper figure shows the high-temperature region, and the lower one shows the low-temperature region.

At the low-temperature region, a Bi-2212 phase with a large grain size formed, and the impurity phase disappeared near the oxide/silver interface. Most of the impurity phase existed in the middle of the oxide layer. At the high-temperature region, on the other hand, numerous impurities were observed. The grain growth of the Bi-2212 phase started at the low-temperature region of the tape, and the Bi-2212 phase grew toward the high-temperature region of the tape. As a result, large in-plane textured domains of Bi-2212 were obtained. Such in-plane textured domains were sometimes obtained by the conventional heat treatment under a homogeneous temperature. However, in-plane textured domains obtained under a temperature gradient were much larger than those obtained under a homogeneous temperature.

The tapes fabricated under the temperature gradient have well-aligned, in-plane textured grains with a large size. Solidification of Bi-2212 in this experiment is basically a unidirectional solidification, and in-plane texturing can be explained by this mechanism. At the early stage of the solidification of Bi-2212, nucleation and grain growth start at the low-temperature region. The orientation of the Bi-2212 nuclei was random; however, the nuclei whose *a*- or *b*-axis was parallel to the temperature gradient would preferentially grow toward the high-temperature region. Thus, Bi-2212 large grains whose *a*- or *b*-axis is parallel to the temperature gradient can be obtained.

## References

- [1] T. Muroga, J. Sato, H. Kitaguchi, H. Kumakura, K. Togano, M. Okada, *Physica C* 309 (1998) 236.
- [2] A. Matsumoto, H. Kitaguchi, H. Kumakura, K. Togano, *Physica C* 350 (2001) 147.
- [3] R.D. Ray II, E.E. Hellstrom, *Physica C* 251 (1995) 27.
- [4] T. Hasegawa, H. Kobayashi, H. Kumakura, K. Togano, *Supercond. Sci. Technol.* 7 (1994) 579.
- [5] A. Matsumoto, H. Kitaguchi, H. Kumakura, K. Togano, *IEEE Trans. Appl. Supercond.* 11 (2001) 3046.
- [6] A. Matsumoto, H. Kitaguchi, H. Kumakura, K. Togano, *Physica C* 341–348 (2000) 2435.
- [7] J. Kase, T. Morimoto, K. Togano, H. Kumakura, D.R. Dietderich, H. Maeda, *IEEE Trans. Magn.* 27 (1991) 1254.