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Preparation and Critical Current Density of Bi-based Superconducting Whisker Composites

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Abstract: $Bi_2Sr_2CaCu_2O_x$ (Bi-2212) superconducting whisker composites densified and textured by hot pressing have been prepared. The composites consist of Bi-2212 whiskers and Bi-2212 powder and include the whiskers by 5.0 and 10 wt%. The *ab*-plane of the whiskers and the grains is aligned parallel with the pressed plane of the composites. Although zero resistance temperature ($T_{c,zero}$) is not so different between the composites and the sample without the whiskers, critical current density (J_c) for the 10 wt% composite is 14 times larger than that for the sample without the whiskers at 77 K under zero magnetic field. The increase in J_c is caused by an improvement of the grain growth and alignment around the whiskers. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Wires, magnets and magnetic shielding materials composed of superconducting cuprates are the sintered ceramics at present. In order to obtain the materials with high critical current or good magnetic shielding properties, it is necessary to achieve highly aligned and densified states. Many methods for preparing these materials have been reported. The Ag-sheathed method (powder in tube method)[1–3] and the doctor-blade casting method of Ag sheets with partial melting process[4] are advantageous to a good alignment. The hot pressing method is useful to prepare densified samples.[5] Moreover, this method is favorable to align the superconducting grains because of their anisotropic grain morphology, particularly in $Bi_2Sr_2CaCu_2O_x$ (Bi-2212) and $Bi_2Sr_2Ca_2Cu_3O_x$ (Bi-2223) compounds.

The growth of ribbon-like Bi-2212 whiskers of single crystals with the dimensions of 2–10 μm thick, 10–300 μm wide and 3–15 mm long has been reported.[6] Because the whisker has a good transport property (critical current density, $J_c \approx 10^4$ A/cm^2 at 77 K under zero magnetic field),[7] a high J_c is expected in materials prepared by connecting or sintering the whiskers. However, it is difficult to connect or sinter the whiskers directly without damaging them. Therefore we aim at achieving a high J_c by incorporation of the whiskers into Bi-2212 polycrystalline ceramics. It is expected that Bi-2212 grains are grown and aligned well along the whiskers because of the shape of the whiskers as mentioned above, and consequently the J_c values increase in these composites. Therefore it is important for the grain alignment to align the whiskers well in the composites. We have prepared the densified Bi-2212 superconducting whisker composites in which the whiskers and the grains are aligned well by hot pressing. The effect of the incorporation of the whiskers into the Bi-2212 bulk compound on transport property is investigated from the viewpoint of the grain alignment.

2 EXPERIMENTAL

In this study, a commercially available Bi-2212 powder (DOWA, 3 N, average particle size

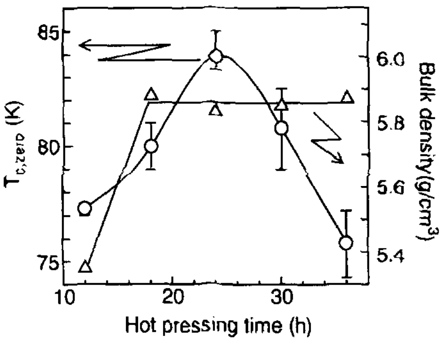

Fig. 1. Hot pressing time dependence of $T_{c,zero}$ (○) and bulk density (△) for the samples without whiskers.

< 3 μm) was used. No impurity phases in this powder were found by X-ray diffraction analysis. The Bi-2212 whiskers were prepared by heating melt-quenched glass plates with the composition of $BiSrCaCu_2Al_xO_y$ ($0.5 < x < 0.75$) in a stream of O_2 gas at 865°C for 80 h.[6] The powder and the whiskers were mixed so as not to damage the whiskers. The whisker contents were 5.0 and 10 wt%. Both mixtures had a total weight of 5.0 g. The mixtures and the Bi-2212 powder (whisker content, 0.0 wt%) were pelletized, covered with gold foil, and hot pressed for 24 h and for 12–36 h at 815°C under 12 MPa, respectively. The diameter for the hot pressed samples was about 2.0 cm and the thickness was 0.20–0.25 cm.

Pressed planes (perpendicular to the pressing direction) and cross-sectional planes (parallel to the pressing direction) for the samples were observed by a scanning electron microscope (SEM). Temperature dependence of resistivity and J_c were measured by a standard four-probe method. For the resistivity measurement, silver paste was used for the connections at both voltage and current terminals. For the J_c measurement, the current terminals were covered with silver layers by vacuum evaporation and metallic solder was used for both voltage and current terminal connections. The J_c values were measured at 77 K under zero magnetic field. Criterion for the determination of J_c was 1.0 μV/cm.

3 RESULTS AND DISCUSSION

The samples without whiskers have been prepared using different hot pressing time at 815°C under 12 MPa. The zero resistivity temperature ($T_{c,zero}$) and bulk densities for these samples are shown in Fig. 1. Although the onset temperature is close for all the samples, $T_{c,zero}$ spreads within 75.8–83.9 K and has a maximum value for the sample hot pressed for 24 h, as shown in Fig. 1. Broadening of the resistivity–temperature curve (R–T curve) appears near $T_{c,zero}$ and results in lowering $T_{c,zero}$ for the samples hot pressed for 12 and 36 h. In contrast, broadening does not appear for the other samples. The bulk densities do not change with increasing hot pressing time for the samples hot pressed for more than 18 h and they are 90–92% of the Bi-2212 powder density (6.50 g/cm^3).[8] However, the bulk density for the sample hot pressed for 12 h is low, as shown in Fig. 1. In this case, sintering is not sufficient because of the lack of the hot pressing time, which causes the low $T_{c,zero}$ compared with the other samples. As the samples are sintered almost completely by hot pressing for more than 18 h, the lower $T_{c,zero}$ of the sample hot pressed for 36 h probably results from a decomposition of the Bi-2212 phase. According to these results, the composites have been hot pressed for 24 h.

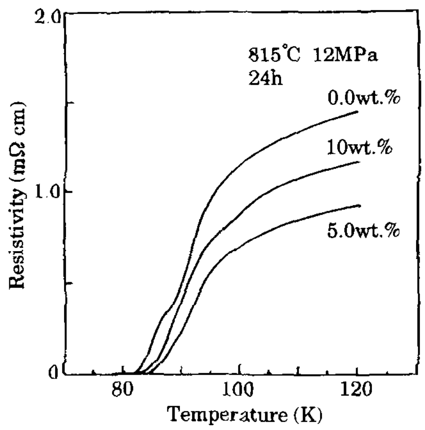

Fig. 2. Resistivity–temperature curve (R–T curve) for the 0.0 wt% sample, the 5.0 wt% and the 10 wt% composites hot pressed at 815°C under 12 MPa for 24 h.

Table 1. $T_{c,zero}$ **and bulk density for the 0.0 wt% sample, the 5.0 wt% and the 10 wt% composites**

Sample whisker content (wt%)	$T_{c,zero}$ (K)	Bulk density (g/cm^3)
0.0	83.9	5.83
5.0	83.1	5.95
10	83.7	5.81

Figure 2 shows the R–T curve for the sample without whiskers (hereafter abbreviated as 0.0 wt% sample), the 5.0 wt% and the 10 wt% composites. All samples have been hot pressed at 815°C under 12 MPa for 24 h. $T_{c,zero}$ is 83–84 K for these samples (Table 1). The bulk densities are also listed in Table 1. The composites are densified, as well as the 0.0 wt% sample.

SEM images of the cross-sectional planes for the 5.0 wt% and the 10 wt% composites are shown in Fig. 3. It is clear that the grains are grown and

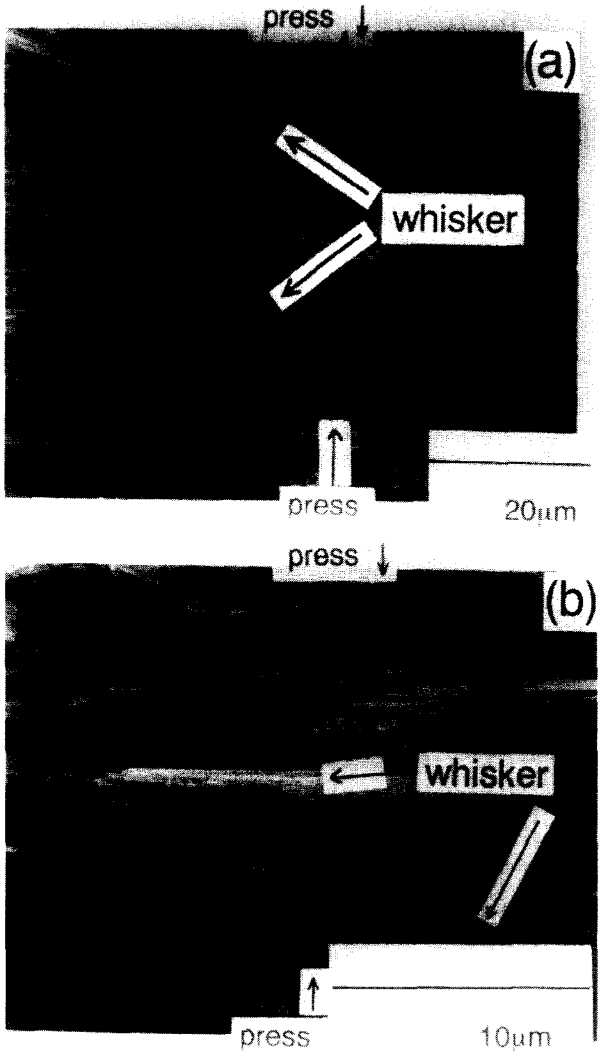

Fig. 3. Scanning electron micrographs of the cross-sectional planes for the 5.0 wt% (a) and the 10 wt% composites (b).

textured well for both the composites. The *ab*-plane of the grains is aligned parallel to the pressed plane. The stacking layered structure of the whisker is observed. This side of the whisker corresponds to the *ac*- or the *bc*-planes. The *ab*-plane of the whisker is aligned parallel to the pressed plane during hot pressing because the whisker has a ribbon-like shape with the well grown *ab*-plane. Although most whiskers are aligned parallel to the pressed plane, some whiskers are curved such as the upper whisker in Fig. 3(a). The grains around this whisker have been curved and grown along it. Moreover, the grains between the whiskers are grown and well aligned compared with the grains apart from the whiskers, as shown in Fig. 3(b). It is evident from the SEM images that the whiskers encourage the grain growth and alignment along them. Although hot pressing is effective for the grain growth and alignment and the densification of the samples, the grains are grown and aligned better by incorporation of the whiskers into the bulk samples.

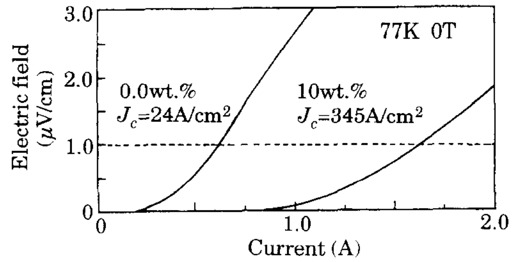

Fig. 4. Current–electric field curve for the 0.0wt.% sample and the 10wt.% composite.

Figure 4 shows the current–electric field curve. J_c for the 10 wt% composite is about 14 times larger than that for the 0.0 wt% sample. Considering $T_{c,zero}$ for the whiskers is 77–78 K, they do not act as current paths which are effective for an increase in J_c at 77 K. As mentioned above, the grain growth and alignment around the whiskers are better than those for the sample without the whiskers. The increase in J_c can be explained by the improvement in the grain growth and alignment.

4 CONCLUSIONS

Bi-2212 superconducting whisker composites with a Bi-2212 whisker content of 5.0 and 10 wt% have been prepared. The densified and textured composites can be obtained by hot pressing. The *ab*-plane of the whiskers and the grains are aligned parallel with the pressed plane in the composites. Although $T_{c,zero}$ is not so different between the composites and the 0.0 wt% sample, J_c for the 10 wt% composite is 14 times larger than that for the 0.0 wt% sample at 77 K under zero magnetic field. This increase in J_c is caused by an improvement in the grain growth and alignment by incorporation of the whiskers.

REFERENCES

1. HEINE, K., TENBRINK, J. & THÖNER, M., *Appl. Phys. Lett.*, **55** (1989) 2441.
2. HALDAR, P., HOEHN, J. G., Jr & RICE, J. A., *Appl. Phys. Lett.*, **60** (1992) 495.
3. NOMURA, K., SEIDO, M., KITAGUCHI, H., KUMAKURA, H., TOGANO, K. & MAEDA, H., *Appl. Phys. Lett.*, **62** (1993) 2131.
4. KASE, J., IRISAWA, N., MORIMOTO, T., TOGANO, K., KUMAKURA, H., DIETDERICH, D. R. & MAEDA, H., *Appl. Phys. Lett.*, **56** (1990) 970.
5. MURAYAMA, N., SUDO, E., AWANO, M., KANI, K. & TORII, Y., *Jpn J. Appl. Phys.*, **27** (1988) L1856.
6. MATSUBARA, I., TANIGAWA, H., OGURA, T., YAMASHITA, H., KINOSHITA, M. & KAWAI, T., *Jpn J. Appl. Phys.*, **28** (1989) L1121.
7. MATSUBARA, I., TANIGAWA, H., OGURA, T., YAMASHITA, H., KINOSHITA, M. & KAWAI, T., *Appl. Phys. Lett.*, **57** (1990) 2490.
8. NOMURA, S., YAMASHITA, T., YOSHINO, H. & ANDO, K., *J. Am. Ceram. Soc.*, **74** (1991) 2711.