Synthesis of Hg(Re)1223 Tapes by PIT Method Using NiO / Ni Sheath

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Abstract. Fabrication of Hg$_{1-x}$Re$_x$Ba$_2$Ca$_2$Cu$_3$O$_y$ [Hg(Re)1223] tapes has been attempted by the PIT(Powder-In-Tube) method using a NiO/Ni sheath. It is confirmed that Hg(Re)1223 tapes with a high Re substitution level, 25% for Hg, showed sharp superconducting transitions at ~134 K and high irreversibility fields up to ~9 T at 77 K. In addition, application of magnetic grain alignment was effective for development of c-axis oriented Hg(Re)1223 tapes showing high transport properties.

1.  Introduction

The Re doping to the Hg-based superconductors is effective for improving both chemical instability and flux pinning properties at high temperatures without losing their originally high $T_c$'s[1,2]. Among them, Hg(Re)1223 is the most promising compound applicable at 77 K because of its high $T_c$ and high irreversibility field, which originates from the lowered electromagnetic anisotropy by Re substitution at Hg(O) layers. In our previous study, Hg(Re)1223 thick film tapes were prepared on hastelloy or NiO / Ni substrates. However, the resulting tapes exhibited low $J_c$ performance at 77 K due to the porous microstructure of the Hg(Re)1223 layer, i.e. poor grain coupling of Hg(Re)1223[3]. In this study, in order to make dense Hg(Re)1223 layer for improvement of $J_c$, we have attempted to synthesize Hg(Re)1223 tapes by the PIT(Powder-In-Tube) method using NiO / Ni sheath.

2.  Experimental

The precursor material with a nominal composition of Re$_{0.25}$Ba$_2$Ca$_2$Cu$_3$O$_y$ was prepared from high purity powders of ReO$_3$, BaCO$_3$, CaCO$_3$ and CuO. Appropriate amounts of these powders were mixed and calcined at 900°C for 20 h in air. The calcinations process was repeated twice. The precursor material was mixed with HgO, pressed into pellets and sintered at 900°C for 15 h in sealed quartz ampoules. The obtained Hg(Re)1223 [Hg$_{0.75}$Re$_{0.25}$Ba$_2$Ca$_2$Cu$_3$O$_y$] pellets were ground and filled into surface oxygenated Ni tubes. The tube was pressed uniaxially by a pressure of 330 MPa to a tape shape, and then sintered at 850 – 870°C for 1 ~ 10 h in the evacuated quartz ampoule together with Hg-containing oxide pellets for controlling vapor pressure of mercury during sintering. The pellets used as for the Hg vapor source were prepared from a powder mixture of HgO(0.2 g) and Re$_{0.1}$Ba$_2$Ca$_3$Cu$_4$O$_{12}$ (0.6 g), which was prepared in similar way as the Re$_{0.25}$Ba$_2$Ca$_2$Cu$_3$O$_y$ precursor. For improving the density and c-axis orientation of the tapes, intermediate pressing was applied for some tapes.
For further enhancement of the c-axis orientation, the magnetic grain alignment technique was applied for the synthesis of green Hg(Re)1223 tapes with ~ 60 μm thickness from a slurry containing Hg(Re)1223 powders and organic solvents. After drying and removing organic components by heating at 400°C for 5 h under flowing gas of O₂ 20%/ Ar (80%), the tapes were wrapped in surface oxygenated Ni foil, pressed with 330 MPa and sintered at 850 ~ 900°C for 1 ~ 10 h.

Constituent phases of the superconducting layer were analysed by X-ray diffraction. Microstructures of the surface and cross-sections of the tapes were observed by scanning electron microscopy (SEM). The electrical transport properties of the tapes were measured by the conventional four-probe method under fields up to 9 T applied vertical to the tape surface. The irreversibility field, \( H_{irr} \), was defined by applying a criterion resistivity of 1 μΩcm in the transport measurements. Critical current properties, \( I_c \) and \( J_c \), were defined by a criterion of 10 μV/cm.

3. Results and Discussion

3.1. Development of Hg(Re)1223 tapes by the PIT method

Through numerous attempts to synthesize PIT-processed Hg(Re)1223 tapes by sintering for various temperatures and times, the Hg(Re)1223 phase was found to be stable in a sintering temperature range of 840 ~ 870°C. Figure 1 shows a typical surface X-ray diffraction pattern of the Hg(Re)1223 tape taken after removal of the Ni sheath. The dense and predominantly c-axis oriented Hg(Re)1223 tapes with a typical grain size of 10 μm was successfully obtained by sintering at ~ 850°C with an intermediate pressing process as shown in Fig. 1(b). The secondary electron image for the tape surface also indicated that the c-axis orientation was well developed at the surface of the Hg(Re)1223 layer. However, microstructural observation performed for the cross section of the layer revealed that the c-axis grain orientation was achieved only near the surface region and the internal part of the oxide layer was composed of randomly oriented Hg(Re)1223 polycrystals.

![Fig. 1. (a) Powder and (b) surface X-ray diffraction patterns for a Hg(Re)1223 tape sintered at 850°C for 2 h with intermediate pressing.](image)

The Hg(Re)1223 tapes sintered at 840 ~ 870°C showed sharp superconducting transitions with \( T_{c,ons} \approx 134 \) K in the resistivity measurements. Temperature dependences of \( H_{irr} \) for Hg(Re)1223 tapes are summarized in Fig. 2. The \( H_{irr} \) at 77 K of the tape synthesized through the intermediate pressing was approximately 7 T, while that of a tape without intermediate pressing process was ~5 T. In
addition, normal-state resistivity, \( \rho \), at 150 K of the tape with intermediate pressing was reduced to 5.3 m\( \Omega \) cm mainly due to improvement of the grain alignment at surface region.

In order to improve electrical properties by strengthening the grain connection of the Hg(Re)1223, the filling powder was changed to the short time calcined powder, which was mainly composed of a Hg(Re)1212 phase, and slow cooling process down to 600°C was added after sintering. \( H_{irr} \) of the tape reached excellent superconducting properties of approximately 9 T at 77 K as show in Fig. 2. Furthermore, normal-state resistivity, \( \rho \) at 150 K decreased to \( \sim 1 \) m\( \Omega \) cm. It is considered that starting from the powder composed of Hg(Re)1212 as a main phase strengthened the intergrain connection of the Hg(Re)1223 crystals. In addition, the slow cooling process is believed to improve the local chemical composition particularly for the Hg composition at the grain boundaries.

**Fig. 2.** Temperature dependence of irreversibility fields for the Hg(Re)1223 tapes.

The \( I-V \) characteristics for Hg(Re)1223 tapes are shown in Fig. 3. Although \( I_c \) of the quenched Hg(Re)1223 tape with intermediate pressing was only 15.2 A/cm-width and corresponding \( J_c \) was 200 A/cm\(^2\), \( I_c \) was improved up to 18.3 A/cm-width and \( J_c \) was 330 A/cm\(^2\) for the tape starting from Hg(Re)1212 contained powder and introduction of slow cooling process. However, these values are not sufficiently high for application as for current leads. This low \( J_c \) is considered to be due to random grain orientation in the internal region.

**Fig. 3.** \( I-V \) characteristics for the Hg(Re)1223 tapes.
3.2. Synthesis of c-axis aligned Hg(Re)1223 tapes by applying magneto-scientific technique

Based on the results on the PIT-processed Hg(Re)1223 tapes, grain alignment by applying strong magnetic fields has been attempted to improve c-axis oriented texture of the Hg(Re)1223 layer. In order to investigate the effect of crystal orientation, as a preliminary examination Hg(Re)1223 powder was mixed with epoxy resin and slowly solidified in magnetic fields. X-ray diffraction analysis revealed that applying a magnetic field of 3 T is enough to achieve c-axis orientation of the powder parallel to the field direction by magnetic anisotropy of the CuO₂ plane.

The Hg(Re)1223 tape fabricated through the coating and drying the slurry on the NiO/Ni substrate under 3 T and pressing with 330 MPa was confirmed to maintain the strongly c-axis oriented microstructure after sintering at 850°C for 1 h as shown in Fig.4(b), while the tape synthesized without magneto-scientific technique were composed of randomly oriented grains as shown in Fig. 4(a). It is confirmed that application of the magnetic alignment technique is effective for promoting c-axis orientation in a large part of the oxide layer. $J_c$ of this c-axis oriented Hg(Re)1223 tape showed higher values of 660 A/cm² than that of the PIT method tapes, whereas all the effective methods to enhance critical current properties found for PIT-processed tapes, such as intermediate pressing, starting from Hg(Re)1212 containing powder and slow cooling, were not applied for it. This result suggests that further enhancement of the superconducting properties can be expected by optimization of the sintering process and components in starting calcined powder.

![Fig. 4. Secondary electron images for the fracture cross sections of the Hg(Re)1223 tapes sintered at 850°C for 1 h initially coated and dried under 0 T (a) and 3 T (b).](image)

4. Conclusions

Improvement of the critical current properties of PIT-processed Hg(Re)1223 tapes applicable for a practical use, such as current leads, was attempted in the present study. The dense Hg(Re)1223 tapes with strongly c-axis oriented surfaces were obtained from a sintering temperature range of 840 – 870°C. Introduction of the intermediate pressing, starting from Hg(Re)1212 containing powders and slow cooling processes were found to improve grain coupling, resulting in an enhancement of $J_c$ and achieving very high irreversibility fields up to ~9 T at 77 K. In addition, application of the magnetic grain alignment technique essentially improved the c-axis orientation in a whole part of the Hg(Re)1223 layer.

References

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