Microstructure controls and their effects on the properties of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ superconductors

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Abstract. This paper reports our recent progresses in the development of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x/\text{Ag}$ tape conductors for the applications of magnetic field generation in liquid helium or around 20 K, using a refrigerator. We have carried out extensive work to optimize the processing parameters, investigating the relationship between the microstructure and transport J_c . We have found that the partial melting in oxygen atmosphere is effective to have large transport J_c with good reproducibility. The pre-annealing and intermediate rolling (PAIR) process has been successfully applied to the multilayer conductors to improve the grain alignment and transport J_c . The J_c of $5 \times 10^5 \text{ A/cm}^2$ at 4.2 K and 10 T has been achieved, which is the highest value reported so far. Two magnets fabricated by using different types of Bi-2212/Ag conductors were tested. One is a magnet designed as an insert magnet for a 18 T-class large bore Nb–Ti/Nb₃Sn superconducting magnet. The conductor of this magnet was multifilamentary tape processed by powder-in-tube method. The I_c was 98 A in the backup field of 18 T, which generated the self field of 1.79 T. A large pancake coil was fabricated with multilayer conductor and tested under the operation of cryocooler system. The coil was stably operated up to the J_c of the coil at the temperatures below 30 K.

Keywords. $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ superconductor; grain alignment; critical current density; tape; magnet.

1. Introduction

Among the many high temperature superconductors, $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ (Bi-2212) is one of the most promising materials for practical application because of its extremely high transport critical current density (J_c) at low temperatures even in strong magnetic fields. In recent years, many investigations of magnet fabrication using Bi-2212 superconducting tapes have been reported (Balachandran *et al* 1994; Shibutani *et al* 1994; Tenbrink and Krauth 1994; Tomita *et al* 1994, 1995; Okada *et al* 1996). Bi-2212/Ag tapes were prepared by applying a melt-solidification method, which produced an excellent microstructure of highly oriented Bi-2212 crystals (Kase *et al* 1991). Due to this preferable microstructure, they show excellent critical current density (J_c) values higher than 10^5 A/cm^2 , even in magnetic fields above 25 T (Tesla) at 4.2 K. In the previous work (Okada *et al* 1996), we fabricated small magnets composed of pancake type coils using Bi-2212/Ag multifilamentary tapes prepared by the powder-in-tube method and melt-solidification process. Those small magnets were tested at 4.2 K as the insert magnet of a Nb–Ti/Nb₃Sn superconducting magnet system and one of the magnet generated about 1.8 T in the

back-up field of 21 T, so that the whole system achieved the highest magnetic field of 22.8 T generated only by superconducting state. Although the magnet had a small size (13 mm inner dia., 49 mm outer dia. and 55 mm height), the result suggested that the combination of Bi-2212 and conventional metallic superconductor would be very promising to construct a high-field superconducting magnet system, such as a high-field NMR magnet.

Another interesting application of Bi-2212 is a magnet operated at elevated temperatures. For example, at 20 K where the efficiency of a Gifford–McMahon (GM) cryocooler becomes high enough, Bi-2212 also shows excellent J_c values. In general, Bi-2212/Ag tape conductors are more easily synthesized than Bi-2223/Ag conductors because of simpler fabrication procedure. These suggest that the Bi-2212 is another candidate for a conductor of a cryogen-free superconducting magnet operated with cryocooler.

In this paper, we report our recent progresses in the development of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x/\text{Ag}$ tape conductors for the applications of magnetic field generation in liquid helium or at below 20 K by using a refrigerator. We have carried out an extensive work to optimize the processing parameters to have large J_c with good reproducibility, investigating the relationship between the microstructure and transport J_c . The paper also reports

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the results of coil tests in liquid helium and cryocooler operation.

2. Fabrication of Bi-2212/Ag tape

We are developing three processes to fabricate Bi-2212/Ag long tape and its coil, which are dip-coating, powder-in-tube (PIT), and lamination processes. Figure 1 shows the schematic diagram of these three processes. In the dip-coating process, Ag tape is continuously dipped into the slurry to be coated with the mixture of oxide and organic binders. The lamination process is the modification of the dip-coating process, in which several coated tapes are stacked and wrapped by Ag or Ag-alloy foil. The assembly is then cold rolled into a tape with multilayer structure.

In all these processes, the tape is given the heat treatment of partial melting and slow cooling in order to achieve good grain alignment of Bi-2212. We found that the partial melting and slow solidification in pure oxygen atmosphere brings about a larger transport J_c than in ambient atmosphere with good reproducibility as shown in figure 2 (Kumakura *et al* 1996). The investigation by high resolution transmission electron microscopy indicated that the partial melting and slow solidification in low oxygen partial pressure results in the formation of amorphous layer at the grain boundary, resulting in the weak coupling (Fujii *et al* 1997). Figure 3 shows the typical transport J_c as functions of magnetic field and temperatures. The tapes have high transport J_c which exceeds well over 105 A/cm^2 in applied magnetic fields at the temperatures below 30 K.

Recently, we have developed the pre-annealing and intermediate rolling (PAIR) process in order to improve the gain alignment. Figure 4 shows the procedure of the PAIR process, which is particularly effective when applied for lamination process (Miao *et al* 1998a). Figure 5 shows the effect of pre-annealing (PA) and intermediate annealing (IR) on the transport J_c of the Bi-2212/Ag multilayer tape processed by lamination process. These results indicate that the application of PAIR process to conventional partial melting process increases the J_c to about 3 times. Very recently, we achieved critical current density of $5 \times 10^5 \text{ A/cm}^2$ at 4.2 K and 10 T by optimizing the PAIR process and conductor fabrication procedure, which is the highest critical current density of the tape reported so far (Miao *et al* 1998b). This large increase of J_c was caused by the large improvement of grain alignment of Bi-2212 as shown in figure 6.

3. Coil test in liquid helium to generate high magnetic field

Bi-2212/Ag multifilamentary tapes with 19 oxide cores, whose size was 0.15 mm in thickness, 5 mm in width and 50 m in length were prepared by the powder-in-tube method (Okada *et al* 1995). The tapes were then wound in a double pancake form, partially melted at around 880°C and then furnace cooled in a flowing pure oxygen atmosphere. Alumina paper was used as an insulator. Finally, the coils were annealed in the atmosphere of low oxygen partial pressure in order to optimize the carrier concentration. After the heat treatment, the coils were impregnated with an epoxy resin with low viscosity.

Figure 1. Schematic diagrams of three processes for the fabrication of long Bi-2212/Ag tape and coils.

Then, ten double pancake coils were stacked to fabricate an insert magnet. Figure 7 shows the photograph of an insert magnet, which was 125 mm in height, 129 mm in outer diameter and had a clear bore of 25 mm. The magnet was encased in a metal former and impregnated with epoxy resin for the support to strong electromagnetic force. Voltage terminals were soldered on the outermost

turn of each double pancake coil and also on the current leads. The critical current of I_c of the coil was defined by 10^{-13} ohm-m criterion. The critical current density of the coil $J_{c\text{-coil}}$, was calculated from I_c and the overall cross section of the conductor. The J_c of the Bi-2212 oxide core, $J_{c\text{-oxide}}$ was also calculated from I_c and the cross sectional area of the oxide core. The generated magnetic field of the magnet was measured by using a Hall sensor. Backup magnetic fields up to 18 T were applied using a large bore Nb-Ti/Nb₃Sn superconducting magnet at Tsukuba Magnet Laboratories of National Research Institute for Metals.

The $J_{c\text{-oxide}}$ calculated from the I_c defined by the 10^{-13} ohm-m criterion is plotted as a function of the centre magnetic field in figure 8. In the backup field of 18 T, the insert magnet showed I_c value of 98 A,

Figure 2. Critical current density J_c at 4.2 K and 10 T as a function of maximum temperature of the heat treatment schedule. The heat treatment of the partial melting and solidification was performed under several oxygen partial pressure.

Figure 3. Typical transport J_c of the Bi-2212/Ag superconducting tape as functions of applied magnetic field and temperature. The magnetic field is applied parallel to the tape surface.

Figure 4. Procedure of the pre-annealing and intermediate rolling (PAIR) process.

Figure 5. Effect of pre-annealing (PA) and intermediate rolling (IR) on J_c of the Bi-2212/Ag multilayer tape.

which corresponds to the $J_{c-oxide}$ of about 3×10^4 A/cm² and the J_{c-coil} of 3.6×10^3 A/cm². At this current, the self-field of the insert magnet was 1.79 T, resulting in a total magnetic field of about 19.8 T. The J_{c-coil} is 1/3–1/4 of that of the small coils which was reported in previous work (Okada *et al* 1996), and we are now improving the performance of the large magnets.

4. Coil tests under cryocooler operation

The Bi-2212 coil used for the cryocooler test was fabricated by a react and wind method using Bi-2212/Ag multilayer composite tapes prepared by the lamination process. Ag tapes of 20 μ m in thickness and 3 mm width were coated with slurry and those tapes were stacked together and wrapped with 25 μ m thick Ag-0.2%Mg alloy tape. The mechanical strength of the tape was much enhanced by using this Ag-0.2%Mg alloy. This multilayer tape was continuously heat treated by travelling the tape through a long pipe furnace having a precise temperature gradient. This heat treatment gave a partial

melting and subsequent slow cooling. We have fabricated 100 m long tapes with excellent J_c properties and uniformity. After the heat treatment, the tape was coated

Figure 7. Bi-2212 test magnet designed as an insert magnet of the Nb-Ti/Nb₃Sn superconducting magnet.

Figure 6. SEM micrographs observed on the longitudinal cross section of the Bi-2212/Ag multilayer tape processed without (a) and with (b) PAIR process.

Figure 8. J_c for the oxide core of the Bi-2212 test magnet shown in figure 7 defined by the 10^{-13} ohm-m criterion as a function of the centre magnetic field (= applied field (Nb-Ti/Nb₃Sn) + self field (Bi-2212)). The previous result (Okada *et al* 1996) for smaller coil is also shown for comparison.

with polyimide for insulation, and then wound around a Cu tube to make a double pancake coil. Voltage terminals were soldered on the outermost turn of the coil and on the Ag current leads. The coil was encased in a stainless steel frame and was impregnated with epoxy resin. The details of the tape and magnet fabrication process have been described elsewhere (Hasegawa *et al* 1997). The magnet has a clear bore of 60 mm diameter, outer diameter of 128 mm and 9.3 mm in height and was installed in a GM cryocooler system as shown in figure 9 to be tested at various temperatures. For comparison, conventional slow cooling heat treatment was also carried out using a box furnace for short tapes cut from the long tape.

We measured the voltage of the magnet at several temperatures as a function of time with various constant applied current. There was a critical current above which the voltage and temperature continue to go up with time, finally resulting in a thermal runaway of the magnet. Below this critical current, the voltage initially goes up slightly due to the heat generation at the current leads, however, the voltage saturates and becomes constant in a few minutes. We measured the voltage and temperature for 24 h, and no changes were observed. Figure 10 shows the plot of this critical current as a function of operation temperature. At higher temperature region, the voltage increases and, hence, the temperature rise of the magnet

were slow due to the larger heat capacity of the magnet, and thermal runaway was observed several hours after the current was applied. Up to about 30 K, the stable operating current density was equal or slightly lower than J_c values. Above 30 K, however, stable operating current density was higher than J_c . The stable operating current density extrapolated to 4.2 K was lower than that obtained in liquid helium. This indicates that the heat transfer from the coil to cooling stage was smaller than that from the coil to liquid helium. At higher temperature region, heat generation in the magnet, $I_c \times V$, was small due to the low J_c values which led to a stable operating current density higher than J_c .

The highest stable operating current density of the coil at 20 K was $4.6 \times 10^4 \text{ A/cm}^2$ ($I = 95 \text{ A}$) which is high enough for practical applications. At this current, the generated magnetic field was 0.78 T. Calculation indicates that a magnet consisting of twelve double pancake coils with the same dimension generates about 3 T which is high enough for practical applications.

5. Conclusions

In this paper, we have reported our recent progresses in the development of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x/\text{Ag}$ tape conductors for the applications of magnetic field generation in liquid helium or at below 20 K by using a refrigerator. We

Figure 9. Test system of Bi-2212 coil under cryocooler operation.

Figure 10. Plot of the current density I_s which is the broader of the stable operation and thermal runaway. The J_c of the coil ($J_{c\text{-coil}}$) defined by the 10^{-13} ohm-m criterion is also plotted for comparison.

have carried out an extensive work to optimize the processing parameters, investigating the relationship between the microstructure and transport J_c . We have found that the partial melting in oxygen atmosphere is effective to have large transport with good reproducibility. The pre-annealing and intermediate rolling (PAIR) has been successfully applied to the multilayer conductors to improve the grain alignment and transport J_c . The J_c of 5×10^5 A/cm² at 4.2 K and 10 T has been achieved, which is the highest value reported so far.

Two magnets fabricated by using different types of Bi-2212/Ag conductors were tested. One is a magnet designed as an insert magnet for a 18 T-class large bore Nb-Ti/Nb₃Sn superconducting magnet. The conductor of this magnet was multifilamentary tape processed by powder-in-tube method. The magnet consists of ten double-pancake coils, and was tested in liquid helium in bias fields up to 18 T. The I_c was 98 A in the backup-field of 18 T, which corresponds to the $J_{c\text{-oxide}}$ of about 3×10^4 A/cm² and the $J_{c\text{-coil}}$ of 3.6×10^3 A/cm². At this current, the self-field of the insert magnet was 1.79 T. A large pancake coil was fabricated with multilayer conductor and tested under the operation of cryocooler system. Below about 30 K, the highest operating current densities for which the magnet was stably operated with GM cryocooler were almost equal to $J_{c\text{-coil}}$ values defined by 10^{-13} ohm-m. At 20 K, maximum stable operating current density was 4.6×10^4 A/cm² which was about

70% of those at 4.2 K, suggesting that a few Tesla will be easily attained by cryocooler operation by stacking many pancakes of Bi-2212 conductors.

References

- Balachandran U, Iyer A N, Halder P, Hoehn J G, Motowidlo L R and Galinski G 1994 *Appl. Supercond.* **2** 251
- Fujii H, Kumakura H and Togano K 1997 *J. Jap. Inst. Metals*, **61** 856
- Hasegawa T, Hikichi Y, Koizumi T, Imai A, Kumakura H, Kitaguchi H and Togano K 1997 *IEEE Trans. Appl. Supercond.* (in press)
- Kase J, Morimoto T, Togano K, Kumakura H, Dietrich D R and Maeda 1991 *IEEE Trans. Magn.* **24** 1254
- Kumakura H, Kitaguchi H, Togano K and Sugiyama N 1996 *J. Appl. Phys.* **80** 5162
- Miao H, Kitaguchi H, Kumakura H, Togano K and Hasegawa T 1998a *Physica* **C301** 116
- Miao H, Kitaguchi H, Kumakura H, Togano K, Hasegawa T and Koizumi T 1998b *Physica* **C303** 81
- Okada M, Tanaka K, Sato J, Awaji S and Watanabe K 1995 *Jpn J. Appl. Phys.* **34** 4770
- Okada M et al 1996 *Jpn J. Appl. Phys.* **35** L623
- Shibutani K, Hase T, Egi T, Hayashi S, Ogawa R and Kawate Y 1994 *Appl. Supercond.* **2** 237
- Tenbrink J and Krauth H 1994 *Adv. Cryogenic Eng.* **40** 305
- Tomita N et al 1994 *Appl. Phys. Lett.* **65** 898
- Tomita N et al 1995 *IEEE Trans. Appl. Supercond.* **5** 520