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To cite this article: H S Kim *et al* 2009 *Supercond. Sci. Technol.* **22** 125016

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The influence of heat-treatment and oxygenation annealing on the superconducting properties of YBCO coated conductors

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Received 12 July 2009, in final form 22 September 2009

Published 23 October 2009

Online at stacks.iop.org/SUST/22/125016

Abstract

The superconducting properties of YBCO (yttrium barium copper oxide) coated conductors (CCs) are strongly dependent on their oxygen content. Degradation of the superconducting properties of a YBCO CC can occur due to a phase/structure transition caused by the oxygen diffusion out of the YBCO during heat-treatment or soldering, which is an inevitable process during the creation of a superconducting joint. Such variations in phase/structure are generally functions of temperature and oxygen partial pressure (P_{O_2}). Therefore, in order for a superconducting joint of YBCO CC to be feasible, it is important to examine the changes in the microstructure and oxygen diffusion behavior for YBCO CCs. This study examined the superconducting properties of YBCO CCs before and after a heat-treatment under a reduced P_{O_2} followed by an oxygenation annealing process in an oxygen rich environment. Partial melting of YBCO without melting of the silver stabilizer layer was obtained for a sample heat treated for 60 s at 820 °C and $P_{O_2} \simeq 1 \times 10^{-2}$ Torr. The superconducting properties of the sample heat treated at 820 °C were fully restored by an oxygenation annealing treatment for 15 h at 600 °C.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, there has been considerable interest in YBCO coated conductors (CCs) for various high temperature superconducting (HTS) applications on account of its high critical current density, high index number (n -value), less dependency of the critical current on an external magnetic field, good mechanical properties and reasonable prime cost. However, a joining technique for the YBCO CCs is essential for HTS magnet applications due to the technical difficulties in lengthening YBCO CCs. This should also contribute to the establishment of a superconducting closed loop for a persistent current mode operation and interconnections between HTS magnet coils.

Some studies on the non-superconducting joints of YBCO CC have been carried out using solder as a connector

between the superconducting layers [1–4]. In the case of a non-superconducting joint, it is inevitable that contact resistance will occur across the connection. Therefore, the development of superconducting joints, i.e. superconductor to superconductor connections, is essential for HTS applications, particularly when operated in persistent current mode, such as nuclear magnetic resonance (NMR), magnetic resonance imaging (MRI) and superconducting magnet energy storage (SMES). However, there are no reports on the superconducting joints of YBCO CC.

In ambient air ($P_{O_2} \simeq 160$ Torr), a superconducting joint of YBCO CC is rarely obtained without melting the silver stabilizer layer that protects the superconducting layer because the melting temperature of YBCO is higher than that of silver, as shown in figure 1. However, a successful superconducting joint can be obtained without deformation of the YBCO CCs by reducing the P_{O_2} , which helps reduce the melting temperature of YBCO (see figure 1) [5–14]. On

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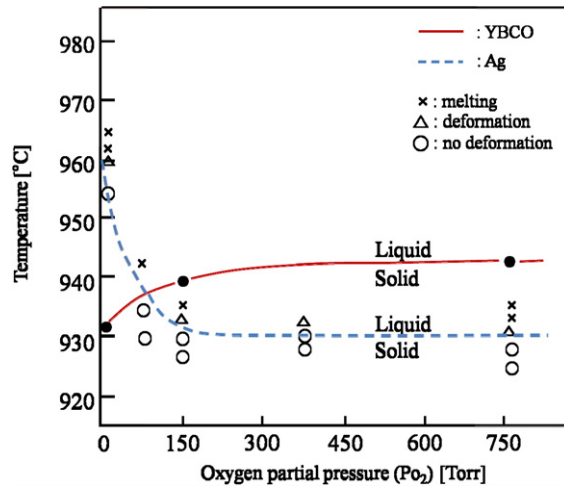


Figure 1. Changes in the melting temperatures of YBCO and silver as a function of P_{O_2} [5].

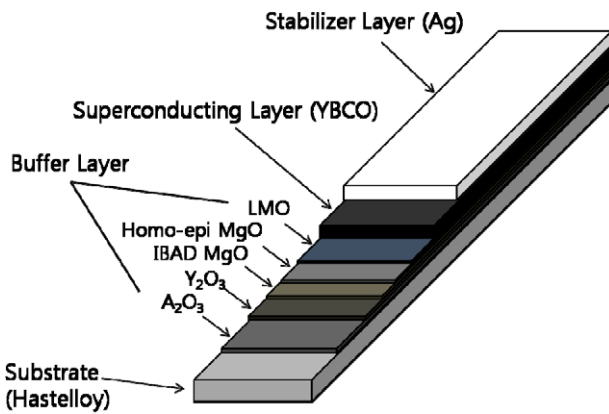


Figure 2. Schematic drawing of the YBCO coated conductor (CC).

the other hand, heat-treatment under a reduced P_{O_2} , which is controlled directly by the out-diffusion of oxygen, can degrade the superconducting properties. The structure and superconducting properties of YBCO are strongly affected by the oxygen stoichiometry. Accordingly, an oxygen

deficiency causes a phase transition from a superconducting orthorhombic phase to a non-superconducting tetragonal phase. The orthorhombic-to-tetragonal phase transition is strongly dependent on the temperature and P_{O_2} . This phase transition in an atmosphere containing oxygen is reversible with changes in temperature. However, it is irreversible in a vacuum state, resulting in a tetragonal phase that remains stable after heat-treatment at high temperatures [15–19]. Therefore, it is important to develop an optimal additional oxygenation annealing process at low temperatures (500–600 °C) in an oxygen rich environment to restore the oxygen stoichiometry and superconducting properties.

This paper discusses the changes in microstructure and superconducting properties of YBCO CC after heat-treatment under a reduced P_{O_2} ($\sim 1 \times 10^{-2}$ Torr) and an additional oxygenation annealing process in an oxygen rich environment in terms of the feasibility of a superconducting joint. The optimal conditions for the first heat-treatment and oxygenation annealing process, such as heat-treatment temperature, time and environment were evaluated by examining the superconducting properties of YBCO CC.

2. Experiment

Figure 2 shows a schematic drawing of the YBCO CC ('SF4050' from IGC-Superpower) used in this study. For a HTS–HTS superconducting joint in the case of a face-to-face junction, the silver (Ag) stabilizer layer on top of the YBCO needs to be eliminated. A chemical etching method was used to remove the Ag stabilizer layer. The etchant (Gold Etchant TFA from Transene Co.) was diluted with distilled (DI) water (50% by weight) to moderate the etching reaction in order to achieve a homogeneously etched surface [20].

Figure 3 shows the heat-treatment cycles for the first heat-treatment (HT1) and additional oxygenation annealing (OA) process. As mentioned earlier, heat-treatment was performed in two steps. In the first step, heat-treatment (HT1) for the joining two YBCO CC tapes, the samples were heat treated to various temperatures (T_{HT1}) at 5°C min^{-1} under a reduced P_{O_2} ($\sim 1 \times 10^{-2}$ Torr) and held at that temperature for 60 s.

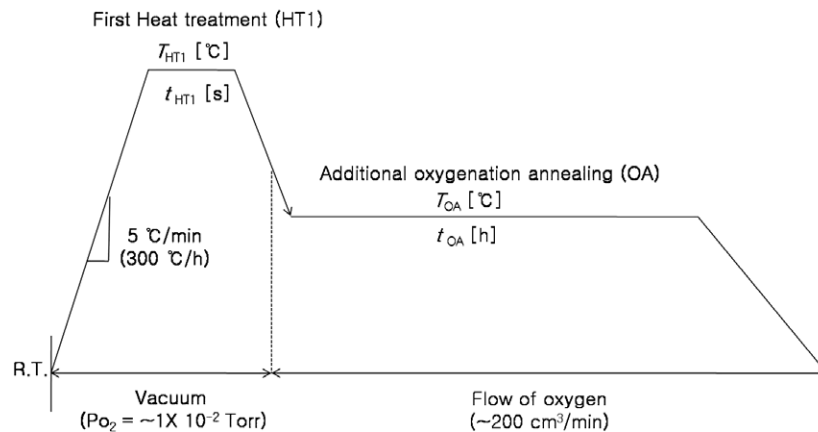


Figure 3. Heat-treatment cycles for the first heat-treatment (HT1) and additional oxygenation annealing (OA). T_{HT1} : temp. of HT1, t_{HT1} : duration time of HT1, T_{OA} : temp. of OA, t_{OA} : duration time of OA.

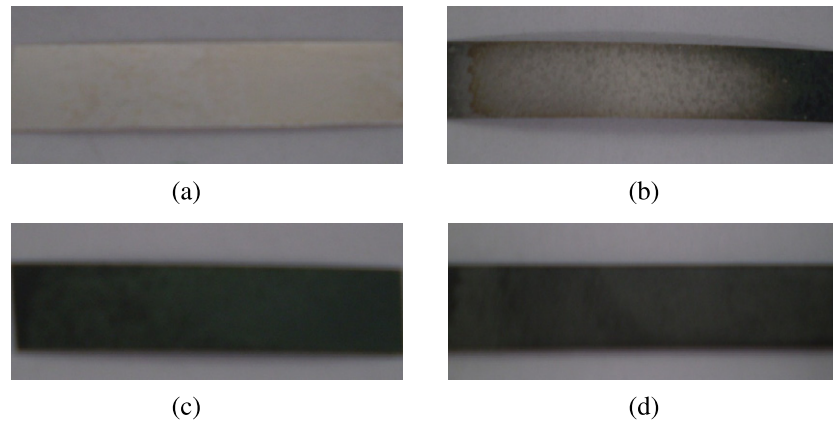


Figure 4. Photographs of YBCO CC after heat-treatment at $P_{O_2} = \sim 1 \times 10^{-2}$ Torr. (a) 800 °C, (b) 850 °C, (c) 900 °C, (d) 950 °C.

After the first heat-treatment, the samples were furnace cooled under a reduced P_{O_2} until 700 °C. In the second step, an additional oxygenation annealing process (OA) to restore the oxygen stoichiometry was performed at temperatures (T_{OA}) ranging from 500 to 600 °C under a flow of pure oxygen ($\sim 200 \text{ cm}^3 \text{ min}^{-1}$) for various times (t_{OA}).

The self-field critical current (I_c) values of the YBCO CC samples were measured in a bath of liquid nitrogen (LN2) using a $1 \mu\text{V cm}^{-1}$ criterion. The morphology and structure of the samples was analyzed by scanning electron microscopy (SEM) and x-ray diffraction (XRD), respectively.

3. Results and discussion

For the feasibility of a superconducting joint of YBCO CC, it is important to determine the optimal heat-treatment conditions, where the reactions of YBCO, melting or diffusion, can occur without melting the silver stabilizer layer. In order to extract the appropriate heat-treatment temperature ranges for the first heat-treatment (HT1), four samples without removing the silver layer were heat treated for 60 s at 800, 850, 900, and 950 °C. Figure 4 shows photographs of the YBCO CCs after heat-treatment at P_{O_2} of $\sim 1 \times 10^{-2}$ Torr. The silver layer on the YBCO CC sample heat treated at 800 °C was intact, while it was partially melted at 850 °C, and completely melted after heat-treatment at 900 °C or above. Therefore, a heating temperature < 850 °C was chosen as the first heat-treatment step.

Figure 5 shows XRD patterns of a virgin sample before heat-treatment along with samples heat treated at various temperatures. The XRD peaks of all samples, corresponding to the major peaks of YBCO, indicate a strong preferential c -axis orientation. No peaks for impurity phases were detected.

Figure 6 shows typical SEM images of the surface morphology of the virgin sample and heat treated sample at 820 °C under a reduced P_{O_2} of $\sim 1 \times 10^{-2}$ Torr. As shown in figure 6(b), the surface of the YBCO CC was partially melted. From these results, it was expected that the joint of two YBCO CCs, without melting the silver layer, could be obtained by heating at ≥ 820 °C and $P_{O_2} = \sim 1 \times 10^{-2}$ Torr. In addition, the lower P_{O_2} decreased the melting temperature of YBCO

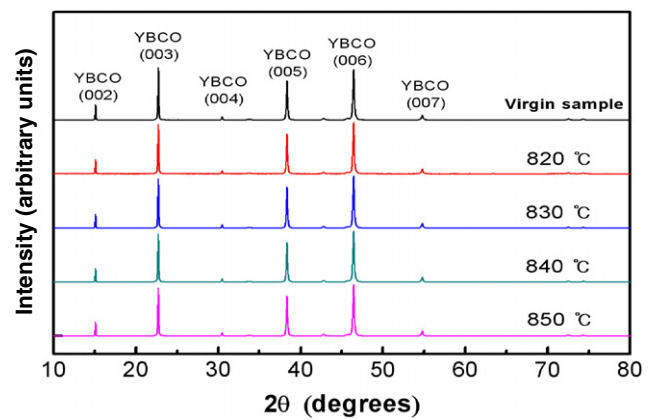


Figure 5. XRD patterns of the virgin sample and samples heat treated at various temperatures.

CC, which could make it possible to join the YBCO layers at lower temperatures than at higher P_{O_2} and increase the reaction kinetics of YBCO CC.

Figure 7 shows the V – I curve of the virgin sample. The I_c and n -values of the virgin sample were 130 A and 49, respectively. Figure 8 shows the ratios of the I_c values before (I_c^{before}) and after (I_c^{after}) the first heat-treatment step at 820, 830, 840 and 850 °C. After the first heat-treatment, the samples showed I_c degradation. The I_c value of the sample heat treated at 820 °C was 24% lower than the virgin sample. The samples heat treated at 830 °C or above showed ohmic behavior, which indicates that these samples are non-superconductors. As stated earlier, a transition of YBCO occurs during the first heat-treatment and is irreversible due to the reduced P_{O_2} . This suggests that an additional oxygen annealing process will be necessary to restore the superconducting properties of the first heat treated samples.

The oxygenation annealing process was performed at various temperatures to examine the effects of the oxygenation annealing temperature on the superconducting properties of the YBCO CCs. Figure 9 shows the V – I curves of the samples after an oxygen annealing process for 15 h at 500, 550 and 600 °C after the first heat-treatment step at 840 °C. The sample

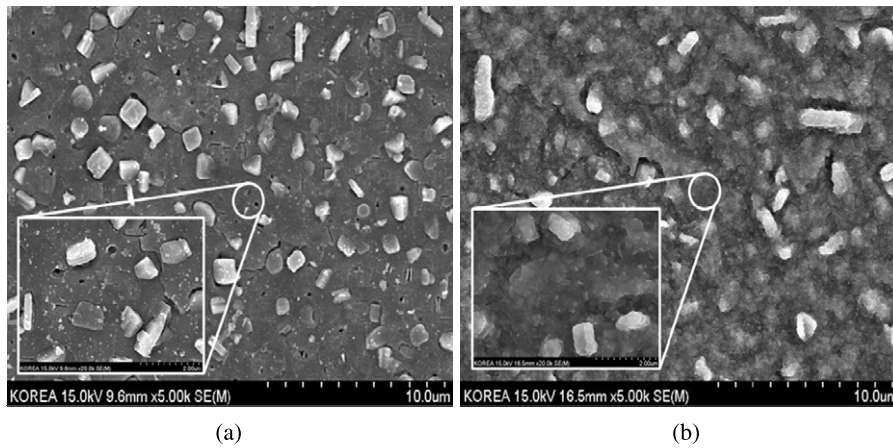


Figure 6. Typical SEM images of the surface of YBCO CC: (a) virgin sample and (b) sample heat treated at 820 °C under a reduced P_{O_2} of $\sim 1 \times 10^{-2}$ Torr.

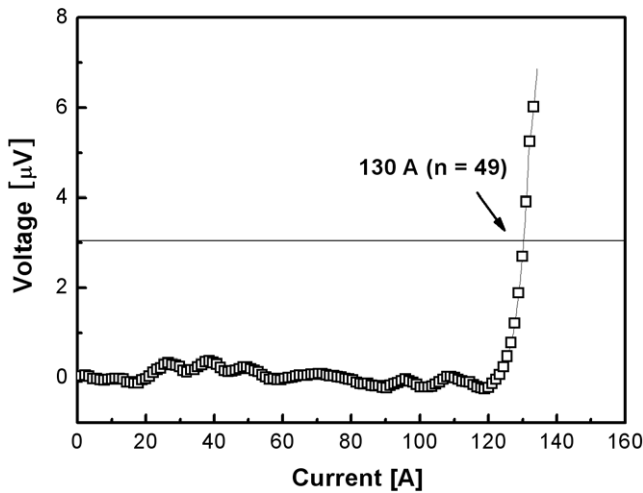


Figure 7. V – I curve of the virgin sample.

annealed at 600 °C had a higher I_c value than those annealed at 500 and 550 °C. At a fixed annealing duration, the oxygenation annealing process at higher temperatures is more favorable for restoring the superconducting properties.

The effect of the duration time of the oxygenation annealing process on the superconducting properties of the YBCO CCs was also examined. Figure 10 shows the V – I curves of the samples annealed for 5, 10, and 15 h at 500 °C after being heat treated at 830 °C. The I_c value of the samples annealed for 5, 10, and 15 h were 18, 46, and 85 A, respectively. The I_c values of the samples increased with increasing oxygenation annealing duration. This means that the oxygen that had diffused out during the first heat-treatment was restored during the subsequent oxygenation annealing process.

Figure 11 shows the V – I curves of the virgin sample and samples heat treated at 820 °C and annealed for 15 h at 600 °C. The I_c (129 A) value of this sample was similar to that of the virgin sample (130 A), which suggests that the superconducting properties had been fully restored.

Table 1. Superconducting properties of the samples after oxygenation annealing at 500 °C.

T_{HT1} (°C)	820		830			840			850		
t_{OA} (h)	5	10	5	10	15	7	10	15	10	15	30
I_c (A)	>115 (burn-out)	118	18	46	85	36	44	50	12	15	31
n -value	—	15	13	25	18	26	24	37	3	7	6
$I_c^{\text{after}}/I_c^{\text{before}}$ (%)	88	91	14	35	65	28	34	38	9	12	24

Table 2. Superconducting properties of the samples after oxygenation annealing at 600 °C.

T_{HT1} (°C)	820	830	840			850	
t_{OA} (h)	15	15	15	20	30	30	60
I_c (A)	129	117	69	98	>108 (burn-out)		55 100
n -value	41	28	25	17	—		20 28
I_c^{after}/I_c^{before} (%)	99	93	53	78	83		44 77

Tables 1 and 2 list the superconducting properties of the samples heat treated at various temperatures and annealed at 500 and 600 °C, respectively. As expected, the I_c values of the samples increased with increasing oxygenation annealing time. Generally, the n -values of the samples also increased with increasing duration.

However, it is certain that the results cannot be applied directly to superconducting joints because of the influence of the different boundary conditions for the oxygen atmosphere in a superconducting joint. In this case, the oxygen has to diffuse in the plane and has no easy access to the YBCO layer as in the single coated conductor. Assuming that both the solubility and diffusivity of oxygen in the buffer and substrate materials are very low, only two sides (few μ m thick) between the YBCO–YBCO joint serve as conduits for oxygen during the oxygenation annealing process to restore the superconducting properties. Therefore, an oxygenation annealing process at higher P_{O_2} and longer durations might be necessary.

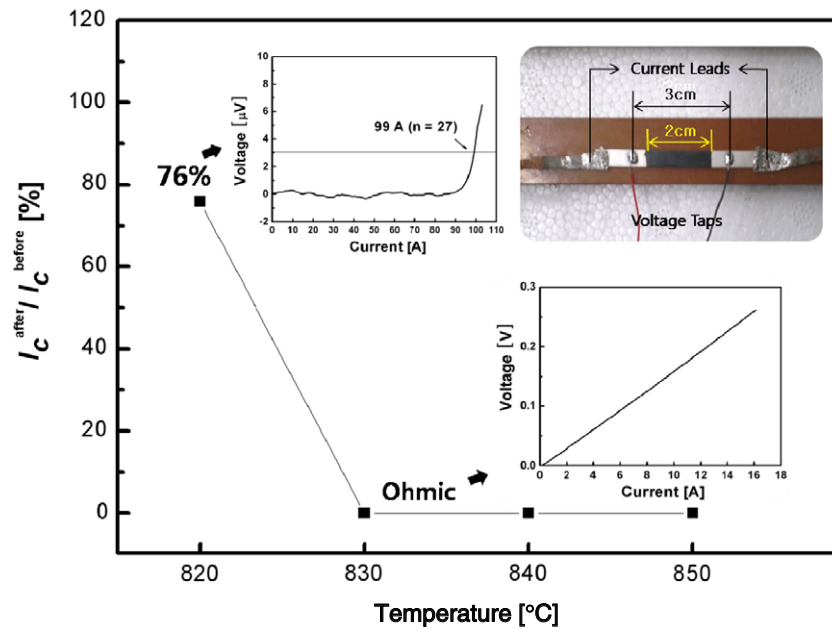


Figure 8. Ratios of the I_c values before and after the first heat-treatment at various temperatures.

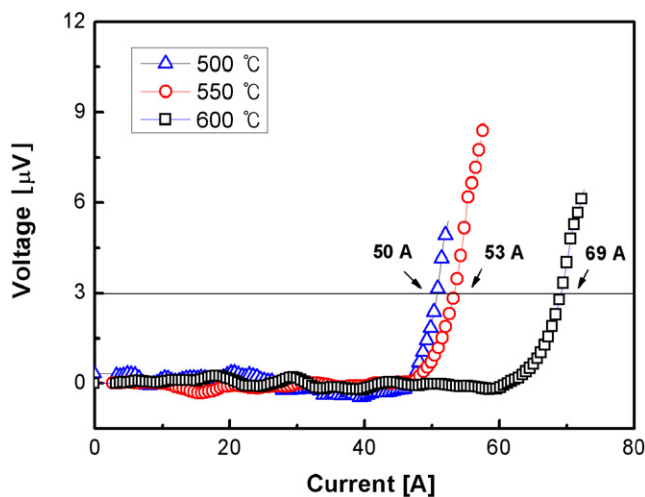


Figure 9. V - I curves of the samples annealed for 15 h at 500, 550 and 600 °C after the first heat-treatment at 840 °C ($T_{HT1} = 840$ °C, $T_{OA} = 500, 550$ and 600 °C, $t_{OA} = 15$ h).

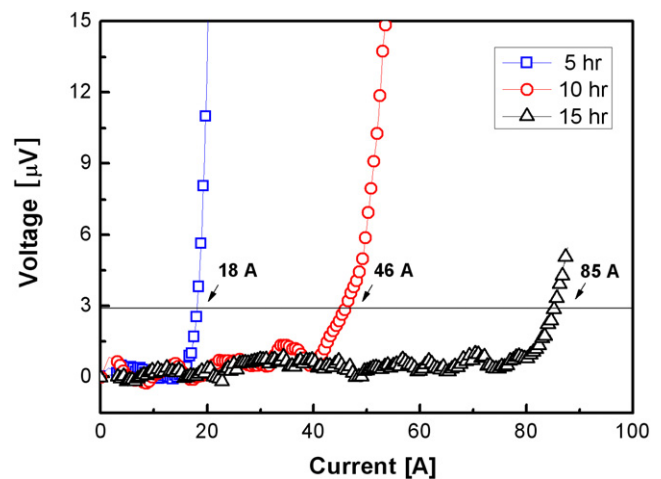


Figure 10. V - I curves of the samples annealed at 500 °C for 5, 10 and 15 h after the first heat-treatment at 830 °C ($T_{HT1} = 830$ °C, $T_{OA} = 500$ °C, $t_{OA} = 5, 10$ and 15 h).

4. Conclusion

This study examined the optimal heat-treatment and oxygenation annealing conditions for a superconducting joint of YBCO CC. The first heat-treatment under a reduced P_{O_2} was effective in obtaining a partially melted YBCO without melting the silver stabilizer layer. The oxygenation annealing process makes it possible to restore the superconducting properties. Moreover, an oxygenation annealing process at higher temperatures and longer durations is more favorable for restoring the superconducting properties of YBCO CC. A partially melted YBCO CC without melting the silver stabilizer layer was obtained in the sample heat treated for 60 s at 820 °C and

$P_{O_2} = \sim 1 \times 10^{-2}$ Torr. The superconducting properties of the sample heat treated at 820 °C were fully restored after an oxygenation annealing process for 15 h at 600 °C. Studies on the optimal processes for the superconducting joints of YBCO CC are currently underway.

Acknowledgments

This study was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MEST 2009-0085369), and the Electric Power Industry Technology Evaluation and Planning. It was also supported by a grant from the center for Applied

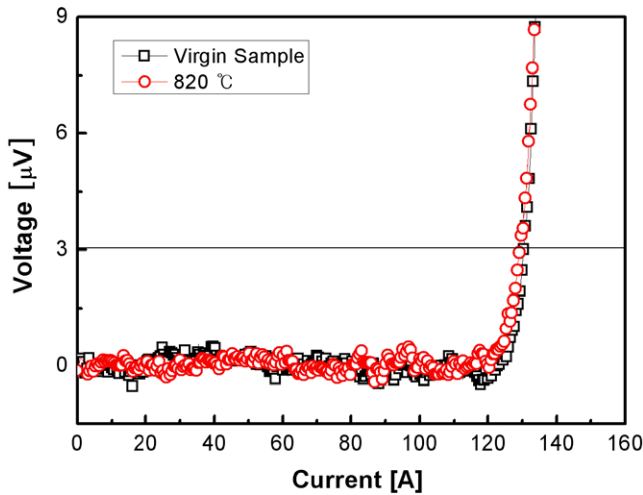


Figure 11. V – I curves of the virgin sample and sample heat treated at $T_{HT1} = 820\text{ }^{\circ}\text{C}$, $T_{OA} = 600\text{ }^{\circ}\text{C}$, $t_{OA} = 15\text{ h}$.

Superconductivity Technology of the 21st Century Frontier R&D Program funded by the Ministry of Education, Science and Technology, Korea.

References

- [1] Kim H S, Kwon N Y, Chang K S, Ko T K, Kim H M, Kim W S, Park C and Lee H G 2008 Joint characteristics of the YBCO coated conductor (CC) by chemical etching *IEEE Trans. Appl. Supercond.* **19** 2835–8
- [2] Park D K, Ahn M C, Kim H M, Lee H G, Chang K S, Lee S J, Yang S E and Ko T K 2007 Analysis of a joint method between superconducting YBCO coated conductors *IEEE Trans. Appl. Supercond.* **17** 3266–9
- [3] Chang K S, Kim H K, Park D K, Ko T K, Ahn M C, Ha D H, Song J B, Lee S J, Kim H M and Lee H G 2008 Joint characteristics of YBCO coated conductor by removing a metallic stabilizer *IEEE Trans. Appl. Supercond.* **18** 1220–3
- [4] Kato J Y, Sakai N, Tajima S, Miyata S, Konishi M, Yamada Y, Chikumoto N, Nakao K, Izumi T and Shiohara Y 2006 Diffusion joint of YBCO coated conductors using stabilizing silver layers *Physica C* **445–8** 686–8
- [5] Masuda Y, Matsubara K, Ogawa R and Kawate Y 1992 Production of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thick films on Ag metal substrate controlled by oxygen *Japan. J. Appl. Phys.* **31** 2709–15
- [6] Chen N, Shi D and Goretta K C 1989 Influence of oxygen concentration on processing $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ *J. Appl. Phys.* **66** 2485–8
- [7] Kim J H and Lee H G 2008 Oxygen out-diffusion in partially melted $\text{YBa}_2\text{Cu}_3\text{O}_{y-0.325}\text{Ag}$ superconductor at reduced oxygen partial pressure *Met. Mater. Int.* **14** 673–8
- [8] Fischer K, Chebotaev N M and Naumov S 1993 Isothermal crystal growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ in BaO – CuO – $\text{CuO}_{0.5}$ flux melts at reduced oxygen partial pressures *J. Cryst. Growth* **132** 444–50
- [9] Feenstra R, Lindemer T B, Budai J D and Galloway M D 1991 Effect of oxygen partial pressure on the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin films by post-deposition annealing *J. Appl. Phys.* **69** 6569–85
- [10] Sinha S N and Lee H G 1993 Bulk $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ –Ag superconductor via synthesized precursor containing $\text{BaCuO}_{2.5}$ *IEEE Trans. Appl. Supercond.* **3** 1161–4
- [11] Park H W and Lee H G 2001 Synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_y$ superconductors via attrition-milled intermediate oxide precursor containing $\text{BaCuO}_{2.5}$ *Met. Mater. Int.* **7** 269–79
- [12] Lee H G, Park H W and Lee D Y 2000 Synthesis of yttrium barium copper oxide–0.325Ag superconductors via intermediate precursor with overall composition $\text{Y}:\text{Ba}:\text{Cu}:\text{O} = 1:2:3:y$, $y > 7$ produced by high-energy attrition milling *Met. Mater.* **6** 473–89
- [13] Lee H G and Sinha S N 1994 Synthesis of melted $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ –0.325Ag superconductor contained in solid silver via synthesized precursor containing $\text{BaCuO}_{2.5}$ *Physica C* **231** 50–62
- [14] Lee H G and Park H W 2003 Synthesis of melted yttrium barium copper oxide–0.325Ag superconductors contained in a solid silver cladding at reduced oxygen partial pressures *Japan. J. Appl. Phys.* **42** 6841–7
- [15] Manthiram A, Swinnea J S, Sui Z T, Steinfink H and Goodenough J B 1987 The influence of oxygen variation on the crystal structure and phase composition of the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ *J. Am. Chem. Soc.* **109** 6667–9
- [16] Eatough M O, Ginley D S, Morosin B and Venturini E L 1987 Orthorhombic–tetragonal phase transition in high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ *Appl. Phys. Lett.* **51** 367–8
- [17] Freitas P P and Plaskett T S 1987 High-temperature order–disorder phase transition in the superconductor $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6+\delta}$ observed by electrical resistivity measurements *Phys. Rev. B* **36** 5723–6
- [18] Specht E D, Sparks C J, Dhere A G, Brynstad J, Cavin O B and Kroeger D M 1988 Effect of oxygen pressure on the orthorhombic–tetragonal transition in the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_x$ *Phys. Rev. B* **37** 7426–34
- [19] Ekin J W, Clickner C C, Russek S E and Sanders S C 1995 Oxygen annealing of *ex situ* YBCO/Ag thin-film interfaces *IEEE Trans. Appl. Supercond.* **5** 2400–3
- [20] Kwon N Y, Kim H S, Kim K L, Yim S W, Kim H-R, Hyun O-B, Kim H M and Lee H G 2009 Influence of stabilizer thickness on over-current test of YBCO-coated conductors *Supercond. Sci. Technol.* **22** 045003