

Effects of carbon nanotube addition on superconductivity in Y-Ba-Cu-O bulk superconductors

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Abstract. Bulk Y-Ba-Cu-O superconductors have significant potential for engineering applications due to high critical current density, which is attributed to the presence of pinning centers such as Y_2BaCuO_5 . The introduction of nano-sized secondary phase is known to act as more effective pinning center than those in micron sizes. The diameter of carbon nanotube (CNT) is close to that of the coherence length of high-temperature superconductors, which is expected to improve the flux pinning performance. We have investigated the effects of CNT addition on the microstructure, superconducting transition temperature (T_c), and critical current density (J_c) of $\text{YBa}_2\text{Cu}_3\text{O}_x$ (Y123) based bulk superconductors. SEM observation showed the distribution of needle-like particles around 100 nm in length in the Y123 matrix for the CNT added samples. The highly porous texture was also observed for the excess addition of CNT. T_c was enhanced from 90.5 K to 91.8 K with increasing CNT addition. It is probable that carbon originated from CNT suppressed oxidation and carrier doping. J_c exhibited the highest value for 0.25 wt% CNT added sample. This suggests that nano-sized needle-like particles act as effective pinning centers. However, a further increase of CNT led to the decline of J_c , which suggests that there is an optimum amount of CNT for the improvement of J_c . The secondary peak was observed for the sample with 1 wt% CNT addition, where CO_3 substitutions with Cu site at the Cu-O chain might induce oxygen vacancies leading to the field induced pinning.

1. Introduction

Melt-processed Y-Ba-Cu-O superconductors have significant potential for engineering applications due to high critical current density (J_c) and high trapped magnetic fields, which is attributed to the presence of the pinning centers such as the micro-sized secondary phase Y_2BaCuO_5 (Y211) in the $\text{YBa}_2\text{Cu}_3\text{O}_x$ (Y123) matrix. It is known that J_c values are inversely proportional to the size of pinning centers. Nano-sized secondary particles are known to be more effective as the pinning center than those in micron sizes. It has been reported that J_c values were enhanced with the addition of nano-sized secondary phases such as ZrO_2 [1], Nb_2O_5 [2], TiO_2 [3], and $\text{Y}_2\text{Ba}_4\text{CuMO}_y$ (Y-2411) ($M = \text{Nb}, \text{W}, \text{Ag}, \text{Bi}, \text{etc.}$) [4] as well as Y211 [5] into the Y123 materials.

We focus on carbon nanotube (CNT) as another candidate of nano-sized pinning centers. The diameter of CNT is close to the coherence length of the high-temperature superconductors, which may influence the flux pinning behavior. It was reported that in the Y123 polycrystals CNTs are segregated along grain boundaries, which leads to the increase in J_c [6].



We have fabricated the melt-processed Y-Ba-Cu-O bulk samples with the addition of CNT and investigated the superconductivity and microstructure in order to elucidate the effects of CNT on the pinning performance.

2. Experimental

Y123 and Y211 powders were mixed in a molar ratio of Y123:Y211 = 10:4 with the addition of 1 wt% CeO₂. The multi-wall CNT was added to the mixture and ultrasonically dispersed with an organic solvent. The amount of CNT was varied from 0 to 1 wt%. The resulting liquid mixture was then dried and uniaxially pressed into pellets. We have fabricated bulk Y-Ba-Cu-O samples with the cold seeding method. Nd-Ba-Cu-O seed crystal was placed on the top of a precursor pellet at room temperature. The typical heat schedule for growing bulk superconductors is as follows. At first, the precursor sample was heated to the maximum temperature 1040°C and held for 1 hour. After the sample was decomposed, it was cooled to the growth temperature 995°C and held for 25 hours. The melt grown samples were annealed at 400°C for 100 hours in flowing oxygen.

Microstructures were observed with a scanning electron microscope (SEM). J_c was estimated from magnetization hysteresis loops measured with a Quantum Design MPMS-XL SQUID magnetometer. The hysteresis curves were measured at 77 K. The superconducting transition temperature (T_c) was also estimated with the same SQUID magnetometer. The magnetic field was applied parallel to the c -axis.

3. Results and discussion

Figures 1 show the top surfaces of the melt-grown Y-Ba-Cu-O samples with 0, 0.25, 0.5, and 1 wt% CNT additions. A single domain was formed without spontaneous nucleation of other grains at 0, 0.25, and 0.5 wt% CNT samples. In the case of 1.0 wt% CNT-added sample, the nucleation of other grains was observed. The size of single domain becomes slightly smaller with increasing the content of CNT. This suggests that the crystal growth rate is reduced by adding CNT.

Figure 2 shows SEM photographs of the cleavage plane for bulk Y-Ba-Cu-O samples fabricated with the addition of 0.25 and 1 wt% CNT. One can observe needle-like particles with around 100 nm in length finely dispersed in the Y123 matrix. These fine particles seem to be originated from CNT since they were not observed in undoped sample. CNT raw material originally has the length of several microns. Presumably, high temperature melt process caused thermal decomposition and the fragmentation of CNT.

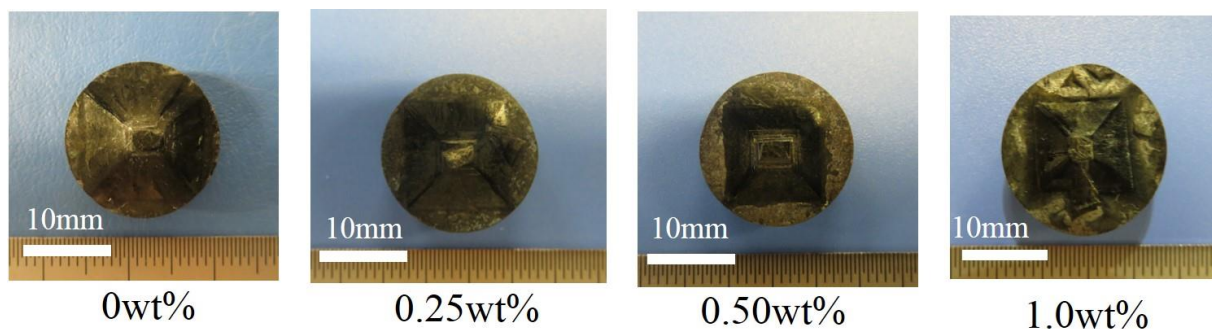


Figure 1. Top surfaces of melt-grown Y-Ba-Cu-O samples with 0, 0.25, 0.5, and 1 wt% CNT additions.

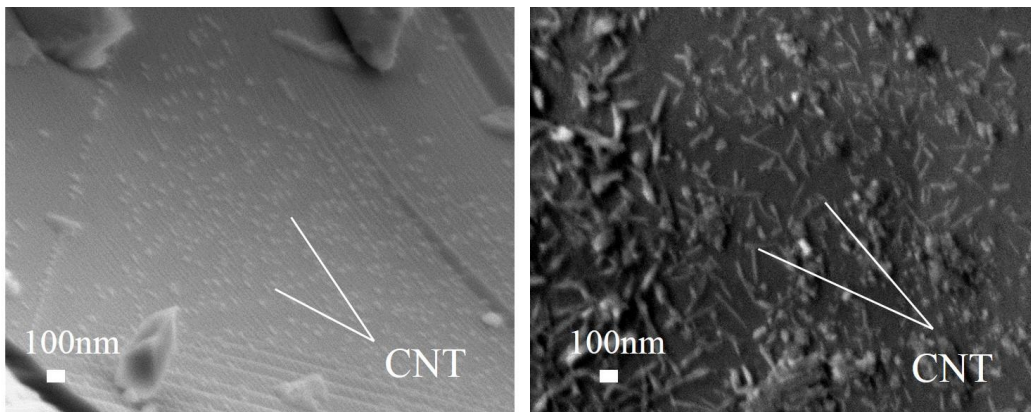


Figure 2. SEM photographs of the cleavage plane for the bulk Y-Ba-Cu-O samples fabricated with the addition of 0.25wt% (left) and 1 wt% CNT (right).

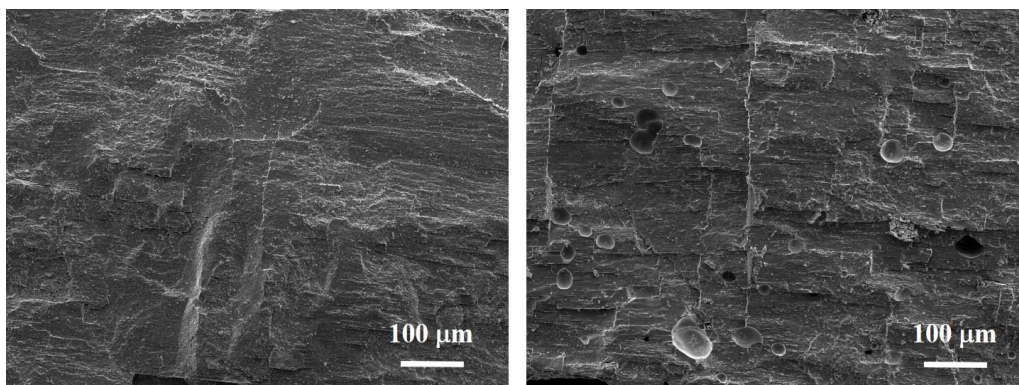


Figure 3. SEM photographs at a low magnification for the bulk samples fabricated with the addition of 0.25wt% (left) and 1 wt% CNT (right).

The fine particles are densely distributed in the central region, but their density is low in the peripheral part for the sample with 0.25 wt% CNT. On the other hand, they are distributed in the whole region for the sample with 1 wt% CNT. In local areas one can find fine particles overlapped each other and in disorder. The sample with 1 wt% CNT contains a number of particles longer than 200 nm unlike 0.25 wt% CNT sample. These results suggest that the addition of highly concentrated CNT do not inhibit the grain growth of Y123 phase and remain as CNT even after the melt-process.

Figure 3 shows SEM photographs at a low magnification for bulk samples fabricated with the additions of 0.25 and 1 wt% CNT. The voids and cracks were observed for the sample with 1 wt% CNT in contrast to 0.25 wt% CNT with relatively dense texture. Sofie *et al.* [7] reported that a bulk sample has the highly porous texture due to CO₂ gas released from BaCO₃ used as a raw material. In the present Y-Ba-Cu-O samples, similar effect might occur due to CO₂ originated from thermally decomposed CNT.

Figure 4 shows the temperature dependence of magnetization under 10 Oe for the samples with the addition from 0 to 1 wt% CNT. The sharp transitions were observed even for the CNT-added samples. T_c was enhanced from 90.5 K to 91.8 K as the addition of CNT was increased up to 1 wt%.

It is known that the oxygen annealing at 400 °C results in the overdoped state in the Y123 system [8]. Our pristine bulk samples are also considered to be overdoped. It is reported that carbon suppresses oxidation or carrier doping in the polycrystalline [9] and melt-processed samples [7, 10]. There are two possible effects of carbon on oxidation. One is that the diffusion of oxygen is prevented by carbon at grain boundaries. The other is that the substitution of CO₃ group with Cu site at the Cu-O chain reduces the oxygen content. Such substitution is revealed by the structure analysis of the neutron powder diffraction for carbon-doped YBa₂Cu_{2.85} (CO₃)_{0.15}O_{6.73} phase [11]. Although the correlation between oxygen (or carrier) and carbon has not been clarified, the thermal equilibrium state of oxygen content might be affected by the modification of crystal structure due to the incorporated carbon. Nakashima *et al.* [10] have reported that the carrier concentration decreases with increasing carbon content from the results of thermoelectric power measurements for several samples annealed at the same temperature of 400°C. Yamamoto *et al.* [9] have performed the quantitative analysis of oxygen and carbon, and found that an increase in carbon concentration leads to a decrease of oxygen content. They also found that a degree of oxygen deficiency increased for the sample containing carbon from the measurements of the zero-field Cu nuclear quadrupole resonance (NQR) spectra, and discussed that a part of chain site oxygen is pushed out together with Cu, since CO₃ group is located at the Cu chain site.

Reducing carbon by the optimization of calcination and synthesis condition or the use of BaO₂ instead of BaCO₃ as a raw material leads to the promotion of oxidation and thereby overdoping [9, 10]. In the present case, the carrier concentration might be decreased from the overdoped to the optimum doped region with the suppression of oxidation due to partial carbon decomposition from CNT.

The magnetic field dependence of J_c at 77 K are shown in figure 5 for the samples with 0 - 1 wt% CNT additions. J_c is enhanced with the addition of CNT in relatively low magnetic fields. The sample with 0.25 wt% CNT addition exhibited the highest J_c value of about 50000 A/cm² in self field. This suggests that nano-sized needle-like particles are active as pinning centers. However, a further increase of CNT led to the decline of J_c .

It is reported that the highly porous texture due to CO₂ gas released from BaCO₃ results in the decrease of J_c [7]. In our highly CNT-concentrated sample, the porous texture is observed as shown in figure 3. This can be considered as one of the causes for degraded J_c . Another possible cause is the reduction of the superconducting Y123 matrix with increasing the amount of second phase impurities. The area of Y123 matrix is reduced with increasing CNT as shown in figure 2, which might lead to the decline of J_c .

The secondary peak was observed for the sample with 1 wt% CNT addition. Sofie *et al.* [7] have observed the peak effect for the samples with more than 0.8 wt% carbon, but not with 0.475 wt% carbon, and discussed this phenomenon as follows. Y_nBa_{2n}Cu_{3n-1}CO₃O_{7n-1} type oxycarbonate is formed due to CO₃ substitutions with Cu site at the Cu-O chain. This induces oxygen vacancies, which cause the field induced pinning and thus the secondary peak effect [12]. A similar effect might occur for our samples, although a further study will be necessary for the clarification.

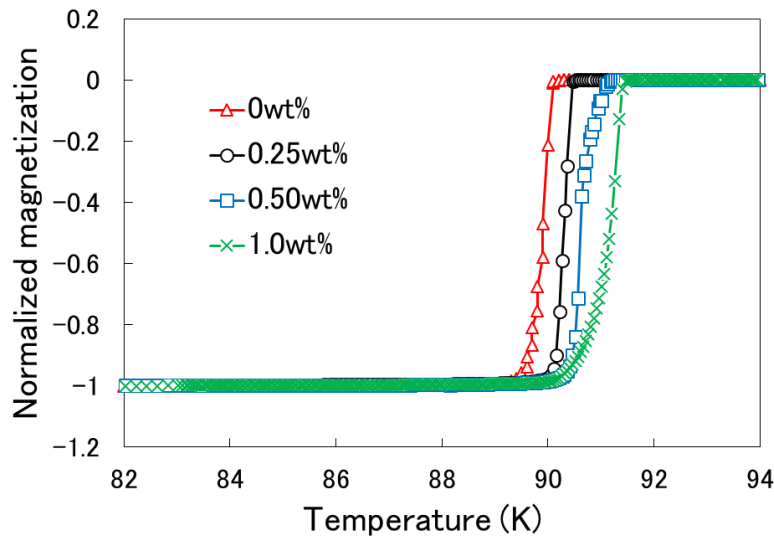


Figure 4. Temperature dependence of magnetization for Y-Ba-Cu-O samples with 0 - 1 wt% CNT additions in the presence of magnetic field of 10 Oe.

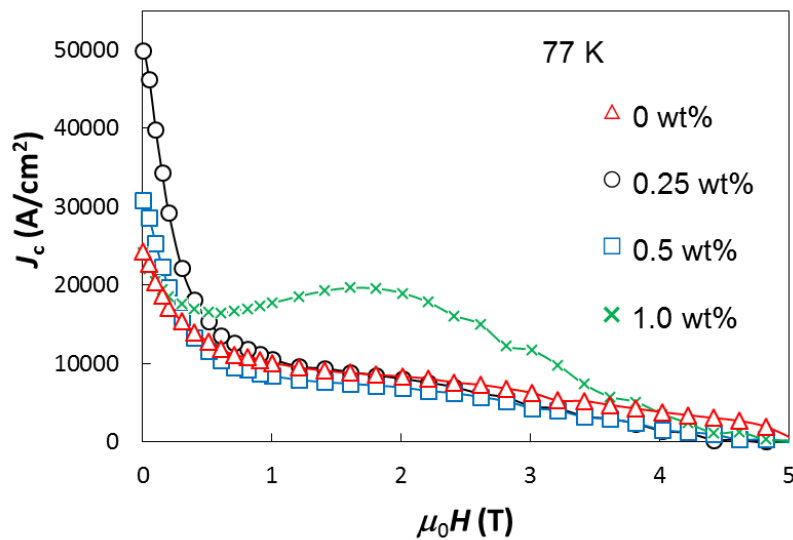


Figure 5. Magnetic field dependence of J_c at 77 K for the samples with the addition between 0 and 1 wt% CNT.

4. Summary

We have investigated the effects of CNT addition on the microstructure and pinning performance in bulk Y-Ba-Cu-O superconductors. It was observed that needle-like particles with around 100 nm in length were distributed in the Y123 matrix. These needle-like particles seem to be originated from CNT. The bulk samples have the highly porous texture for the excess addition of CNT. T_c was increased by 1.3 K with adding CNT. The carrier concentration might be decreased from the overdoped to the optimum doped region by the suppression of oxidation due to carbon decomposition

from CNT. The sample with 0.25 wt% CNT addition exhibited the highest J_c value of about 50000 A/cm² in self field, which is twice as large as that for the undoped sample. This suggests that nano-sized needle-like particles are effective pinning centers. However, a further increase of CNT led to the decrease of J_c because of the increase of the defects and the decrease of Y123 matrix area. The optimum amount of CNT is considered to be around 0.25 wt% for the improvement of J_c .

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