# 부가적인 Annealing이 Josephson weak-links를 통하여 Ceramic 고온초전도체 $YBa_2Cu_3O_{7-\delta}$ 에 미치는 영향

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# Effects of Additional Annealings via Josephson Weak-links on the Electrical Properties of Ceramic $YBa_2Cu_3O_{7-\delta}$

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Single-phase $YBa_2Cu_3O_{7-\delta}$ (YBC) ceramic samples were annealed at 700 °C under a flowing $O_2$ atmosphere for 0, 18, 36, 54 and 72 hours after sintering. The resistivities(ρ) and the critical current densities($J_c$) of the samples were measured in a temperature range 77 to 300 K by a four probe method, using silver paint contacts. The variations of the electrical properties with annealing time are explained in terms of flux pinning, percolation probability and randomness, and alignment of grains and twins. The anomalous increases in $J_c$ and $T_c$ observed in sample annealed for a relatively long time possibly due to alignment of grains and twins, may imply the occurrence of superconducting glass state in high-$T_c$ superconducting ceramic.

## INTRODUCTION

Among the characteristic features of the high-$T_c$ superconductors(HTS), a percolative mechanism through the internal junctions seems to be responsible for their electrical and magnetic properties, due to the granularity and the inherent presence of twins, although it is not related to the nature of the occurrence of the superconductivity.

According as the argument of Deutscher et al.[1], the randomness of the grain sizes in granular superconductors leads to different intergranular coupling strengths, affecting the percolation threshold and probability and resulting in a anomalous difference between the superconducting transition temperature($T_c$) in specific heat and that in electrical resistivity. Rosenblatt et al.[2] discussed the similarity in diamagnetic response of $YBa_2Cu_3O$ (YBC) ceramic to that of Nb grains + epoxy composite, and ascribed it to a 3-D random network of Josephson junctions in YBC ceramic.

Besides the contribution of intergranular couplings to the electrical and magnetic properties of HTS, intragranular couplings through twinboundaries are believed to play an important role to them. Muller et al.[3] suggested a superconducting glass state in HTS which consists of a network of isolated physical superconducting grains through intragranular weak links.[4] Giovannella et al.[5] and Barbara et al.[6] observed the changes in the magnetization and in the ac susceptibility due to the presence of the grainboundaries and twinboundaries, respectively. Rosenblatt et al.[2] predicted the fittness of ordered X-Y model to the ceramic if the twinboundary plays a role of a tunnelling barrier, because of more uniformity in the coupling energy across the twinboundaries than intergranular junctions.

Another important parameter affecting the properties will be the microstructure in the ceramic HTC. Microstructural defects are expected to play a role of pinning points against Lorentz force responsible for the motion of damped vortices. It is expected, thus, that the $J_c$ and magnetic hysteresis increase with increasing pinning strength. In single-phase YBC ceramic samples, Ourmazd et al.[7] reported a hierarchy of pinning strengths of various defects, that is cavities, grainboundaries and twinboundaries in its decrearing order. In addition to those defects, however, it is expected that a strain field resulting from the tetragonal to orthorhombic structural transition plays a role of pinning site, as observed in usual hard superconductors[8].

In this paper, the effects of additional annealings on the electrical properties of HTS ceramic, such as variations of resistivity, $T_c$, superconducting transition width( $T_c$) and $J_c$ as a function of temperature, are investigated. Our results are different from those of Penson et al.[9] Our results, however, are well explained qualitatively in terms of percolation probability and randomness, flux pinning and alignment of grains and twins in a frame of a network of random Josephson junction arrays.

## EXPERIMENTS

6 different samples were made by the conventional powder method. After grinding and mixing powder reagents of $Y_2O_3$, $BaCO_3$, and CuO(asll 99.999%, CERAC) at a stoichiometric ratio 1:2:3, the mixture was pelleted as circular-disc shape at 1.96 x $10^8 N/m^2$ . The disks were calcined at 930 °C for 24 hours in a flowing $O_2$ atmosphere. Then after being ground and pelleted as circular disks with diameter 1.905cm at 2.45 x $10^8 Nm^2$ (except sample no. 54a pelleted at 1.96 x $10^8 N/m^2$ ), the disks were sintered at 950 °C for 12 hours in a flowing $O_2$ atmosphere and cooled to 500 °C at a rate of 2 °C/min, then furnace-coold for 2 hours. 5 disks were heated at an average rate of 5.8 °C/min to 700 °C, hold for 18 hours in a flowing $O_2$ atmosphere, cooled to 497.°C at a rate of 1.7 °C/min, and furnace-cooled to room temperature. The same annealing processes were repeated subsequently with taking one sample each cycle until the last sample had total annealing time of 72 hours. Samples nos. 52, 53, 54b, 55 and 56 correspond to the samples with total annealing time 0, 18, 36, 54 and 72 hours. The samples were cut to dimensions approximately 3 x 3 x 10 $mm^2$ for electrical measurements.

The resistance and $J_c$ of the samples were measured by a four probe technique, using silver paint contacts. An Oxford Instrument CF1200 cryostat, together with the intelligent temperature controller IJC40 was used to control the sample temperature from 77 to 300K. The resistance and $J_c$'s were determined by applying constant currents from 1 to 100mA from a Keithley 224C programmable current source and measuring the voltage drop in the sample with a Keithley 196 nanovolt meter. All the measurements were taken during warming after cooling to liquid nitrogen temperature. In those measurements, special caution was given to distinguish the thermal effect from the contact junction from the voltage drop caused by the destruction of the superconducting state. The resolution limit was $10^{-6}\Omega$.

## RESULTS

As-made samples showed to have a superconducting volume more than 95% as determined by x-ray diffraction method[10]. The variations of $T_{co}$ and $T_{cf}$, a temperature at which $\rho$ = 0 in the resolution limit, with respect to annealing time are plotted in Fig.1. The $T_{co}$ of sample no. 54a is same as that of sample no.54. Fig.2 shows the change of electrical resistivities at 275K, 100K and $T_{co}$ with annealing time, The highest $T_{co}$ was observed in the samples annealed for 18 and 72 hours. The

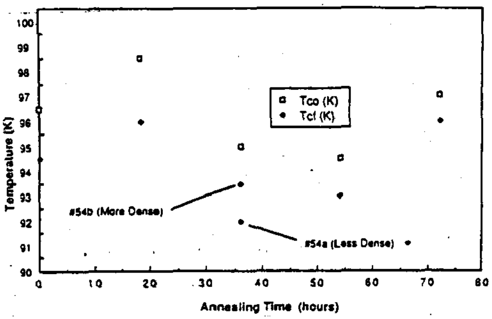


**Fig. 1. Variation of superconducting transition onset ($T_{CO}$) and finishing temperatures with respect to annealing time.**

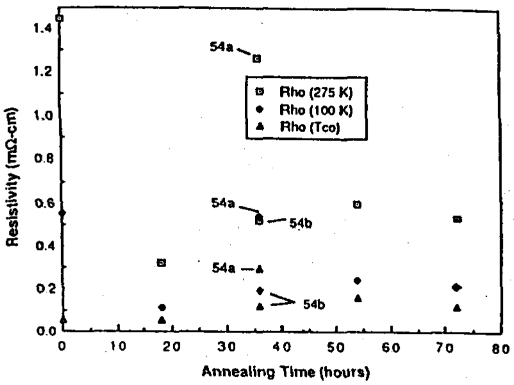


**Fig. 2. Variation of resistivities (Rho = ρ) at 275 K, 100 K and $T_{CO}$ with respect to annealing time.**

sharpest transition, however, was observed in the sample annealed for 72 hours. The lowest $T_{cf}$ and the highest $\rho$ was observed in the sample with the low pelleting pressure and the annealing time of 36 hours.

Fig. 3 shows the change of $J_c$ with respect to annealing time as a function of temperature near the $T_c$. The $J_c$ was decreased with increasing annealing time up to 36 hours, and

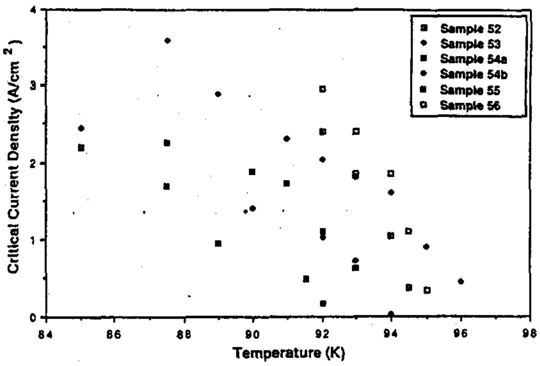


**Fig. 3. Variation of critical current density, as a function of temperature, with respect to annealing time**

then increased with further increase in annealing time. The largest $dJ_c/dT$ near $T_c$ is seen in the sample annealed for 72 hours. The smallest slope is seen in the sample pelleted at low pressure and annealed for 36 hours.

DISCUSSIONS

It was reported that the highest $T_c$ and $\rho$ are observed at $\delta$ =0[11] and there exists a significant non-uniformity of oxygen contents due to an oxygen disordering mainly at : (1/2, 0, 0) and (0, 1/2, 0) sites of the crystal structure, resulting inherently from the tetragonal to orthorhombic transition[11,12]. Thus the highest $T_c$ at the sample annealed for 18 hours is attributed to an increase in temperature at which the coupling probability through the intergranular junctions is equal to a percolation threshold, due to the increases in oxygen content and its uniformity and the reduction of the defect density such as shear strain field expecially near grainboundaries during the 18 hour annealing process.

The further prolonged annealing time is expected to result in a reduced percolation randomness through a spheroidization process of the grains and a reduced defect density. These effects are confirmed by the fact that $\Delta T_c$ decreases with increasing annealing time in a range of 18 to 54 hours.

When the $J_c$'s in Fig.3 were plotted as a function of $T/T_c$ with $T_c$ taken by extrapolating the $J_c$vs. T curve to $J_c$ = 0, they followed near $T_c$ alaw of $J_c(T) = J_0(1-T/T_c)$, where $J_0$ is $J_c$ at T = 0, which is characteristic of a S-I-S Josephson junction[13]. This $1-T/T_c$ dependence of $J_c$ is different from $(1-T/T_c)^2$ expected through a depressed order parameter at the S-I interface in the argument of superconducting glass state due to very small, coherence length [14,15] indicating that the observed temperature dependence of $J_c$ is from the contribution of intergranular junctions. The corresponding $J_0$'s are 73.8± 0.2, 33.5± 0.5, 23.8± 0.2, 27.6± 0.7 and 80.6± 0.2 $A/cm^2$ for the samples annealed for 0, 18, 36, 54 and 72 hours, respectively. These values are within the range(15 to 150 $A/cm^2$ ) of $J_0$ obtained by Senoussi et al. under the assumption of Bean's model in magnetization.

In the samples annealed for more than 18 hours, the extrapolated $J_0$'s are expected to be ones obtained through a competition between two contributions, which are an increase in J* due to the decrease in the percolation randomness and a decrease due to the decrease in the defect density. Thus, up to the annealing time of 36 hours, the contribution of the reduced defect density to $J_0$ seems to be predominant rather than that of the decreased randomness. The increase in $J_0$ obtained in the sample nos. 55 and 56, however, can be explained by an infer that annealing for a long time results in an alignment of the grains and twins. Morgenstern et al.[16] predicted in an argument of superconducting glass model in HYS ceramic that 3-D coupling through an alignment of grains and twins will increases the $T_c$ and $J_c$. Thus, the increases in $T_c$ and $J_c$ may imply a crossover in the coupling dimensionality from a 2-D to a 3-D regime by the alignment of grains and twins, and may be a evidence of the occurrence of the superconducting glass state in HTS ceramic. Note that the increase in $J_0$ occurred earlier than that in $T_c$.

The low $T_{cf}$, normal-state conductivity and $J_c$ observed in sample no.54a, compared to those in sample no.54b, are attributed to relatively low coupling energy resulting from lower pelleting pressure. The details about effects of randomness of grain sized on the electrical and magnetic properties are restricted by a lack of the data from magnetization measurements and microstructural studies.

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