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Preparation of Superconducting $YBa_2Cu_3O_{7-\delta}$ Thin Films by the Dipping-Pyrolysis Process Using Organic Acid Salts

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Thin films of the superconductor $YBa_2Cu_3O_{7-\delta}$ (YBCO) were prepared on yttria stabilized zirconia (YSZ) substrates by the dipping-pyrolysis process. The starting solution, produced by dissolving barium and copper naphthenates and yttrium stearate into an organic solvent, was coated on the substrates and heated up to 800 °C. Resistivities of the films were measured by the four probe method and superconduction was observed at T_c = 90 K (onset) and 60 K (end).

Currently, the layered-structure perovskites such as YBCO[1)] have received a great deal of attention as high T_c superconducting oxides. The fabrication processes of these materials for thin films or wires have also been interested from viewpoints of the electronic devices and electric power transportation. Several studies on the preparation of $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ superconducting thin films by sputtering[2)] or screen printing[3)] have been reported by others, but those by the dipping-pyrolysis process have never been done for these oxide superconductors. This work was undertaken to prepare the superconducting thin films of YBCO by this dipping-pyrolysis process using organic acid salts.[4)]

The commercially available organic acid salts, yttrium stearate (powder), barium naphthenate (liquid), both from Soekawa Chemicals, and copper naphthenate (liquid), Nakarai Chemicals, with chemical pure grade were used as the starting materials. Thermal analysis was performed for each of the organic acid salts with an average sample weight of 100 mg and a heating rate of 100 °C/h in an air stream. The TG-DTA results showed an endotherm with a gradual weight decrease up to 200 °C and a large exotherm with rapid weight loss between 200 and 450 °C; the former is considered to be corresponding to evaporation and/or thermal decomposition of the organic acid salts, and the latter is to an oxidation of the organic component of the salts. The metal content for each of the samples calculated with the TG data was in good accord with the one obtained by chelatometry.

The superconducting YBCO films were prepared in the following way. The prescribed amounts of the organic acid salts (Y:Ba:Cu = 1:2:3 in molar ratio) were dissolved in an organic solvent.[4)] The mixed solution was coated on YSZ (10 mol% Y_2O_3) substrates, 12 mmD × 1 mmt, by dipping. After being dried in air for 0.5 - 1 h, the organic acid salt films with the substrates were heated up to 800 °C in air for 10 min. By repeating the dipping-pyrolysis procedure about 10 times, the thickness of the oxide films was adjusted to 1 - 3 µm. Finally, annealing was carried out in pure oxygen at 800 °C for 80 h. The YBCO films thus obtained were deep black in color.

According to the XRD and thermal analysis described above, the heating process is considered to take place in two stages: (i) removal of the organic components (by pyrolysis or oxidation) at 200 - 500 °C and (ii) solid state reaction of (Y_2O_3-$BaCO_3$-CuO) system at 500 - 800 °C.

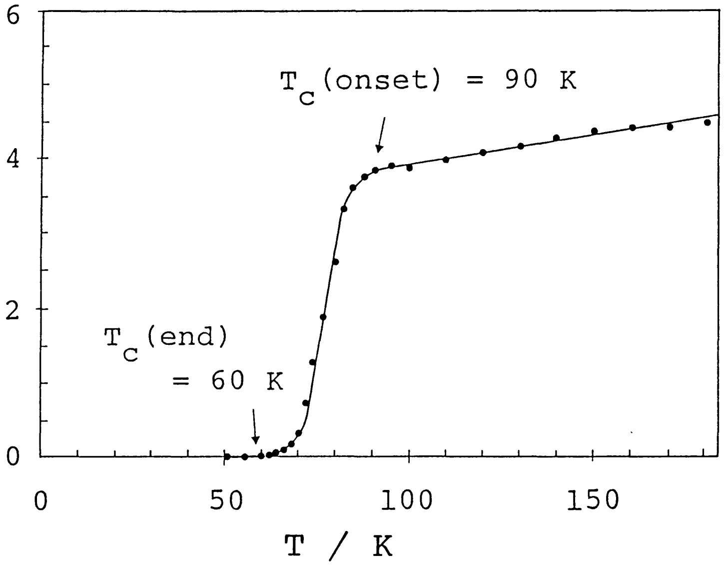

Fig. 1. Resistivity *vs.* temperature relationship for the YBCO thin film.

Resistivities of the coated films were measured in the temperature range of 290 to 10 K by the dc four probe method with point contacted gold electrodes. As Fig. 1 shows, the resistivity (ρ) of the film gradually decreased, indicating metallic behavior, followed by a sharp decrease starting at about 90 K, T_c(onset), and a complete superconduction at 60 K, T_c(end), with an electric current of 10 µA. The value of T_c(end) was found to be greatly dependent on the annealing conditions. The specimen annealed in oxygen at 800 °C for only 2 h showed T_c(end) = 23 K. Studies on the choice of the starting materials or the optimum conditions for heat treatment are in progress.

The advantages of the dipping-pyrolysis process[5,6] are: (i) oxide films are directly formed on the substrates and no powder handling is needed, (ii) composition and texture of the films are homogeneous and easily controlled, (iii) substrates with any kind of shapes are completely coated, (iv) facility investment is small and large scale production is possible, and (v) the temperature required for the solid state reaction is much lower than that of the powder process.

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