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REACTION BETWEEN THE SUPERCONDUCTING OXIDE YBCO AND AMMONIUM BIFLUORIDE

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SUMMARY

The fluorination of YBCO with NH_5F_2 proceeded as a tarnishing reaction. The reaction at 300 °C finished in 3 h consuming quantitatively one hydrogen fluoride in NH_5F_2. Fluorine was introduced into YBCO by using NH_5F_2 less than 0.5 mole for 1.0 mole YBCO to give the orthorhombic $YBCF_xO_y$ which was not distinguished from the structure of the original YBCO. Superconducting properties of the orthorhombic $YBCF_xO_y$ were not observed above liquid nitrogen temperature. Addition of more than 0.5 mole NH_5F_2 brought about the destruction of the YBCO structure to form a passive layer on the surface of YBCO powder particles and left unreacted YBCO inside. No fluorinated product showed a superconducting transition temperature higher than the 93 ± 1 K of the original YBCO.

INTRODUCTION

It was reported that modification involving fluorination of a superconducting oxide, $YBa_2Cu_3O_{7-\delta}$, gave new materials having a noticeably high transition temperature of 155 K [1] and 148.5 K [2]. These reports motivated us to investigate a fluorine containing superconductor with an even higher transition temperature. Many groups have been attempting to reproduce the superconducting phase with Tc:155 K by solid phase preparative techniques using BaF_2, CuF_2 or lanthanide fluorides, but no group has found evidence of a higher transition temperature than 90 K. Several groups have been trying to prepare a single phase of

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fluorine containing YBCO by direct fluorination methods [3-9]. Rao et al. reported their successful attempt to prepare the single phase $YBCF_xO_y$ using ammonium bifluoride [7-9]. We have been also investigating the fluorination of YBCO by the same method, but the results were different from theirs.

In this report, we will discuss the fluorination mechanism of YBCO in the case of the contact reaction with ammonium bifluoride and effects of fluorination on the superconducting properties.

RESULTS AND DISCUSSION

Ammonium bifluoride, NH_5F_2, is well-known as a fluorinating reagent for metal oxides. NH_5F_2 is supposed to react with YBCO according to the following two reactions.

$$YBCO_{6.93} + xNH_5F_2 \longrightarrow YBCF_xO_{6.93-0.5x} + xNH_4F + 0.5xH_2O \qquad (1)$$

$$YBCO_{6.93} + 0.5xNH_5F_2 \longrightarrow YBCF_xO_{6.93-0.5x} + 0.5xNH_3 + 0.5xH_2O \qquad (2)$$

Here the formula $YBCF_xO_{6.93-0.5x}$ ($YBCF_xO_y$) expresses nominal composition in a solid product even if it consists of several phases. Fig.1 shows the relationship between the weight decrease for the fluorination and the nominal fluorine composition of the products. All measured weight decreases agreed well with theory calculated from reaction(1). It means that the fluorination at 300 °C under an oxygen flow finishes in 3 h, consuming quantitatively one hydrogen fluoride in NH_5F_2. The fluorine composition, x in $YBCF_xO_y$ was therefore calculated from the weight decrease according to reaction (1). The x-values were confirmed by fluorescent X-ray analysis. Fig.2 shows the XRD profiles for the products with various fluorine compositions in $YBCF_xO_y$. For products with x-values up to 0.5, XRD profiles were not distinguished from that of the original YBCO. When the products were allowed to stand above 400 °C, they converted into a multiphase one containing barium fluoride as shown by the profile No.3. This fact convinced us that fluorine was introduced into the YBCO crystal lattice. When the x-value exceeded 0.5, new broad and small peaks(○) appeared at $2\theta = 26.3°$,

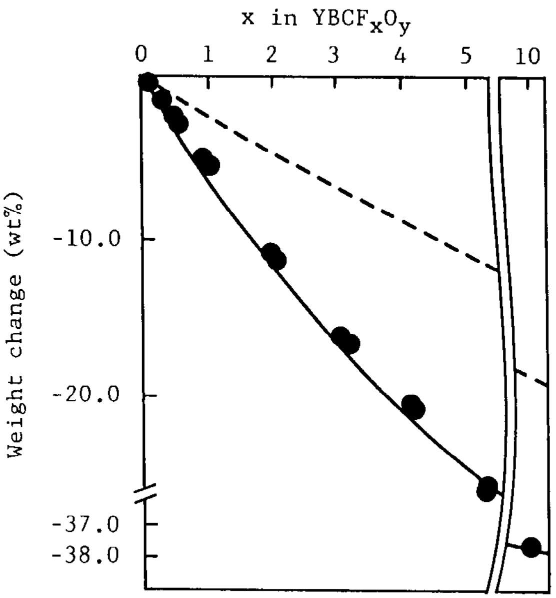

Fig.1. Relationship between the weight change and x-value in $YBCF_xO_y$

Reaction; YBCO + $NH_5F_2 \longrightarrow$

——— : $YBCF_xO_y + xNH_4F + 0.5xH_2O$,

– – – – : $YBCF_xO_y + 0.5xNH_3 + 0.5xH_2O$, (y: 6.93-0.5x)

● : Measured weight change.

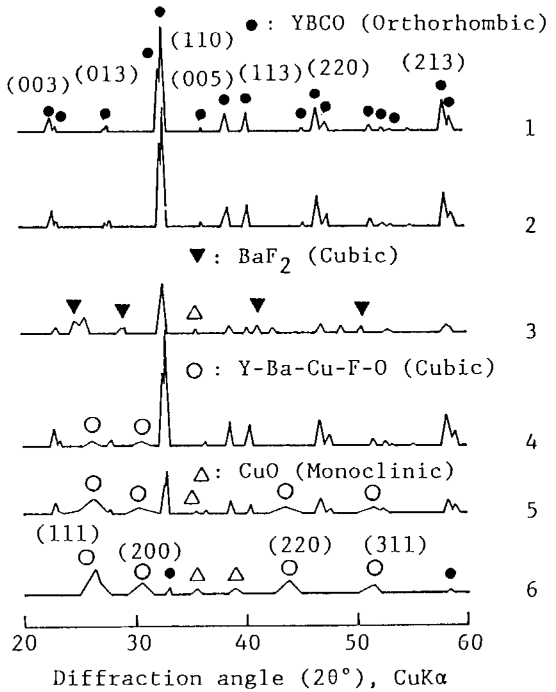

Fig.2. XRD profiles for $YBCF_xO_y$ with various values of x

x in $YBCF_xO_y$; 1 : 0.0 (Original YBCO), 2 : 0.5, 3 : After heat treatment for x=0.5, 4 : 0.9, 5 : 5.3, 6 : 10.1.

30.5°, 43.7° and 51.6°. These became major peaks in the profile of x=10.1 and could be assigned to a cubic structure with the lattice constant a_o; 5.9 Å. This compound seemed to be a Y-Ba-Cu ternary fluoride oxide from ESCA. Diffraction peaks(●) for the orthorhombic structure due to the unreacted YBCO became weaker with increase in x. No transformation of the structure of YBCO was observed in XRD patterns. This is in contrast to the result which we have already reported that the crystal structure of YBCO transformed from orthorhombic into pseudo-tetragonal with a change of x from 0.5 to 1.0 in the case of the reaction between YBCO and elementary fluorine [6].

The aspects of fluorination were noticeably influenced by the activity of HF. In the case of using less than 0.5 mole of NH_5F_2 for 1.0 mole YBCO, the activity was low enough to attack labile oxygens selectively to give orthorhombic $YBCF_xO_y$ with a lattice little different from that of the original YBCO. When NH_5F_2 exceeded 0.5 mole, it seemed that the activity at the reaction grain interface became so high that HF attacked any oxygen sites in YBCO to form a passive layer consisting of copper oxide(II) and the Y-Ba-Cu fluoride oxide. This layer acts as a barrier to fluorine diffusion [10]. As a result, the original YBCO remained in the center of the particle even when fluorination proceeded until the x-value in $YBCF_xO_y$ reached 10.1. That is, the fluorination of YBCO with NH_5F_2 could be explained as a tarnishing reaction.

Next, we examined the magnetic properties of fluorinated powder samples by using the specially designed magnetic balance [6,11]. All samples showed the same on-set temperatures at 93 ± 1 K as shown in Fig.3. Even the x=10.1 sample indicated a Meissner effect due to the original YBCO still present in the particles. Fig.4 shows the relationship between the x-value and the mole fraction of superconducting phase. The fraction in fluorinated products decreased almost linearly with increase in x, although there were anomalies up to x=0.5. A sharp decline around 0.5 suggested that the formation of orthorhombic $YBCF_xO_y$ ($0<x<0.5$) depressed the superconducting transition temperature and that fluorine incorporation reached the inner part of a particle. This fact seemed to correspond to the result that the mole fraction of the superconducting phase

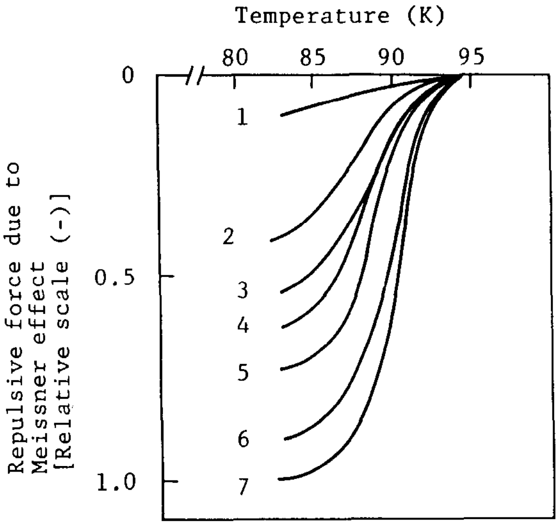

Fig.3. Temperature dependency of the magnetic repulsive force for $YBCF_xO_y$

x in $YBCF_xO_y$;
1 : 10.1, 2 : 5.3, 3 : 3.1, 4 : 0.1,
5 : 0.5, 6 : 0.9, 7 : Original YBCO.

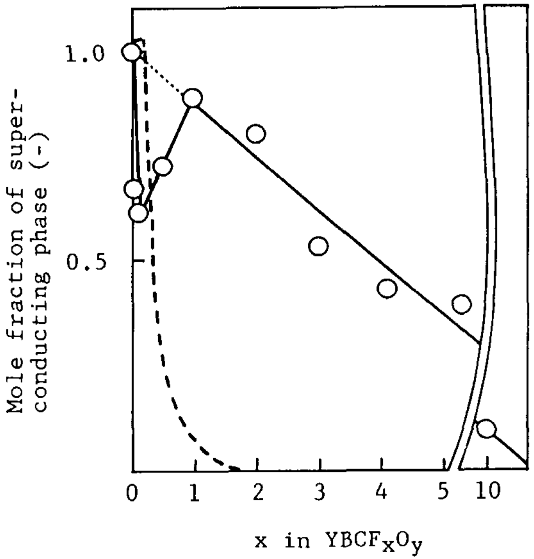

Fig.4. Mole fraction of superconducting phase in $YBCF_xO_y$ measured at 85K

Formation reaction;
—— : YBCO + NH_5F_2, - - - : YBCO + F_2.

reduced drastically after $x=0.5$ when using elementary fluorine as shown by the dashed line in Fig.4.

Fig.5 shows the electrical resistivities measured at every 30 μm from the surface of fluorinated sintered sample. Fig.6 shows the x-value in $YBCF_xO_y$ at each position measured by means of fluorescent X-ray analysis. At the 30 μm position where the x-value was around 8.00, the resistivity was above 10^7 ohm•cm and too high to be measured exactly. Chemical constituents at this position were determined by X-ray diffraction to be copper oxide (II) and the ternary fluoride oxide with a cubic structure. At the position of 100 μm where the x-value was around 1.00, the resistivity showed a semiconducting behavior. At positions over 100 μm where x-values were less than 0.50, the resistivity showed the on-set of a superconducting transition at 90 K, but did not become zero until 50 K. The XRD profiles at this position were similar to those of the orthorhombic YBCO structure. We also observed anomalous behavior in electrical resistivity at 35 K at the positions filed off between 30 μm and 100 μm as shown in Fig.5. It is possible to say that there were fluorine containing phases which showed the superconducting transition at lower temperatures than 90 K. However, the reproducibility and the identification of this phase are not achieved yet.

Rao et al. reported that NH_5F_2 reacted with YBCO to give $YBa_2Cu_3O_{6.5-\delta-0.5x}F_x$ $(0<x<4)$ in which fluorine was coordinated mainly around Y and Ba. This single phase compound had the same T_c as that of the original YBCO [7,9]. In our research there was no indication of their type of $YBCF_xO_y$. Instead, we obtained another kind of $YBCF_xO_y(0<x<0.5)$ in which fluorine would be coordinated around Cu in the 2nd layer of a 3-layered perovskite structure. Its superconducting transition temperature was at least below liquid nitrogen temperature. However, we do not think these two results contradict each other because these contrasts might be ascribed to differences in the reaction condition such as the temperature (327 °C : Rao et al., 300 °C in our case) and the particle sizes of YBCO and NH_5F_2. These different results imply that the reaction between YBCO and NH_5F_2 is very sensitive to the activity of HF and the O-Cu-O chain in the 2nd layer is closely related to the superconducting properties.

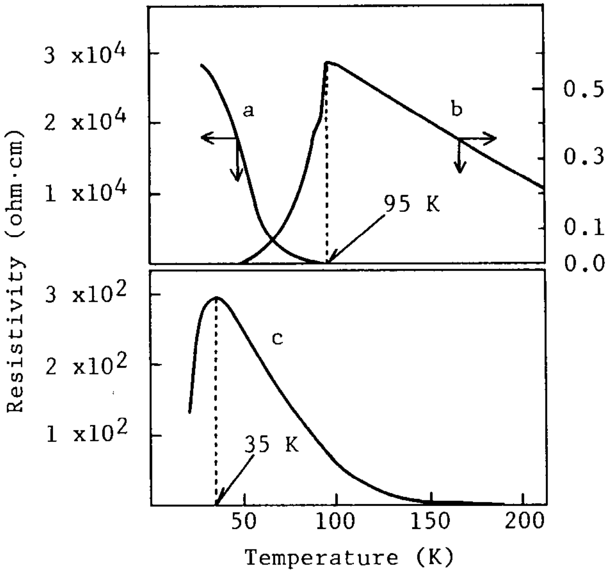

Fig.5. Temperature dependency of the resistivity measured on the surface of fluorinated sintered sample

a : The position up to 100 μm from the surface,
b : Inner position over 100 μm,
c : Special resistivity benavior measured at up to 100 μm.

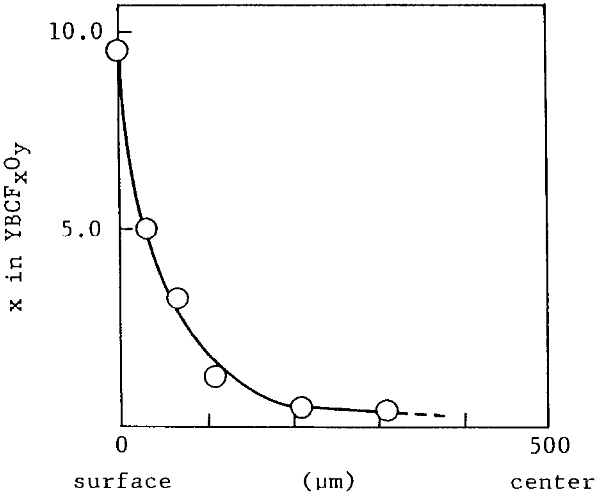

Fig.6. x-Value in YBCF$_x$O$_y$ measured at various positions for fluorinated sintered sample

To study the fluorination mechanism further, the solid-gas reaction between YBCO and HF has been investigating by means of a Chemical Vapor Transport method (CVT) using ammonium bifluoride as a HF source.

EXPERIMENTAL

Preparation and fluorination of YBCO

The superconducting oxides, $YBa_2Cu_3O_{7-\delta}$, used as a starting material was prepared by the usual method. A mixture of Y_2O_3, $BaCO_3$ and CuO (>99.99% pure.)in mole ratios 0.5:2:3 was fired at 920 °C for 6 h in dried air and then slowly cooled down to room temperature in the furnace. The oxygen composition was determined to be $YBa_2Cu_3O_{6.93}$ by iodometry [12]. The resistivity of the original YBCO showed a superconducting transition at 93 ± 1 K and became zero at 89 K. The appropriate powder mixture of YBCO (5 μm in diameter) and ammonium bifluoride was heated at 300 °C for 3 h in an oxygen flow and quenched to room temperature. The products were examined by X-ray diffraction, fluorescent X-ray analyses and ESCA to determine structure and composition.

Measurement of electrical resistivity

The electrical resistivity was measured by the d.c. standard 4-probe method in a liquid helium dewar (20 K < Temp.< r.t.). Since fluorinated powder samples could not be sintered without decomposition, samples for the resistivity measurement were prepared by the fluorination after the original YBCO was sintered into a pellet (13mm diameter). The fluorine composition was controlled by filing from the surface of a pellet sample and determined by fluorescent X-ray analysis.

Evaluation of the perfect diamagnetic transition

Magnetic properties of fluorinated powder samples were examined using the specially designed magnetic balance. This device, named Meissner Effect Evaluating Device(MEED), can detect the superconducting transition temperature at which the sample begins to receive a repulsive force against a magnetic field. The mole fraction can be also evaluated from the calibration line between the fluorine composition and the intensity of the repulsive force relative to that of the original YBCO measured at 85 K [6,11].

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