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Distributions of $Y_2Ba_1Cu_1O_5$ particles in fluorine-doped $Y_1Ba_2Cu_3O_x$ superconductors

T. HAMADA, R. MORIMO, R. OGURA
Department of Electrical Engineering, Miyakonozyo College of Technology, 473-1 Yoshio, Miyakonozyo 885, Japan

An experimental study has been carried out on the relationship between $Y_2Ba_1Cu_1O_5$ particles in $Y_1Ba_2Cu_3O_x$ superconductors and electric furnace cooling rates. As the electric furnace cooling rates decrease, the $Y_2Ba_1Cu_1O_5$ particles become uniformly disperse in fluorine-doped $Y_1Ba_2Cu_3O_x$ superconductors. However, the $Y_2Ba_1Cu_1O_5$ particles do not appear in the undoped $Y_1Ba_2Cu_3O_x$ superconductors.

1. Introduction

Much research has been carried out on oxide superconductors in various fields such as physical science [1–3], and there are many controversial issues regarding the application of the results. One such issue is the fact that oxide superconductors are very inferior to metal superconductors in critical current density [4]. Consequently, efforts have been made to continually improve the quality and the synthesis of oxide superconductors has become more important [5–7]. There are some effective methods of synthesis for oxide superconductors; for example, the quench and melt growth method, the melt powder-melt growth method and the melt textured-growth method and so on. These methods enable the required high critical current density for their application to be attained. The crystals made by these methods contain $Y_2Ba_1Cu_1O_5$ particles which act as one of the pinning centres. It is very important for a high magnetic field material such as $Y_1Ba_2Cu_3O_x$ superconductor to contain $Y_2Ba_1Cu_1O_5$ particles. Although $Y_2Ba_1Cu_1O_5$ particles are observed in crystals obtained by the quench and melt growth method, which is heat treated at temperatures above 1000 °C, the fluorine-doped superconductor has a lower reaction temperature than the undoped one [8]. In addition, fluorine-doped superconductors showed a large magnetization curve, like NbTi [9]. The present authors investigated the electromagnetic properties of fluorine-doped superconductors [10]. No crystal observation, however, was performed on the fluorine-doped superconductors. Therefore, a comparison between fluorine-doped superconductor and an undoped superconductor, in regard to the presence and activity of crystal samples obtained at a temperature below 1000 °C, is of great interest.

The purpose of this work is to illustrate the distribution of $Y_2Ba_1Cu_1O_5$ particles in fluorine-doped $Y_1Ba_2Cu_3O_x$ superconductors. The results have been compared with undoped superconductors in regard to the relationship between the distribution of $Y_2Ba_1Cu_1O_5$ particles in $Y_1Ba_2Cu_3O_x$ superconductors and electric furnace cooling rates. Because oxygen influences oxide superconductors during the reaction, the cooling rates are used some values of cooling rate in this experiment. Crystals were examined by scanning electron microscopy (SEM) on polished mirror-like surfaces, and elements were analysed using an electron probe microanalyser (EPMA).

2. Experimental procedure

The samples used in this study were $Y_1Ba_2Cu_3O_x$ and $Y_1Ba_2Cu_3F_{0.4}O_x$ superconductors. $Y_1Ba_2Cu_3O_x$ superconductor is composed of Y_2O_3, $BaCo_3$ and CuO, each with a purity of 99.99%. The fluorine-doped superconductor is composed of two master compositions, $Y_1Ba_2Cu_3O_x$ and $Y_1Ba_2Cu_3F_4O_x$. $Y_1Ba_2Cu_3F_4O_x$ is composed of Y_2O_3, BaF_2, and CuO, each with a purity of 99.99%. After being weighed and mixed, they were calcined at 900 °C for 8 h in the air and then cooled in an electric furnace to room temperature. The temperature in the electric furnace was measured using platinum thermocouples. The compound was reground using a mortar. The $Y_1Ba_2Cu_3O_x$ powder was then pressed into 15 mm diameter samples with a mould. Fluorine-doped samples were synthesized with powders of $Y_1Ba_2Cu_3O_x$ and $Y_1Ba_2Cu_3F_4O_x$ to approach $Y_1Ba_2Cu_3F_{0.4}O_x$. The fluorine ratio was selected according to the magnetization loops which exhibited maximum hysteresis loops. $Y_1Ba_2Cu_3O_x$ and $Y_1Ba_2Cu_3F_{0.4}O_x$ were sintered at a temperature of 950 °C for 2 h. They were then cooled to room temperature with cooling rates as a function of time (2, 3, 4 and 10 °C h^{-1}). These samples were then hardened with epoxy resins, and their surfaces polished to a mirror finish. Crystal observation was performed using a scanning electron microscope (SEM) and an electron probe microanalyser (EPMA).

3. Results and discussion

Fig. 1 shows scanning electron micrographs of fluorine-doped superconductors at various cooling rates (2,

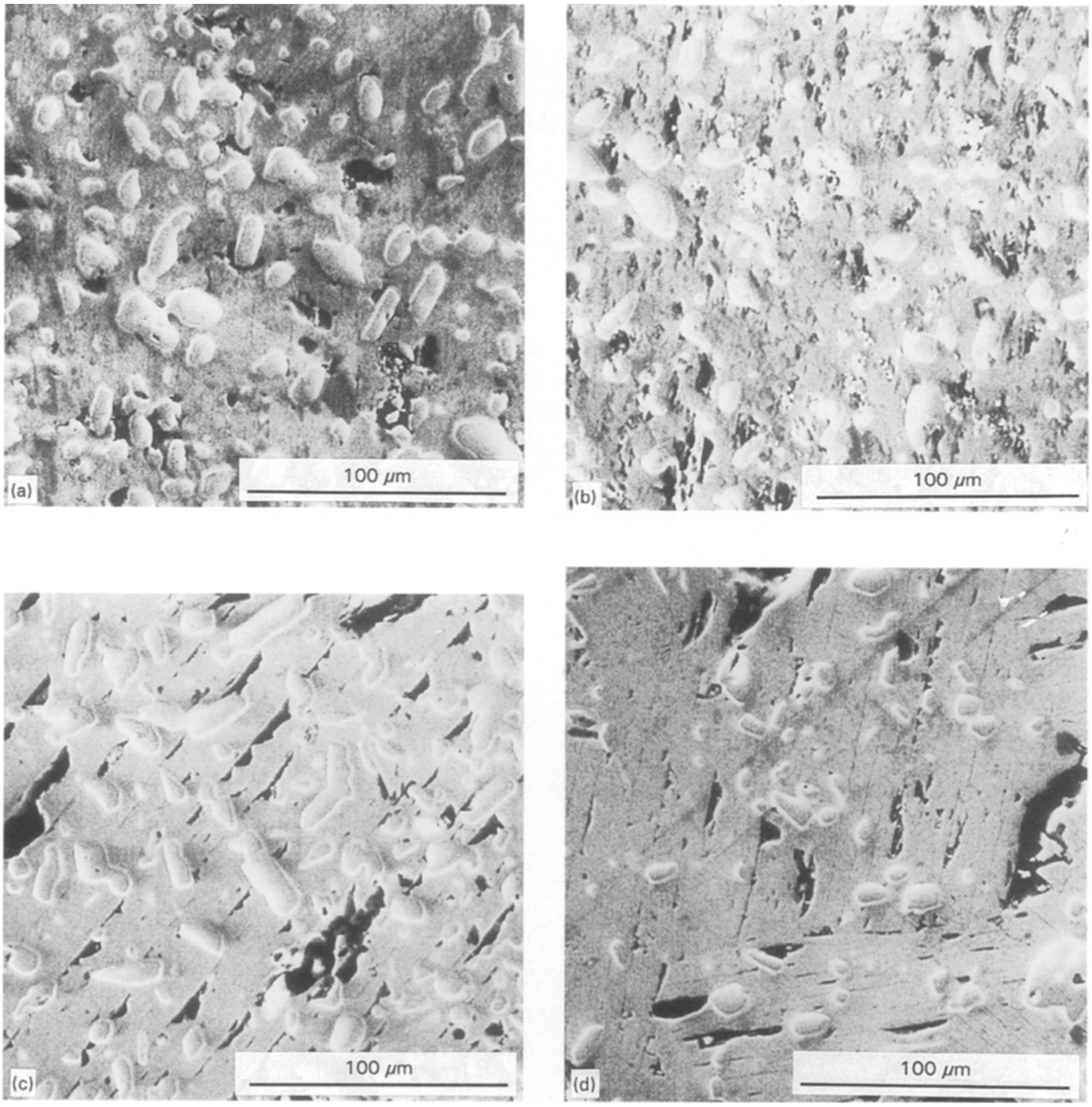

Figure 1 Scanning electron micrographs of fluorine-doped superconductors at cooling rates of (a) 2, (b) 3, (c) 4 and (d) 10 °C h^{-1}. As the cooling rates decrease, particles in the crystal are dispersed uniformly.

3, 4 and 10 °C h^{-1}). The crystals include many particles and grain boundaries. As the cooling rates decreased, the particles in the crystal were dispersed uniformly. In addition, scanning electron micrographs of samples cooled at 2 and 3 °C h^{-1} show a decrease in grain boundaries and gaps in the crystal. Fig. 2 shows the qualitative analysis of elemental yttrium, barium and copper on a fluorine-doped superconductor at a cooling rate of 2 °C h^{-1}. The particles in the crystal responded strongly to the presence of yttrium. In Fig. 3, the particles (B) and the area outside the particles (A) in the crystal were analysed by electron probe microanalysis (EPMA). The results are given in Table I. The ratio of Y:Ba:Cu:O is approximately 2:1:1:5.7. This result suggests that the particles are non-superconducting $Y_2Ba_1Cu_1O_5$ [11]. The elemental oxygen deviates from the theoretical value 2:1:1:5. The reason is thought to be the low cooling rate which results in sufficient absorption of oxygen in the crystal. The area surrounding the particles in the crystal was analysed in the same manner. The ratio of Y:Ba:Cu:O is approximately 1:2:3:8. The deviation of elemental oxygen content was also influenced by the cooling rate. Fig. 4 shows scanning electron micrographs of undoped superconductors at cooling rates of 2, 3, 4 and 10 °C h^{-1}. There are many gaps and grain boundaries in the crystal, and no $Y_2Ba_1Cu_1O_5$ particles were seen. The gaps and grain boundaries in the crystal do not depend on the cooling rates. It is considered that the undoped superconductor does not react sufficiently at the given maximum temperature. Therefore, it is necessary to use a higher treatment temperature for the undoped superconductor in order to obtain high-quality materials. On the other hand, fluorine-doped superconductors do react sufficiently at the given temperature, and include many

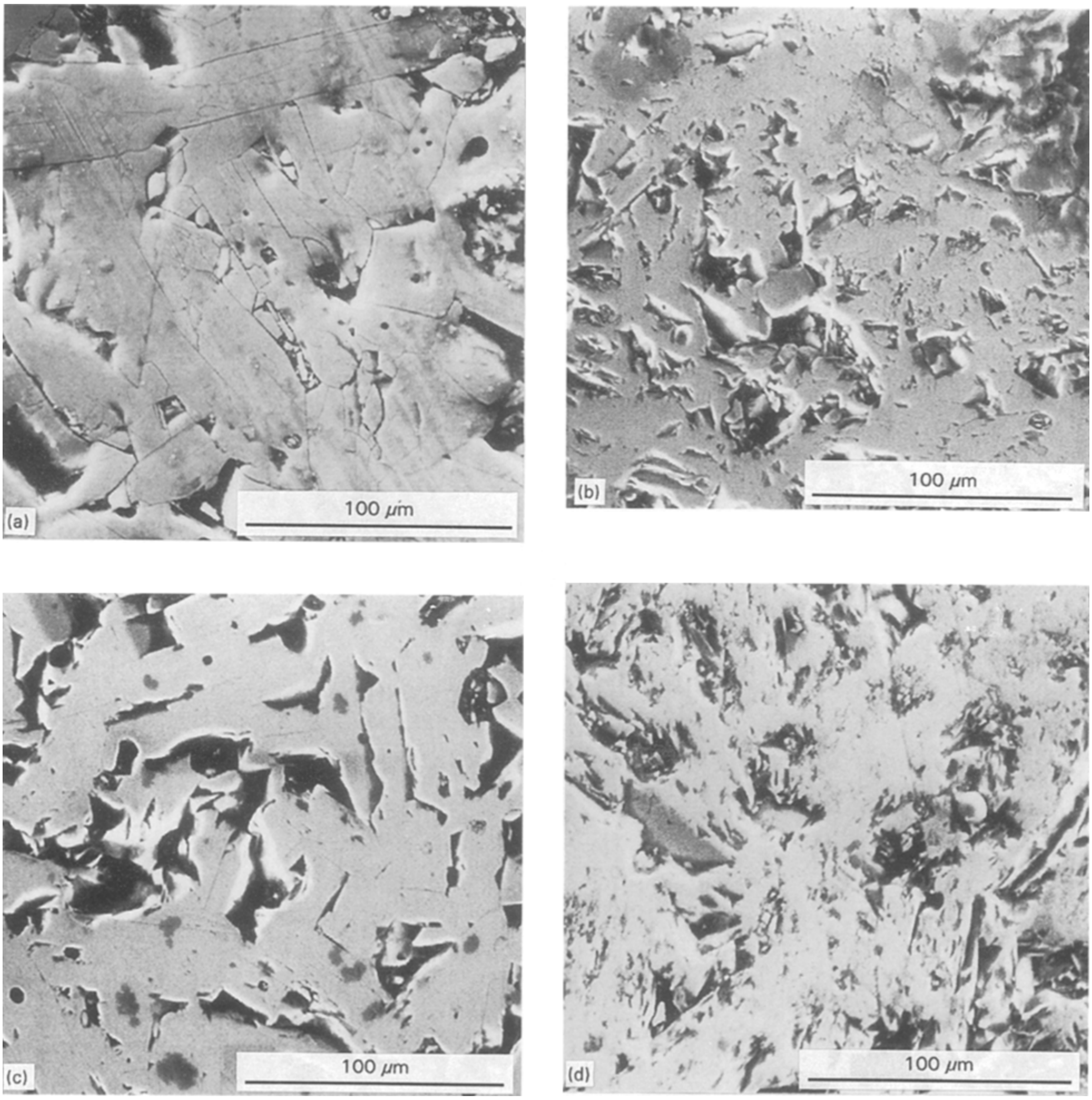

Figure 2 Scanning electron micrographs of undoped superconductors at cooling rates of (a) 2, (b) 3, (c) 4 and (d) 10 °C h^{-1}. There are many gaps and grain boundaries in the crystal, but no $Y_2Ba_1Cu_1O_5$ particles are seen.

TABLE I Quantitative analysis (%) of the fluorine-doped superconductor

	Y	Ba	Cu	O	F
Position A	20.9283	10.1971	11.3128	57.5501	0.0117
Position B	8.0444	14.3206	21.6647	55.9553	0.0150

TABLE II Fundamental data of the fluorine-doped and undoped samples (2 °C h^{-1})

	J_c (A cm^{-2}) (at 77 K and 0.2T)	T_c(K)
Fluorine-doped	6920	90
Undoped	1370	91

$Y_2Ba_1Cu_1O_5$ particles in the crystal which act as pinning centres. Therefore, the use of fluorine in the synthesis of superconductors is considered to be valuable in obtaining high critical current density. The critical current densities were measured by the Campbell method at 77 K. The results are listed in Table II. The samples measured were those coded at 2 °C h^{-1}. Therefore, the fluorine-doped sample included non-superconducting $Y_2Ba_1Cu_1O_5$ particles in the crystal. The fluorine-doped superconductor was compared with undoped superconductors with a critical current density at 77 K. The magnetic field was increased by using the copper magnet in the liquid nitrogen bath. The fluorine-doped sample exhibited a higher critical current density than for the undoped sample. That is, it is considered that the non-superconducting $Y_2Ba_1Cu_1O_5$ particles in the fluorine-doped sample act as effective pinning centres because the critical

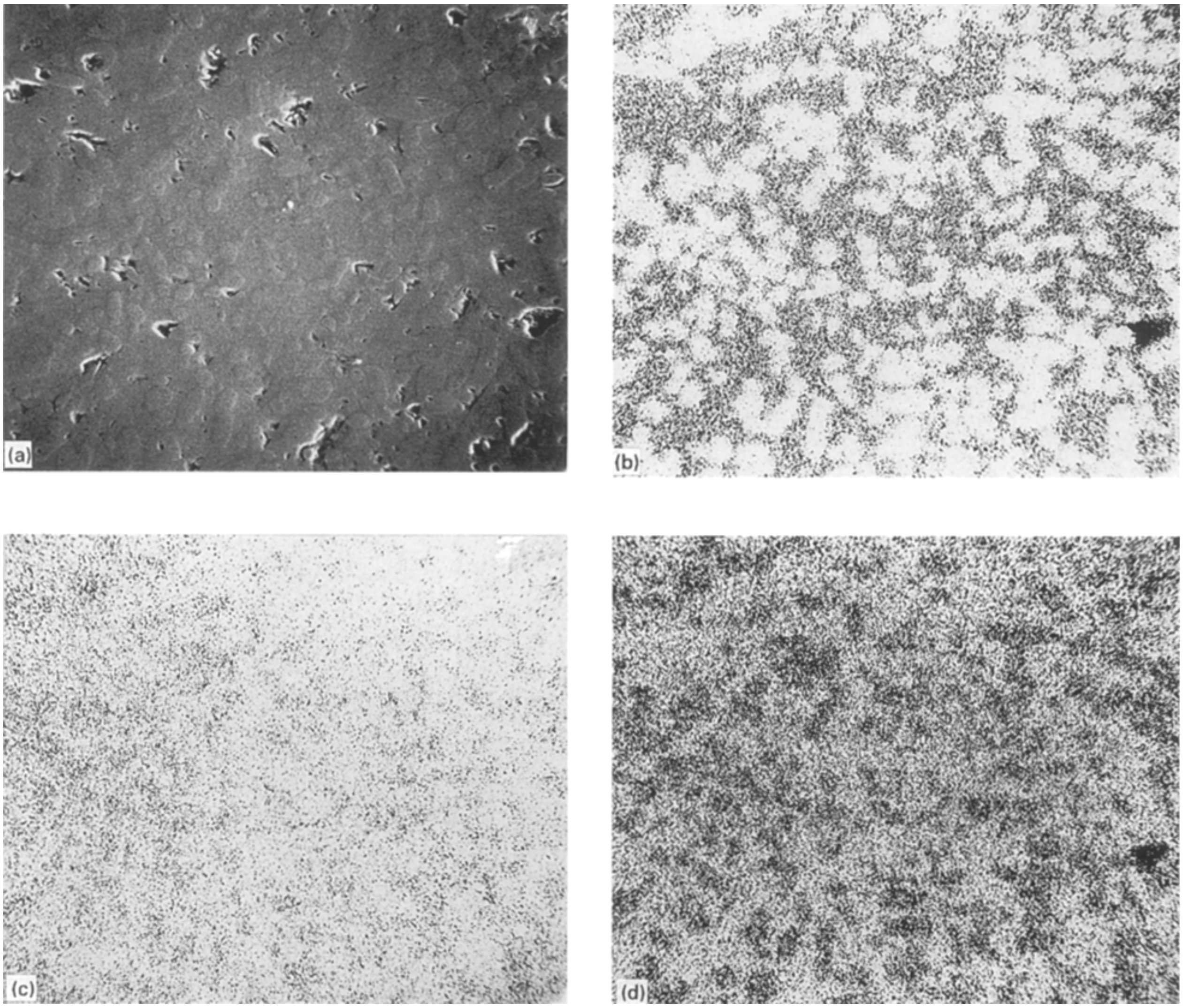

Figure 3 Qualitative analysis of fluorine-doped superconductors. Elemental yttrium barium and copper were analysed. The particles respond clearly to the presence of elemental yttrium. (a) SEM, (b) yttrium, (c) barium, (d) copper.

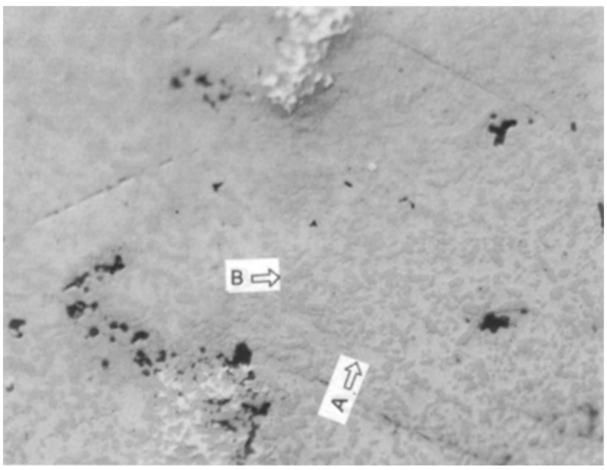

Figure 4 A scanning electron micrograph for quantitative analysis. The cooling rate was $2\,°\mathrm{C\,h^{-1}}$. The results are given in Table I.

current density is increased in comparison with undoped sample. However, the results show that the critical current density is actually inferior to the QMG sample, possibly because the non-superconducting $Y_2Ba_1Cu_1O_5$ particles in the QMG sample are finely distributed in the crystal (less than 1 μm) [12, 13], whereas in the fluorine-doped superconductor, they are distributed as large particles. Therefore, to increase the critical current density, it is necessary for non-superconducting $Y_2Ba_1Cu_1O_5$ particles to be produced in the superconducting phase for fluorine-doped superconductors without using a complicated process like the QMG method. Further study will help to clarify the production mechanism of $Y_2Ba_1Cu_1O_5$ particles using fluorine at a lower temperature than usual.

4. Conclusions

In our research on fluorine-doped $Y_1Ba_2Cu_3O_x$ superconductors and undoped superconductors, and the relationship between $Y_2Ba_1Cu_1O_5$ particles in $Y_1Ba_2Cu_3O_x$ superconductor and the electric furnace cooling rates, the following results were obtained.

1. As electric furnace cooling rates decreased, the $Y_2Ba_1Cu_1O_5$ particles dispersed uniformly in fluorine-doped $Y_1Ba_2Cu_3O_x$ superconductors.

2. No $Y_2Ba_1Cu_1O_5$ particles were present in undoped superconductors.

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