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Plasma Sprayed Y-Ba-Cu-O System Superconductor†

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KEY WORDS : (Y-Ba-Cu-O System Superconductor) (Oxide Superconductor) (Plasma Spraying) (LPC Plasma Spraying)

After the discovery of high T_c La-Ba-Cu-O system superconductor¹⁾, many works have been performed for searching new superconductive oxide systems and to develop its applications. For this purpose, some new oxide superconductor systems, such as the La-Sr-Cu-O²⁾ system, the Y-Ba-Cu-O³⁾ system, the Bi-Sr-Ca-Cu-O⁴⁾ system etc., were discovered. Usually, the oxide superconductors are produced by sintering, PVD, CVD etc.. Also, some attempts to produce oxide superconductors by thermal spraying were reported⁵⁾⁻⁹⁾.

As spraying powders for the Y-Ba-Cu-O system, perovskite type powders were usually used. To prepare the perovskite type powders, a cycle of calcination, sintering and grinding was repeated a few times. Even using perovskite type powders, as sprayed coatings did not show superconductivity, except when the substance was kept at 873K during spraying⁹⁾. Post-annealing was found to be necessary to yield superconductivity.

As original materials, Y_2O_3 , BaCO_3 and CuO powders were used. The powders were mixed in the correct proportion, i.e. the ratio of $\text{Y}:\text{Ba}:\text{Cu} = 1:2:3$. As mixed powders could not be sprayed since they could not be supplied to spraying gun. Therefore, the powders were calcined before spraying. After calcination at 1273K for 6 hours in air, the resulted powders could be sprayed, but the structure was not perovskite type. To prepare perovskite type spraying powders, 3 times of calcination and a time of sintering had to be carried out. **Figure 1** shows the X-ray diffraction patterns of spraying powders both non perovskite type and perovskite type. As shown in Fig. 1 (a) there is no perovskite type structure since the calculation temperature was high, but (b) has a perovskite type structure.

Prepared spraying powders were grinded and sieved. The powders passed through a 100 micron mesh were used for plasma spraying. Both air ambient plasma

spraying and LPC (Low Pressure Condition) spraying were carried out. Spraying conditions are shown in Table 1. As substrate plates, blasted SUS304 steel (5 × 50mm) plates were used. Figure 2 shows the X-ray diffraction patterns of as air ambient plasma sprayed coating surfaces (a) using non perovskite type spraying powders and (b) perovskite type spraying powders. Comparing (a) and (b) in Fig. 2, they shows almost same pattern and there is no perovskite type structure. It was considered that their ori-

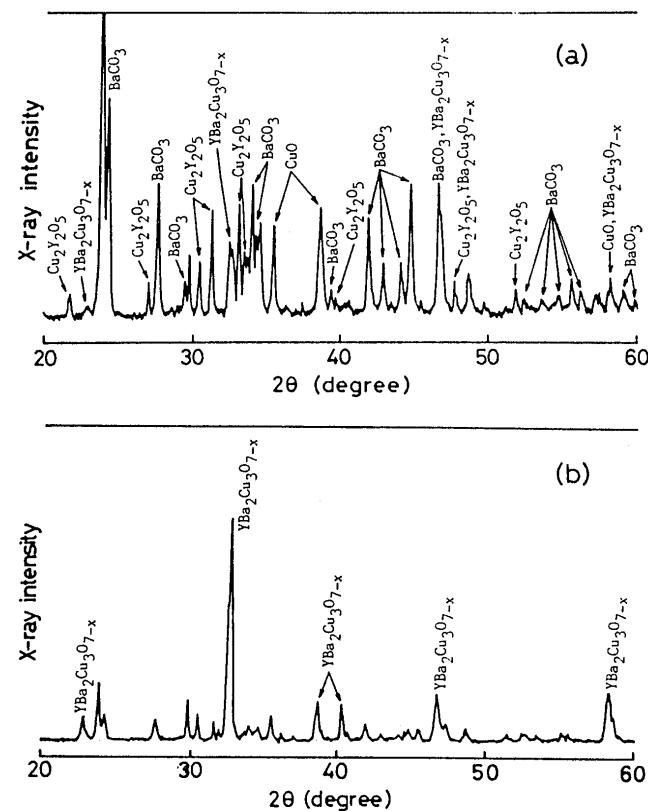


Fig. 1 X-ray diffraction patterns of (a) non perovskite type spraying powders and (b) perovskite type spraying powders.

† Received on October 31, 1988.

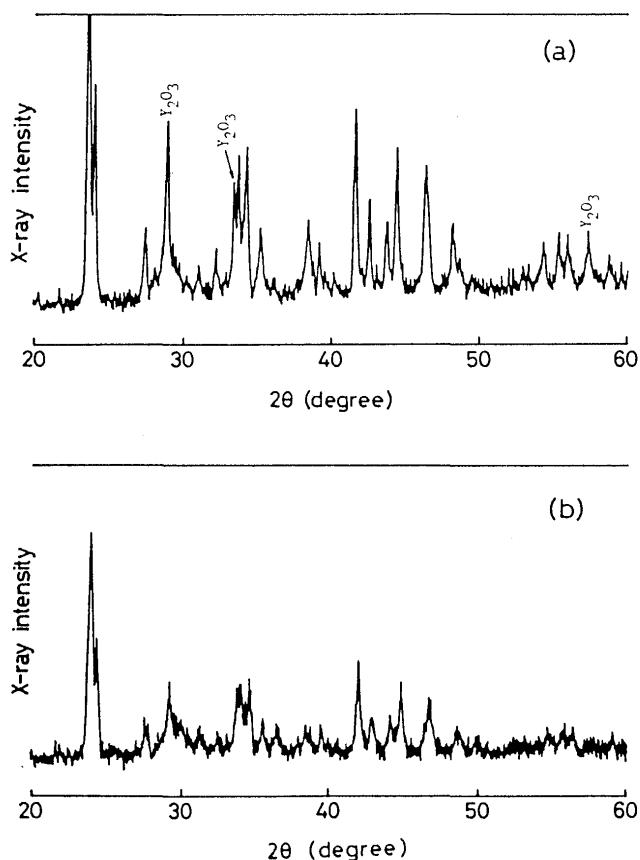
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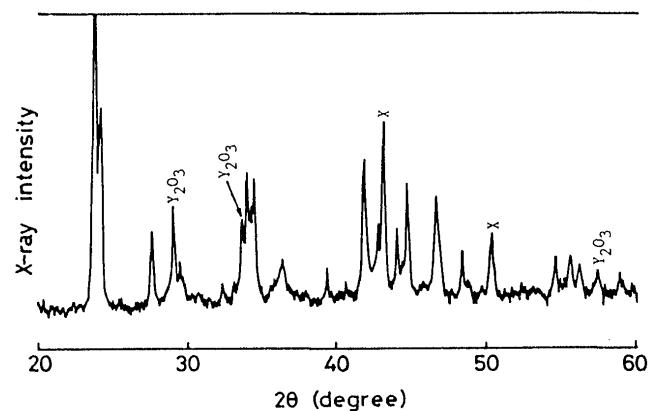
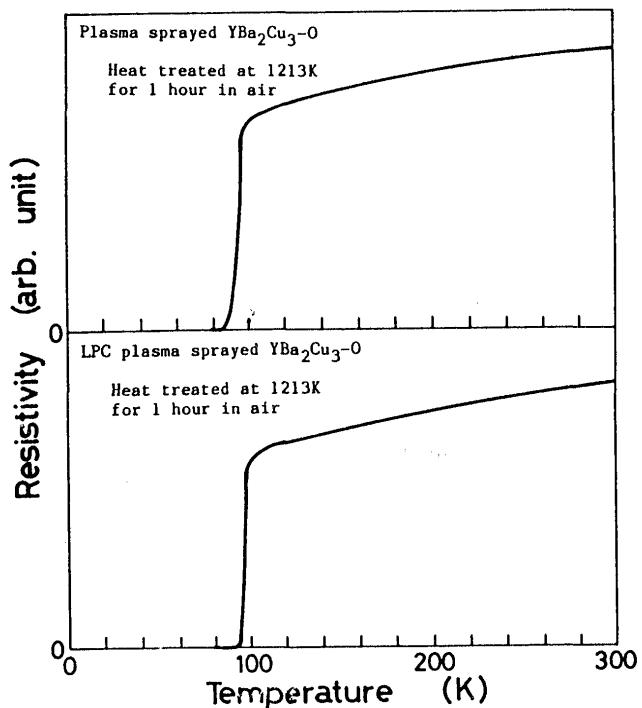
Table 1 Spraying conditions

	Plasma spraying (in air)	LPC plasma spraying
Spraying atmosphere	Atmospheric air	Ar:100torr
Plasma gas(Ar)	47.2 l/min	47.2 l/min
Auxiliary gas(H ₂)	1.9 l/min	7.1 l/min
Plasma power	35 kW	30 kW
Spraying distance	80 mm	150 mm

**Fig. 2** X-ray diffraction patterns of as-sprayed surface of air ambient plasma sprayed coatings, (a) using non perovskite type spraying powders and (b) using perovskite type spraying powders.

ginal structures were destroyed in the high temperature plasma jet during plasma spraying. Temperature dependence of resistivity was measured by dc four-probe method down to liquid nitrogen temperature. As-sprayed coatings did not show superconductivity. Resistivity increased with decreasing the temperature.

Figure 3 shows the X-ray diffraction pattern of as LPC

**Fig. 3** X-ray diffraction patterns of as-sprayed surface of LPC plasma sprayed coatings using non perovskite type spraying powders.**Fig. 4** Temperature dependence of resistivity for plasma sprayed Y-Ba-Cu-O system coatings, after heat treatment in air.

plasma sprayed coating surface using non perovskite type spraying powders. In Fig. 3, there is no perovskite type structure too, and some distinct peaks marked with x, which are not seen in Fig. 2, are recognized. Same peaks were recognized when perovskite type powders were heated in vacuum¹⁰. LPC plasma spraying was carried out in a low pressure condition (Ar: 100 Torr), i.e. in a reductive atmosphere, so decomposition of original structure must be easier than the air ambient plasma spraying. It

was considered that the magnitude of the decomposition of original structures was related to the spraying conditions.

Since as plasma sprayed coatings did not show superconductivity, yielded coatings were heat-treated in air. Before the heat treatment, plasma sprayed coatings were separated from the substrate plates to avoid the reaction between coating and substrate metal. The separated coatings were heat-treated at an elevated temperature for some hours in air and cooled in furnace. **Figure 4** shows examples of temperature dependence of resistivity for heat treated plasma sprayed coatings. The upper profile is for air ambient plasma sprayed coating and the lower profile is for LPC plasma sprayed coating. As shown in Fig. 4, they shows superconductivity and the resistivity becomes zero at around 90K. It was recognized that plasma sprayed coatings could become superconductor at the heat treatment temperature range of 1173K to 1223K. Heat treated plasma sprayed coatings had perovskite type structure as shown in **Fig. 5**.

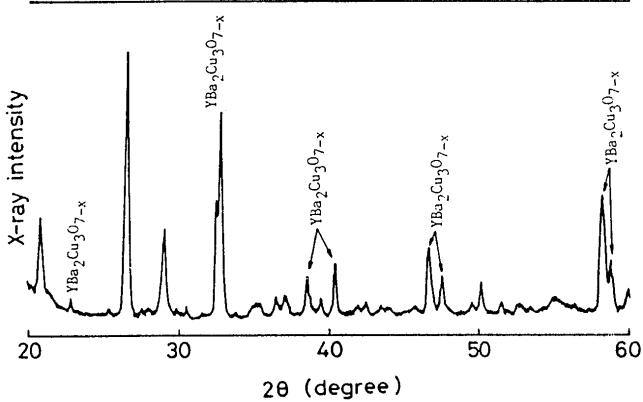


Fig. 5 An example of X-ray diffraction pattern of heat treated plasma sprayed coating.

From the results described above, original structure of the spraying powders was destroyed in a high temperature plasma jet during plasma spraying. Therefore, it is not necessary to use perovskite type spraying powders for spraying. By using non perovskite type powders, almost same coatings are yielded. As-sprayed coatings were not superconductor and did not have perovskite structure, but it can be changed to superconductive perovskite type structure by heat treatment in air.

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