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# Formation of YBaCu-O System Superconductor by Thermal Spraying<sup>†</sup>

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## Abstract

The YBaCu-O and Bi(Pb)SrCaCu-O system superconductor coatings by thermal spraying are described. YBaCu-O system superconductor coatings are sprayed by using perovskite type and non-perovskite type powders. As sprayed coatings are not superconducting and there is no perovskite structure even when perovskite type powders are used, but they become superconducting after heat treatment in air. An electro-chemical method was also employed, to obtain a high quality superconductor applying an electric field treatment. Bi(Pb)SrCaCu-O system superconductor coatings are sprayed by changing the starting composition. As-sprayed coatings were not superconducting, but they become superconducting after heat treatment in air like the YBaCu-O system. The  $T_c$  of the sprayed coatings using  $(Bi_{1-x}Pb_x)_5Sr_3Ca_2Cu_3O$  powders is higher than the  $T_c$  of sprayed coatings using  $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O$  powders.

**KEY WORDS:** (Plasma spraying, YBaCuO-system, Bi(Pb)SrCaCu-O system, Superconductor)

## 1. Introduction

After the discovery of the high  $T_c$  oxide superconductors of the LaBaCu-O system<sup>1)</sup>, many studies have been performed to discover new oxide superconductor systems. As a result, some new oxide superconductor systems, such as the LaSrCu-O system<sup>2)</sup>, YBaCu-O system<sup>3)</sup>, BiSrCaCu-O<sup>4)</sup> system etc., have been discovered. For the BiSrCaCu-O system, the  $T_c$  was increased by partial replacement of Bi with Pb<sup>5)</sup>. Usually, the oxide superconductors are produced by sintering, PVD, CVD etc.. Also, some attempts to produce oxide superconductors by thermal spraying have been reported<sup>6-11)</sup>.

Powders used for spraying from the YBaCu-O system are usually of the perovskite type. To prepare the perovskite type powders, a cycle of calcination, sintering and grinding was repeated a few times. Even using perovskite type powders, the sprayed coatings did not show superconductivity, except when the substrate was kept at 873K during spraying<sup>10)</sup>. Post-annealing was found to be necessary to yield superconductivity. For Bi(Pb)SrCa-O system there are few reports on spraying<sup>11)</sup>. As the sprayed coatings did not show superconductivity, post-annealing was necessary similar to YBaCu-O system. The  $T_c$  of sprayed

coating was much lower than that of sintered pellet, though the  $T_c$  of sprayed coatings and sintered pellets was almost the same as for the YBaCu-O system.

In this report, the formation of YBaCu-O system and Bi(Pb)SrCaCu-O system superconductors by thermal spraying is described. Atmospheric plasma spraying and LPC (Low Pressure Condition) plasma spraying apparatus were used to perform the experiments described here. For the YBaCu-O system, both perovskite type and non-perovskite type powders were used for spraying. To yield a higher  $T_c$  for Bi(Pb)SrCaCu-O system, the starting composition of spraying powders are modified. To supply active oxygen to superconductive material, an electro-chemical method, using oxygen supplied from stabilized zirconia under an electric field, is described.

## 2. Experiment

$Y_2O_3$ ,  $BaCO_3$  and  $CuO$  powders were used to produce YBaCu-O, while  $(BiO)_2CO_3$ ,  $PbO$ ,  $SrCO_3$ ,  $CaCO_3$  and  $CuO$  powders were used to produce Bi(Pb)SrCaCu-O. The powders were mixed in the correct proportions and calcined in alumina crucibles at an elevated temperature in air. Then the calcined powder was ground and sieved. Only

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the powder that passed through a 100 micron mesh was used for spraying. Both conventional plasma spraying and LPC (Low Pressure Condition) plasma spraying were carried out.

For spraying powders of the  $\text{YBaCu-O}$  system, two types of powders were prepared, one with and the other without the perovskite type structure. Perovskite type powder was prepared by calcination 3 times at 1223K for 6 hours in air and sintering at 1223K for 6 hours in air, though non-perovskite type powder could be prepared with only 1 time calcination at 1273K for 6 hours in air.

For spraying powders of the  $\text{Bi}(\text{Pb})\text{SrCaCu-O}$  system, 4 different compositions of starting powders were prepared. The first reported composition for the  $\text{BiSrCaCu-O}$  system was  $\text{BiSrCaCu}_2\text{-O}^4$ . It has also been reported that the compositions  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{-O}$  and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{-O}$  have a high  $T_c$  phase and low  $T_c$  phase, respectively<sup>12, 13</sup>. So, the following starting compositions were used.

- (a)  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{-O}$
- (b)  $(\text{Bi}_{0.8}\text{Pb}_{0.2})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{-O}$
- (c)  $\text{Bi}_5\text{Sr}_3\text{Ca}_2\text{Cu}_3\text{-O}$
- (d)  $(\text{Bi}_{0.8}\text{Pb}_{0.2})_5\text{Sr}_3\text{Ca}_2\text{Cu}_3\text{-O}$

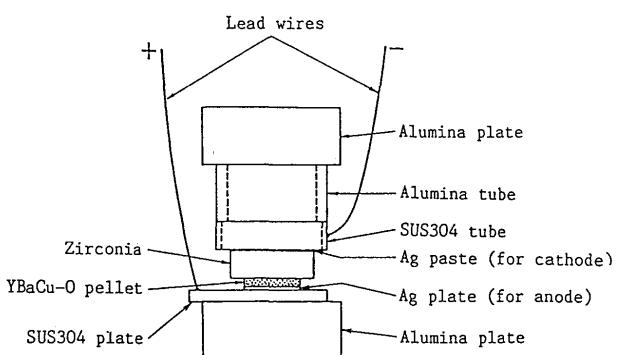
(a) was reported as having a high  $T_c$  phase composition<sup>13</sup>. (b) was a composition reported as being able to achieve a high  $T_c$  phase<sup>5</sup>. (c) and (d) were modified compositions from (a) and (b) for spraying.

The powders were cooled in a furnace, after keeping them at 1123K for 6 hours in air.

The prepared powders were sprayed using the conditions shown in **Table 1**. Blasted SUS304 steel ( $5 \times 50$  mm) plates were used as substrates. After spraying, the sprayed coatings were separated from the substrate. The sprayed coatings were heat treated at elevated temperature for some hours in air and then cooled in a furnace. Resistivity vs. temperature was measured by the dc four-probe method down to liquid nitrogen temperature for the  $\text{YBaCu-O}$  system and down to 10K for the  $\text{Bi}(\text{Pb})\text{SrCaCu-O}$  system.

**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( $\text{H}_2$ )	1.9 l/min	7.1 l/min
Plasma power	35 kW	30 kW
Spraying distance	80 mm	150 mm



**Fig. 1** Schematic diagram of electric field treatment for applying oxygen supplied from stabilized zirconia.

For comparison, 10 mm in diameter, 1 mm thick pressed pellets were sintered using same powders as used for spraying. The samples were characterized by X-ray diffraction and WDX analysis.

An electric field treatment was performed to supply active oxygen to the superconductive  $\text{YBaCu-O}$  system. **Figure 1** shows the assembly of equipment used for this method. Oxygen ions move to the anode side from the cathode side in stabilized zirconia under an electric field. This method has been applied to the bonding of stabilized zirconia to metals<sup>14</sup>. Therefore the electric field was applied to the  $\text{YBaCu-O}$  pellet with active oxygen ions from stabilized zirconia.

### 3. Results and Discussion

#### 3.1 $\text{YBaCu-O}$ system

**Figure 2** shows the experimental procedure and conditions with a summary of results for the  $\text{YBaCu-O}$  system. Mixed powders of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$  could not be sprayed since they could not be supplied to the spraying gun. Therefore, the powders were calcined before spraying. After calcination at 1273K for 6 hours in air, the resulting powders could be sprayed, but the structure was non of the perovskite type.

To prepare perovskite type powders, calcination and sintering had to be carried out 3 times as illustrated in Fig. 2.

**Figure 3** shows the X-ray diffraction patterns of the prepared powders and the surface of as-sprayed coatings both for perovskite type and non-perovskite type powders. Comparing (a) and (c) in Fig. 3; in (a) there is no perovskite type structure since the calcination temperature was high, but (c) has a perovskite type structure. (b) and (d) were X-ray diffraction patterns of as-coated surface using (a) and (c) powders, respectively. Comparing (b) and (d) in Fig. 3; they show almost the same pattern and there is no perovskite structure. It was considered that their original

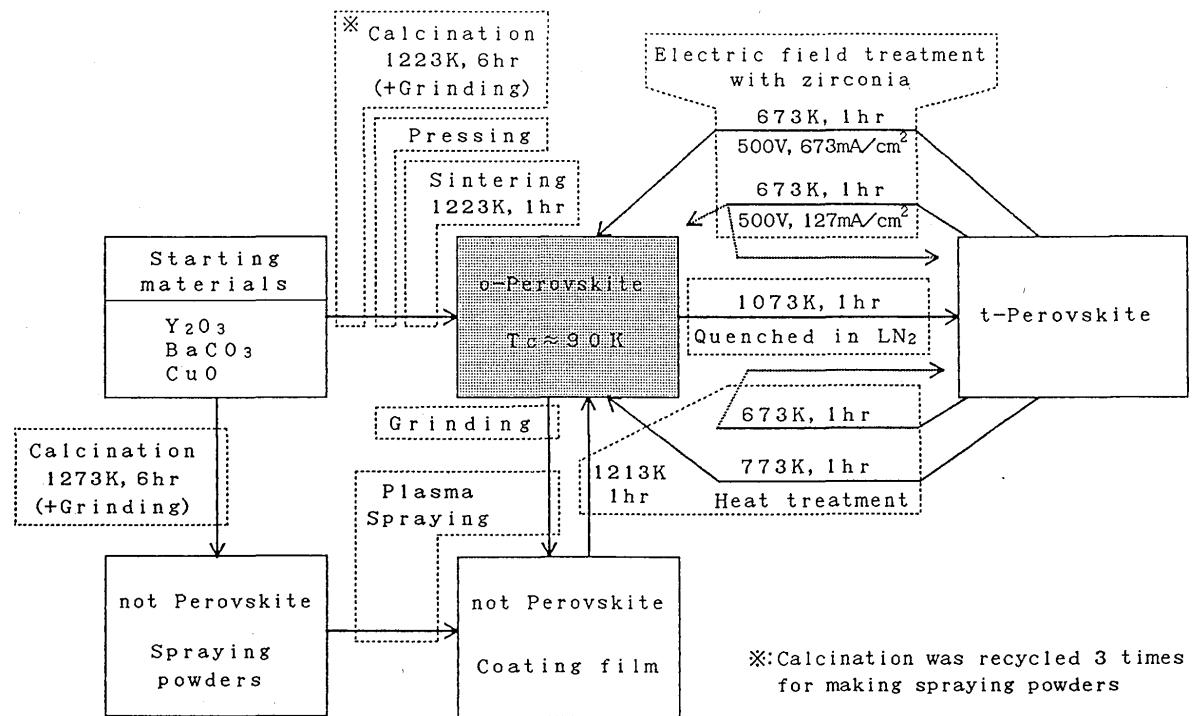
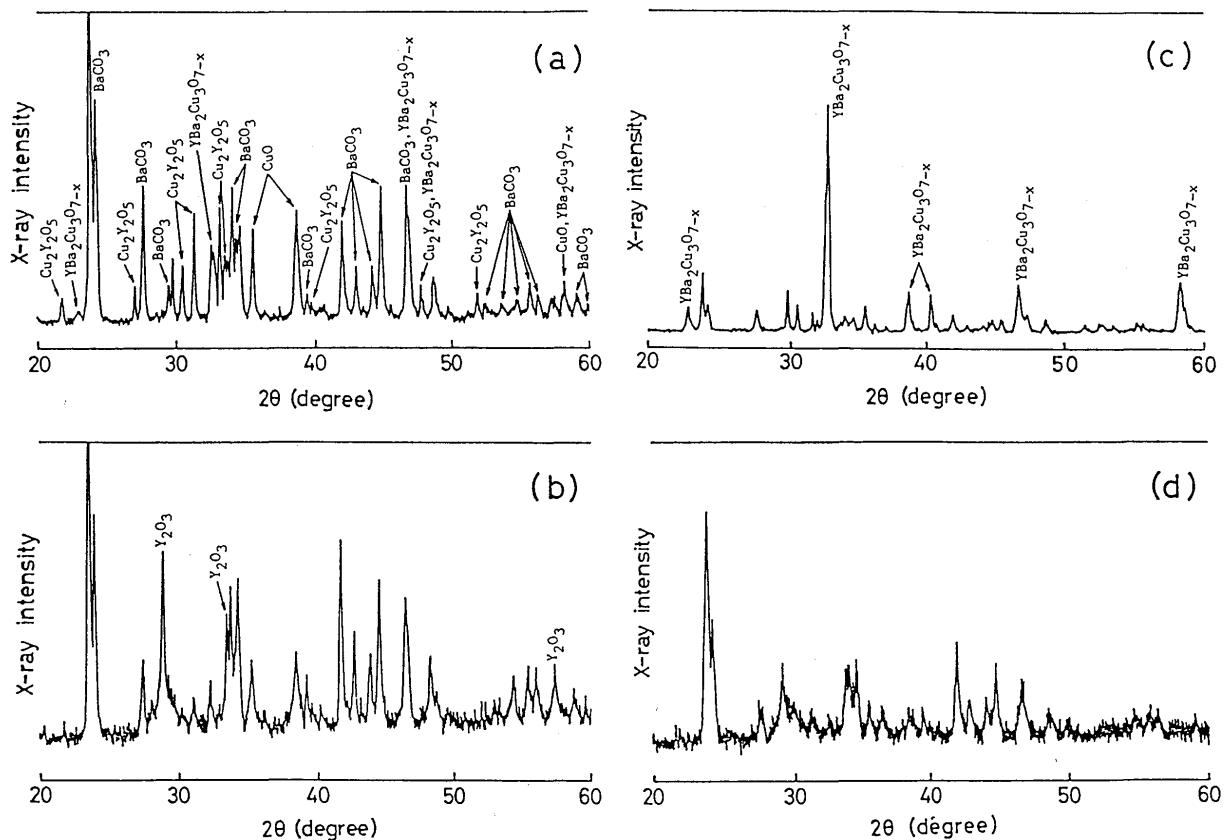


Fig. 2 Schematic diagram of preparation process for YBaCu-O system samples with a summary of the results.

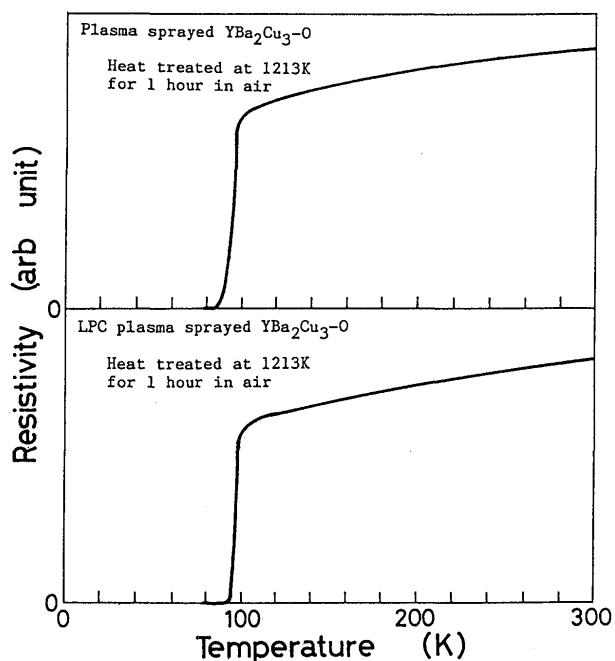


**Fig. 3** X-ray diffraction patterns of spraying powders and air ambient plasma sprayed coatings. (a): non-perovskite type spraying powders, (b): surface of coating using (a) powders, (c): perovskite type spraying powders, (d): surface of coating using (c) powders.

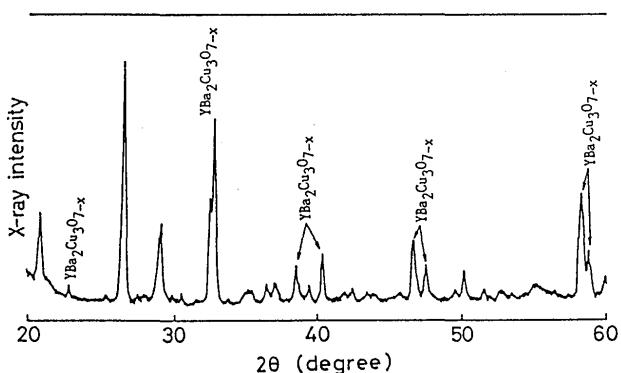
structures were destroyed in the high temperature plasma jet during spraying.

As sprayed coatings did not show superconductivity. The resistivity increased with decreasing the temperature. **Figure 4** shows the temperature dependence of resistivity on heat treated plasma sprayed coatings. The upper profile is for an air ambient plasma sprayed coating, while the lower profile is for an LPC plasma sprayed (sprayed in Ar: 100torr) coating. In Fig. 4, they showed superconductivity and the  $T_c$  was around 90K.  $T_c$  is almost the same to that of sintered pellets. In this report,  $T_c$  is the temperature at which the zero resistance is displayed. Heat treated plasma sprayed coatings had a perovskite type structure as shown in **Fig. 5**.

As an additional experiment, electric field treatment of

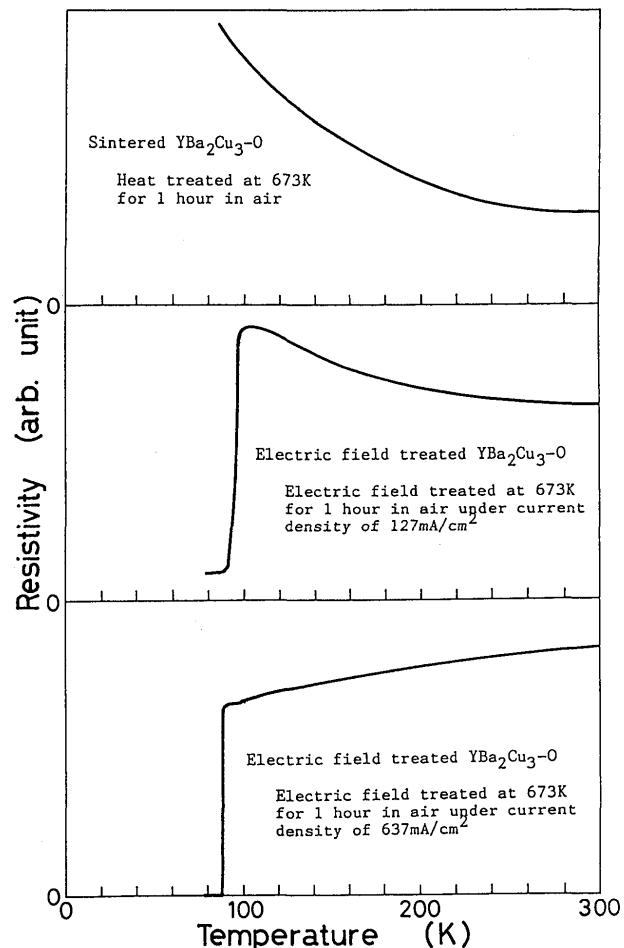


**Fig. 4** Temperature dependence of resistivity for plasma sprayed YBaCu-O coatings, after heat treatment in air.



**Fig. 5** X-ray diffraction pattern of plasma sprayed YBaCu-O coating surface after heat treatment in air.

$\text{YBa}_2\text{Cu}_3\text{-O}$  pellet was carried out. This method involved the use of the electric field assisted bonding of stabilized zirconia to metals, in which active oxygen ions move from the cathode side to the anode side under an electric field, which results in the formation of a metal oxide at an anode side interface.<sup>14)</sup> The mobile oxygen ions in stabilized zirconia were supplied by an electric field applied stabilized zirconia to  $\text{YBa}_2\text{Cu}_3\text{-O}$  pellet. Before the electric field treatment, the  $\text{YBa}_2\text{Cu}_3\text{-O}$  pellet was quenched in liquid nitrogen after it keeping at 1073K for 1 hour. The quenched  $\text{YBa}_2\text{Cu}_3\text{-O}$  pellets had a tetragonal perovskite structure and they did not show superconductivity. The results are shown in **Fig. 6** with changing treatment conditions. When an electric field was not applied (i. e. only heat treatment), the quenched pellets became superconducting and the structure changed to orthorhombic perovskite at the treatment temperature of 773K as shown in Fig. 2, but it did not become superconducting at the treatment temperature of 673K, as shown in the upper profile of Fig. 6. The middle and lower profiles of Fig. 6 show the temperature vs. resistivity profiles of electric field treated pellet with differ-



**Fig. 6** Temperature dependence of resistivity for electric field treated pellets.

ent strength electric fields. With a current density of 127 mA/cm<sup>2</sup> at 673K (the middle profile in Fig. 6) a drop in resistance was observed around 90K, but it did not show zero resistance. When the current density was increased to 673 mA/cm<sup>2</sup>, the pellet obtained showed zero resistance at about 90K in spite of 673K heating as shown in the lower profile of Fig. 6. From X-ray diffraction analysis, the electric field treated pellet had orthorhombic perovskite structure. From these results, it was considered that YBaCu-O system superconductors could get oxygen at lower temperature from the stabilized zirconia to which an electric field was applied, and this caused a change in the crystal structure from tetragonal perovskite to orthorhombic perovskite.

The original structure of the spraying powders was destroyed in the high temperature plasma jet during spraying, so it was not necessary to use perovskite type powders for spraying. By using the non-perovskite type powder almost the same coatings were produced. The non-superconductive tetragonal perovskite structure could be changed to a superconductive orthorhombic perovskite structure at lower temperature by using the electrochemical method mentioned above.

### 3.2 Bi(Pb)SrCaCu-O system

It was reported that BiSrCaCu<sub>2</sub>-O showed two step superconductivity at 115K and 75K<sup>4</sup>. Lower Tc and higher Tc phases were reported for Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>-O<sup>12)</sup> and Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>-O<sup>13)</sup>, respectively. By partial replacement of Bi with Pb the ratio of high Tc phase was increased<sup>5)</sup>.

Here, the results of producing Bi(Pb)SrCaCu-O system coatings by thermal spraying are discussed.

Figure 7 shows the experimental procedure and conditions with a summary of the results for the Bi(Pb)SrCaCu-O system. For starting powders, four different compositions were used as mentioned in section 2.

Figure 8 shows the relationship between temperature and resistivity for a sintered pellet, an air ambient plasma sprayed coating and a LPC plasma sprayed coatings with the starting composition of (a). The as-sprayed coatings did not show superconductivity, like coatings of the YBaCu-O system. After heat treatment, they showed superconductivity. The sintered pellet showed a drop in resistance around 110K and zero resistance around 70K. The heat treated sprayed coatings showed a drop in resistance around 110K but Tc was lower than that of sintered pellet. The Tc for air ambient plasma sprayed coatings was about

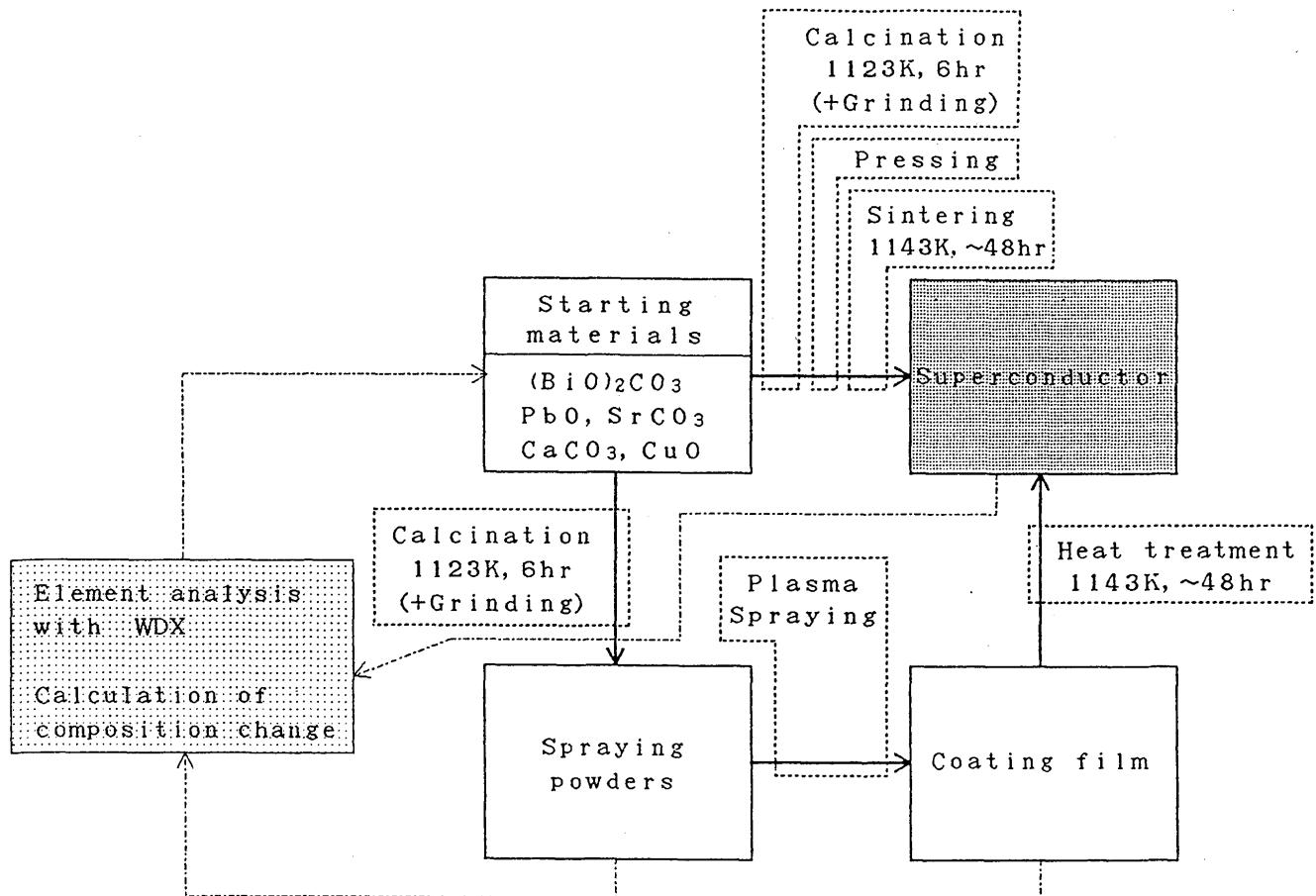
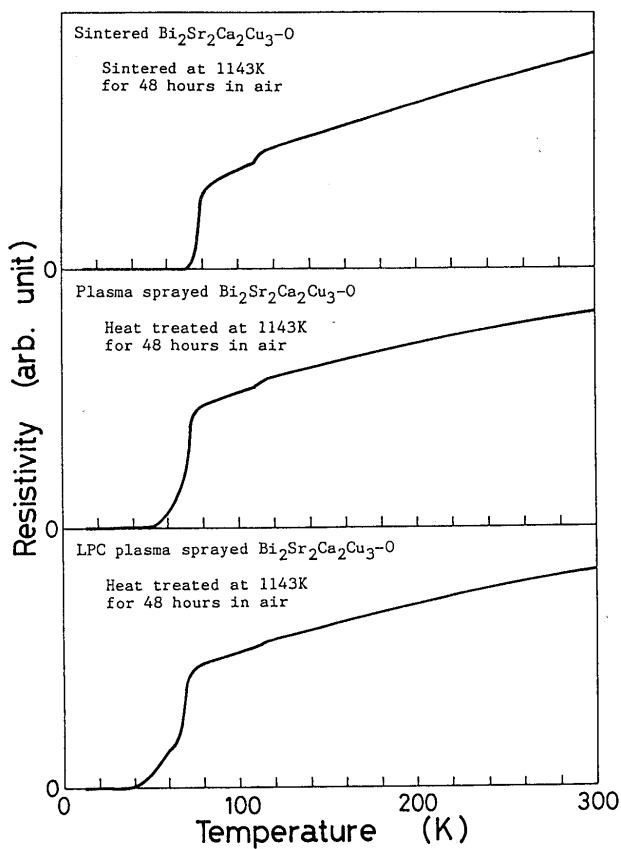


Fig. 7 Schematic diagram of preparation process for Bi(Pb)SrCaCu-O system samples with summary of the results.

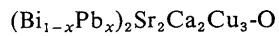


55K, and for LPC plasma sprayed coatings about 30K. The temperature at which the drop in resistance first occurred was almost constant, even when the holding time was increased up to 48 hours. Similar results were obtained for starting compositions of  $\text{BiSrCaCu}_2\text{-O}$  and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{-O}$ .

Figure 9 shows the relation of temperature and resistivity for sintered pellet, air ambient plasma sprayed coatings and LPC plasma sprayed coatings for the starting composition of (b) mentioned in section 2. The left side of Fig. 9 shows that the  $T_c$  increased with the holding time for sintering. The temperature at which the drop in resistance first occurred was almost constant, even when the holding time was increased up to 48 hours. The resistance drop at around 110K was small and the  $T_c$  was around 55K. As seen in the upper and middle profiles, the  $T_c$  was almost the same even when the holding time was increased.

As shown in Figs. 8 and 9, the  $T_c$  of plasma sprayed coatings was lower than that of the sintered pellet. It was considered that the composition must have changed in the high temperature plasma jet during spraying. Therefore, the composition of the spraying powders and surface of as-sprayed coatings was analyzed with WDX analyzer as

indicated in Fig. 7. WDX is not an absolute quantitative analysis technique, but it is possible to estimate the composition change before and after spraying. A point of pressed spraying powders pellet and two points of as-sprayed coatings were analyzed. Yield rates are calculated by assuming the yield rate of Cu was 100%. The results are shown in Table 2. From this table, it appears that relatively large amounts of Bi, Pb and Sr were lost during plasma spraying. From these results, it was decided that for a target composition of



a starting composition of



is suitable. The actual starting compositions for spraying powders were identified as (c) and (d) in section 2.

Figures 10 and 11 show the temperature dependence of resistivity for the starting compositions of powders given in (c) and (d), respectively. They could not be sintered at 1143K since they melt at this temperature, so sintering was done at 1093K. Plasma sprayed coatings did not melt at 1143K. From Fig. 10, sintered pellet shows superconductivity, but  $T_c$  was lower than that of Fig. 8.  $T_c$  of sprayed coating became higher than that in Fig. 8. In Fig. 11, sintered pellet with the starting composition of (d) did not show superconductivity. The  $T_c$  of sprayed coatings was higher than that of Fig. 9. From these results, it was obvious that the superconducting behavior of the  $\text{Bi}(\text{Pb})\text{SrCaCu-O}$  system could be improved by changing the starting composition.

Up to now, the  $T_c$  of sprayed coatings has been lower than that of sintered pellets, but the results of this study show that it can be improved by changing the composition of the starting powders.

#### 4. Conclusion

The results of this work can be summarized as follows,

- (1) For the  $\text{YBaCu-O}$  system, heat treatment was needed to obtain superconductivity for plasma sprayed coatings.

Table 2 Yield rate of elements on spraying

Elements	Yield rate	
Bi	39%	43%
Pb	61%	77%
Sr	71%	92%
Ca	113%	155%
Cu	100%	

Yield rates were calculated as Cu=100% from WDX analysis results

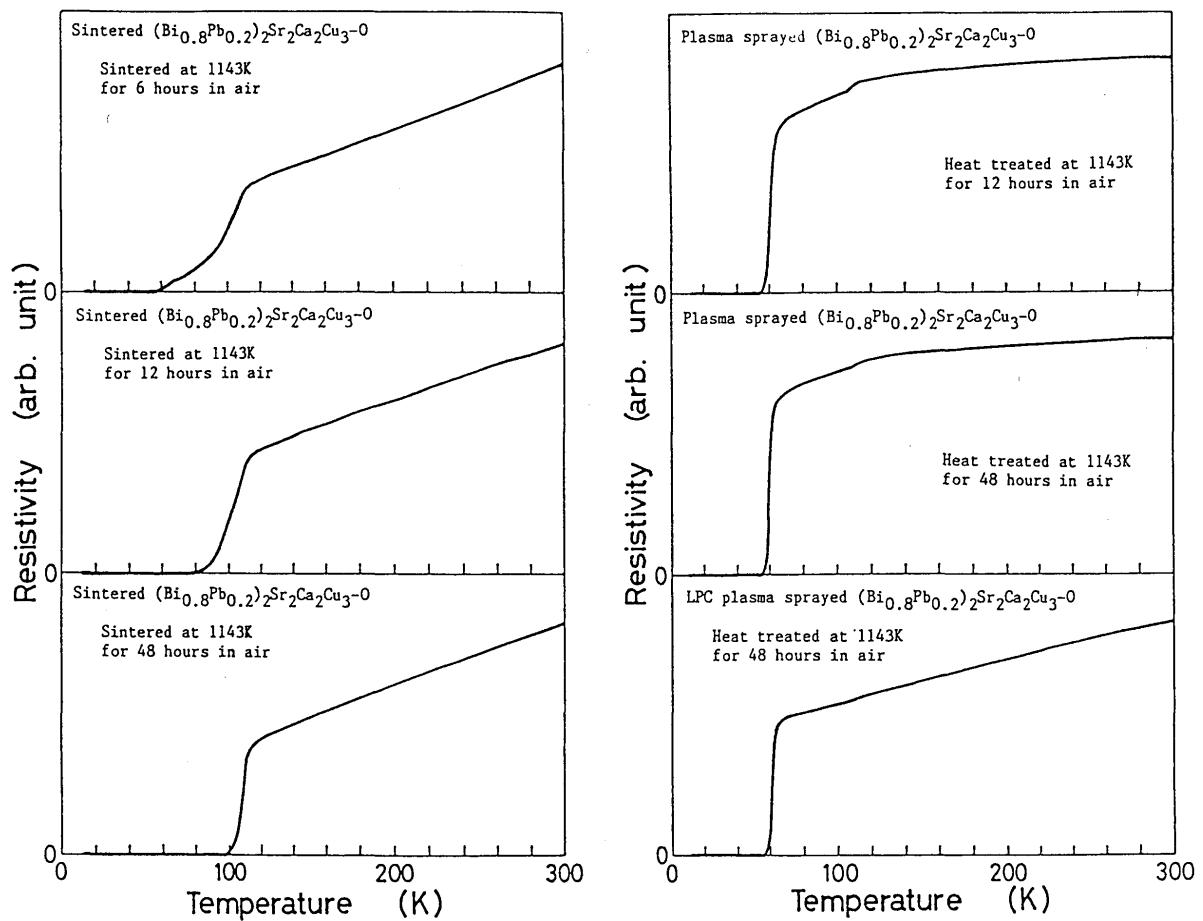


Fig. 9 Temperature dependence of resistivity for heat treated plasma sprayed coatings and for sintered pellets with a starting composition of  $(Bi_{0.8}Pb_{0.2})_2Sr_2Ca_2Cu_3-O$ .

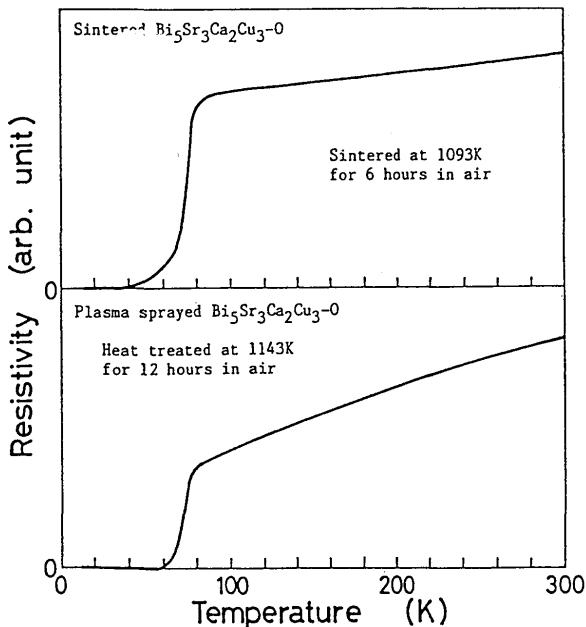


Fig. 10 Temperature dependence of resistivity for heat treated plasma sprayed coatings and with a sintered pellet for starting composition of  $Bi_5Sr_3Ca_2Cu_3-O$ .

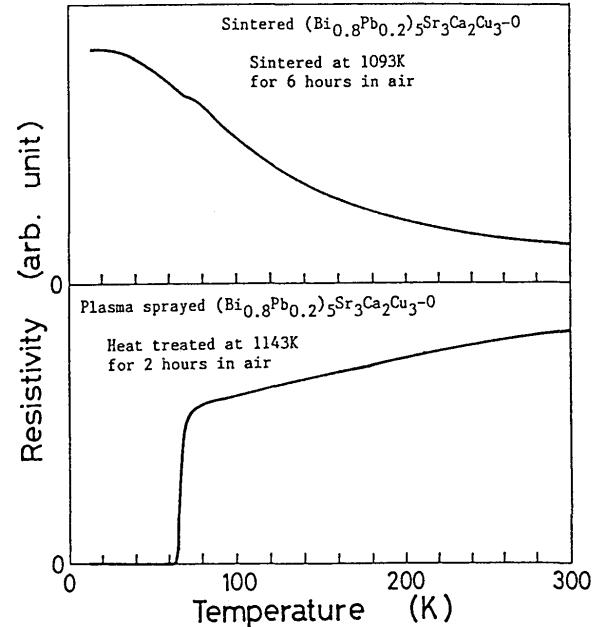


Fig. 11 Temperature dependence of resistivity for heat treated plasma sprayed coatings and with a sintered pellet for starting composition of  $(Bi_{0.8}Pb_{0.2})_5Sr_3Ca_2Cu_3-O$ .

- (2) For the YBaCu-O system, it was not necessary to use perovskite type powder as the spraying powder. Powders that are more easily prepared than perovskite type powder can be used.
- (3) For the YBaCu-O system, a non-superconductive tetragonal perovskite structure could be changed to a superconductive orthorhombic perovskite structure at a relatively low temperature 673K by using an electrochemical method that employs stabilized zirconia and drives oxygen from it to the superconducting material.
- (4) For the Bi(Pb)SrCaCu-O system, heat treatment was needed to obtain superconductivity for plasma sprayed coatings, similarly to the YBaCu-O system.
- (5) For the Bi(Pb)SrCaCu-O system, the Tc of plasma sprayed coatings was lower than that of sintered pellets. However, it could be improved by changing the starting composition of the spraying powders.

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