Applications of Mechanofusion System for the Production of Superconductive Oxides

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1. Introduction

"Mechanofusion" is a technique of creating particulate materials with new properties by mechanochemical surface fusion as a result of certain mechanical energy exerted on the surface of different kinds of particles\(^1\)-\(^2\). In this paper, some examples of application of this technique for the field of superconductive oxides are introduced.

A new Mechanofusion System (AM-20FS) has been developed on the basis of "Angmill", dry attrition type mill. It enables us to grind different kinds of powder materials down to submicron level, to disperse them uniformly and to create composite particles from them. It was made clear from experiments that Mechanofusion was an effective method to prepare the raw powdery materials of superconductive oxides and multi-component targets for superconductive thin films.

2. A new Mechanofusion System "AM-20FS"

Figure 1 shows a picture of this machine. The basic mechanism is the same as conventional types of Mechanofusion system, but it has the following additional features:

- (1) As in most cases fine powders are used as raw materials of oxide superconductors, this apparatus is designed to reduce their adhesion in the Mechanofusion chamber by exerting impact forces to its bottom and vibration forces to the attrition tips fixed on its axis.

- (2) As hazardous powders such as Pb or BaCO\(_3\) are usually used, the air in the chamber is led to an air filter (HEPA filter) to prevent their leakage during its operation. This filter system is set as an option.

Specifications of AM-20FS are summarized in Table 1.

3. Application to produce superconductive oxides\(^3\)

In case of yttrium-based superconductors, each fine powder of Y\(_2\)O\(_3\), BaCO\(_3\) and CuO was weighed to satisfy the mixing ratio of Y : Ba : Cu = 1 : 2 : 3. These powders were treated in a batch operation at a high rotation speed for certain time. The processed powder was calcined in an electric furnace for provided time, and treated by AM-20FS. Then the treated powder was compressed to form a compacted pellet, and sintered for several hours followed by annealing at a certain temperature.

Figure 2 shows an example of temperature dependence of resistivity of the produced samples. It is obvious that the critical temperature reaches 90 K class, and the width of transition

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Table 1 Specifications of AM-20FS

| Specification             | Value                  |
|---------------------------|------------------------|
| Feed charge per batch     | 100 ~ 300 cc           |
| (powder bulk volume)      |                        |
| Power required            | 3.7 kW                 |
| Dimensions of rotating chamber | \(\phi 200 \times 70H\) |
| Chamber rotation          | max. 2,450 r.p.m.      |
temperature is narrow. Figure 3 shows the chart of X-ray diffraction pattern of samples obtained, which shows this sample has the orthorhombic crystal structure of Y-Ba-Cu-O.

Furthermore, the variations in composition of powder treated by the Mechanofusion before calcining were measured to evaluate its uniformity. Each sample of 0.2 g was picked up from the treated powder randomly, and ten samples were analyzed to measure the component ratios of Ba/Y and Cu/Y by an inductively coupled plasma method. As a result, the measured fluctuation coefficient was within 1% in each component ratio. It was found from these experimental results that Mechanofusion was an effective method for preparing Y-Ba-Cu-O superconductors.

As it is well-known, dry mechanical processes such as Mechanofusion method have several advantages compared with wet ones. For example, the former processes do not contain a powder drying operation which is necessary for the latter one. But the dry mechanical processes have much difficulties in treating fine powders properly because of their adhesion phenomena. Table 2 indicates the dependence of treating methods by using dry vibration ball mill on critical temperature $T_c$ of Y-Ba-Cu-O superconductors. Here the same kinds of powders as the case of our method were used as raw materials. When a dry vibration ball mill is substituted for Mechanofusion apparatus, the $T_c$ shows the lower value of 79.3 K. In such a case, a calcining and grinding process must be usually repeated several times to improve the quality of superconductors as shown in Table 2. On the other hand, in case of the process by using Mechanofusion, high quality superconductors were produced through single calcining and grinding process.

Why does Mechanofusion provide such a high quality superconductors effectively? Figure 4 shows the example of SEM and XMA pictures of a composite particle treated by Mechanofusion before calcining. Here Fig. 4(a) is a SEM photograph, and Figs. 4 (b), (c) and (d) are a XMA mapping picture of Y, Ba and Cu respectively. It is obvious from these pictures that a composite particle in (a) is composed of Y, Ba

| No. | Machine              | Production process before forming | $T_c$ (K) |
|-----|----------------------|----------------------------------|-----------|
| 1   | Mechanofusion        | Calcining + Mechanofusion        | 92 ~ 93   |
| 2   | Vibration ball mill (dry type) | Grinding | 79.3 |
| 3   | Vibration ball mill (dry type) | Calcining + Grinding | 84.7 |

Table 2 Effect of mechanical processes of treating powders on critical temperature $T_c$ of Y-Ba-Cu-O superconductors
Fig. 4 Pictures of a composite particle treated by Mechanofusion before calcining
(a): SEM, (b), (c), (d): XMA mappings of Y, Ba, Cu component

and Cu particles ground down to submicron level. Furthermore, as it was already explained, the treated powder has a sufficient uniformity of each component. Therefore, it is considerable that a solid phase reaction of the treated powder is conducted efficiently by the grinding and the mixing effects of Mechanofusion.

As another feature of Mechanofusion, the authors1,2) have already reported that particles of one kind are firmly fixed onto the surface of those of the other kind by exerting certain mechanical forces. It suggests that the contact area of different kinds of particles processed by Mechanofusion is larger than that of the powder mixture under usual compaction. It is thought this effect also might promote the solid phase reaction.

The Mechanofusion is also applied for preparing Bi-based superconductors. Figure 5 shows the example of temperature dependence of resistivity of Bi-Pb-Sr-Ca-Cu-O composite obtained by our process, where the $T_c$-value indicates 106 K. We are now trying to produce Bi-based superconductors which has higher amount of high-$T_c$ phase.

4. Applications to produce superconductive thin films6,7)

Multi-component targets have been widely used to fabricate the thin films of superconducting oxides. As it is well-known, these targets have been produced with a process, which contains the mixing of each component with a ball mill or a co-precipitation method. But when Mechanofusion is applied, it will be a convenient method to produce them.

Figure 6 shows the relationship between the electric resistance and the temperature of a Bi-Pb-Sr-Ca-Cu-O thin film. Here, it was formed by a rf sputtering apparatus with a Bi-Pb-Sr-Ca-Cu-O powder target, and treated in an electric...
furnace for about 170 hours. The powder target was produced by treating raw materials with Mechanofusion and calcining them. As the $T_c$-value shows 102 K, it is proved that this target has also good performance.

As another case, Fig. 7 shows the temperature dependence of resistivity of Y-Ba-Cu-O thin film fabricated by using an ion beam sputtering method. Here the sintered target prepared by Mechanofusion was used as a sputtering resource. As the $T_c$-value indicates 88 K, it is found that this sintered target has a good performance. These experimental results show that Mechanofusion contributes to the production of multi-component targets of superconductive oxides.

5. Conclusions

In this paper, it was summarized that Mechanofusion was an effective method for preparing superconductive oxides, and multi-component targets for superconductive thin films.

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