Densification of Superconducting $\text{Ba}_2\text{YCu}_4\text{O}_8$ Ceramics by Two-Stage Sintering

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二段焼成による $\text{Ba}_2\text{YCu}_4\text{O}_8$ 超伝導セラミックスの緻密化

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Highly dense ceramics of $\text{Ba}_2\text{YCu}_4\text{O}_8$ (Y-124) superconductor were successfully prepared under ordinary pressure of oxygen by the two-stage sintering; the compacted disks of previously prepared Y-124 powders were sintered at 930°C for 2 h, thereafter annealed at 800°C for 200 h. The ceramics thus prepared have relative densities around 95%. It was also confirmed that the Y-124 phase of starting powders was decomposed to $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$ (Y-123) and CuO at 930°C, and then restored in the annealing at 800°C. Liquid-phase sintering may bring about the densification, since partial melt reportedly occurs at 930°C under oxygen pressure of 1013.25 hPa.

Key-words : $\text{Ba}_2\text{YCu}_4\text{O}_8$, Superconducting ceramics, Densification, Two-stage sintering, One atmosphere oxygen pressure

1. Introduction

Because of the higher critical temperature (T_c) than intermetallic compounds and alloys, superconducting cuprate ceramics have been expected to be close to practical use. However, it is required to control the microstructures of superconducting ceramics which strongly affect the superconducting properties. A number of reports have pointed out that a high bulk density as well as oriented microstructure is an important factor in fabricating quality superconducting ceramics. Although the dense bulk specimens of Y-123 have been successfully prepared, it has been still difficult to obtain dense ceramics of Y-124.

Bulk Y-124 specimens prepared under high oxygen pressure or ambient pressure are porous^{1,2)} that their relative densities are about 65%.³⁾ Such low density is unfavorable for the use of Y-124. Williams et al. have recently succeeded in obtaining the dense bulk specimens of Y-124 with relative density of 90%.⁴⁾ The complex sintering process with hot isostatic pressing was employed in their preparation. However, it has been difficult to prepare the dense Y-124 bulk under ordinary pressure of oxygen, since the Y-124 phase is stable only below 850°C at one at-

mospheric oxygen pressure.⁵⁾ In order to prepare the dense Y-124 ceramics under ordinary pressure of oxygen, the present authors employed so-called two-stage sintering: the Y-124 ceramics were fired at 930°C for a short time, and then annealed at 800°C for a long time. This report presents the preparation of dense ceramics of Y-124 by the two-stage sintering. In addition, the microstructure of Y-124 ceramics thus prepared is compared with that of Y-124 ceramics prepared in conventional manner.

2. Experimental

Starting powders prepared through spray-frozen/freeze-drying of the aqueous solution with atomic ratio of Ba : Y : Cu = 2 : 1 : 4 were calcined in flowing oxygen, pulverized, pressed into disks and treated under oxygen pressure of 1013.25 hPa according to the following procedure. The compacted disks were firstly sintered at 930°C for 2 h (called as first-stage) followed by annealed at 800°C for 200 h (called as second-stage) without cooling to room temperature. For comparison, some specimens were sintered at 800°C for 200 h in a similar way reported previously.³⁾

Crystalline phases were identified by X-ray diffraction (XRD) using Cu K α radiation. Microstructural properties were estimated from a measurement of density, scanning electron microscope (SEM) and transmitting electron microscope (TEM) observations. For resistivity measurement with the constant measuring current density of 0.05 A/cm², a standard four-probe method was employed and metal gold was used as the electrode. Temperature was monitored by a silicon diode sensor.

3. Results and discussion

Figure 1 shows the powder XRD patterns of as-calcined specimen (a), sintered specimen after the first-stage (b) and ceramic specimen prepared by the two-stage sintering (c). As-calcined specimen was observed to be of almost Y-124 single-phase. On the other hand, the XRD pattern showed the existence of Y-123 and CuO instead of the Y-124 after

Fig. 1. Powder XRD patterns of as-calcined specimen (a), specimen sintered at 930°C for 2 h (b) and specimen prepared by the two-stage sintering (c).

the first-stage. The decomposition of Y-124 brought about the Y-123 and CuO because the Y-124 is unstable at 930°C in oxygen pressure of 1013.5 hPa.⁵⁾ However, any peaks of Y-123 and CuO are not detectable in the XRD pattern for the specimen prepared by the two-stage sintering, giving only the peaks attributed to Y-124. The zero resistance temperature of the Y-124 ceramics thus prepared was 73 K. Furthermore, the electrical resistivity at 150 K was about one-third as large as that of specimen sintered at 800°C for 200 h. As described later, the densification of Y-124 ceramics achieved by the two-stage sintering led to the low electrical resistivity.

The above results indicate that the Y-124 phase crystallized after the two-stage sintering is formed by the solid-state reaction of Y-123 and CuO. Jin et al. have reported that the Y-124 superconductor is obtained from the mixture of Y-123 and stoichiometric amount of CuO through normal grinding and sintering.⁶⁾

Figure 2 is a TEM photograph of the specimen obtained at the first-stage which consists of Y-123 and CuO. Twin structure can be observed on each grain of the Y-123 phase. On the other hand, spherical fine grains with the diameter of a few hundreds nm were found within the Y-123 matrix. The spherical grains were confirmed to be CuO from an energy dispersive X-ray analysis. A similar texture has been observed

Fig. 2. TEM photograph of the specimen sintered at 930°C for 2 h. (Bar=500 nm)

Fig. 3. SEM photographs of the specimens obtained by sintering at 800°C for 200 h (a) and two-stage sintering (b). (Bars=5 μm)

for specimens prepared by decomposing the Y-124 ceramics.⁷⁾

In Fig. 3, the SEM photograph of the specimen prepared by the two-stage sintering is compared with that of the specimen sintered at 800°C for 200 h. A remarkable difference was confirmed between two SEM photographs. The specimen sintered only at 800°C consists of a number of pores and small grains. The relative density was about 58% which is similar to those reported previously. On the other hand, the specimen prepared by the two-stage sintering has a dense body as can be clearly seen in Fig. 3(b). The bulk density was 5.8 g/cm³, giving 95% of theoretical density. Each grain has a prismatic shape with large dimension. It is clear that the two-stage sintering is an effective method for fabricating dense Y-124 ceramics under ordinary pressure of oxygen.

The first-stage is particularly important for the densification, since the density of specimen displayed in Fig. 2 is almost the same as that of specimen after the second-stage. As Park et al. have pointed out that the decomposition of Y-124 to Y-123 and CuO takes place rapidly around 940°C,⁸⁾ the densification may be promoted under the coexistence of those. According to the ternary phase diagram of $\text{BaO}-1/2\text{Y}_2\text{O}_3-\text{CuO}$ at 950–1000°C by Roth et al., the region at which a melt partially occurs lies on the line from Y-123 to CuO.⁹⁾ Frase et al. and Aselage et al. have observed the melt in 930–940°C on the system Y-123–CuO.^{10),11)} Those reports strongly suggest the appearance of liquid phase in the present two-stage sintering. It is consequently assumed that the origin of densification is a liquid-phase sintering.

4. Conclusion

In this work, the densification of ceramic Y-124 superconductors was carried out under oxygen pressure of 1013.25 hPa by the two-stage sintering, consisted of sintering at 930°C followed by annealing at 800°C. The relative density of about 95% was achieved. The densification brought about the Y-124 showing low resistivity at normal state. It was also observed that Y-124 phase was decomposed to Y-123 and CuO during sintering at 930°C, and again formed at 800°C. The densification is supposed to be

promoted at 930°C by the liquid-phase sintering.

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