

Transition state of phase formation during sintering process inside Ag-sheathed (Bi,Pb)2223 tape

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ABSTRACT A transition state of phase formation inside Ag-sheathed (Bi,Pb)2223 tape during sintering has been reported. XRD measurement was carried out for the powder extracted from a tape. The collected XRD data were analyzed by the Rietveld method. During the sintering, (Bi,Pb)2223, Bi2212, 14-24 and 2-1 were mainly detected together with small amount of CuO at 1093K under 7.8% O₂ atmosphere. And the incubation period of about 36 ks was observed before the start of (Bi,Pb)2223 phase formation. In the incubation period, the Bi2212 phase transition from tetragonal to orthorhombic was observed, that resulted from Pb substitution in Bi site of Bi2212 structure. The preferable secondary phases were gradually shifted from the 14-24 phase to the 2-1 phase.

Key word: (Bi,Pb)2223, phase transformation, powder XRD, Rietveld method

1. INTRODUCTION

Although Ag-sheathed (Bi,Pb)2223 tapes have been fabricated by several industrial companies in recent years, knowledge about the phase transformation during sintering process is still so far from sufficient to establish an effective heat-treatment process for higher *J_c* (Bi,Pb)2223 tapes. For the fabrication of higher *J_c* (Bi,Pb)2223 tapes, it is very important to control not only (Bi,Pb)2223 phase, but also secondary phase formation so that many reports on (Bi,Pb)2223 phase formation have been published [1-5].

To study phase formation in (Bi,Pb)2223 tapes, there are two major methods, SEM/EPMA analysis [1,2] and XRD analysis [3-5]. Although the former is useful to follow secondary phases distribution or (Bi,Pb)2223 grain alignment, it is difficult to get quantitative information about phases in the filament such as the volume fraction. The latter is impossible to detect secondary phase dispersed inside the filament core, because it is used to be performed with superconducting filaments as removed Ag sheath in many cases and the short penetration depth of conventional X-ray such as Cu-K α . It is, however useful to observe texture development of the tapes.

Recently, several researchers have studied about (Bi,Pb)2223 phase formation using neutron or synchrotron X-ray diffraction technique [6-8]. In Refs.[7], they succeeded to follow directly (Bi,Pb)2223 phase formation and secondary phase evolution inside the Ag-sheathed tapes during sintering in air by means

of *in-situ* high temperature neutron diffraction and the Rietveld analysis. However, it is still lacked for quantitative information about the phase transformation in the (Bi,Pb)2223 tape under actual sintering conditions.

We have succeeded to determine quantitatively content of phases in the superconducting filament through the Rietveld analysis on powder XRD data in spite of the *ex-situ* observation using conventional powder XRD technique.

The aim of this study is to clarify the phase transformation and its evolution inside Ag-sheathed tapes by the quantitative determination via the Rietveld method.

2. EXPERIMENTAL

The precursor powder from Merck Corp. was used after re-calcining at 1073 K in air for 72 ks. The chemical composition is $\text{Pb}_{0.33}\text{Bi}_{1.80}\text{Sr}_{1.87}\text{Ca}_{2.00}\text{Cu}_{3.00}\text{O}_x$. Ag-sheathed (Bi,Pb)2223 monofilamentary tapes were prepared by PIT method. The tapes were sintered at 1093 K under Ar-7.8%O₂ atmosphere for 0.6 ~ 360 ks and air-quenched after each sintering.

To extract superconducting filaments, Ag sheath was removed from the sintered tape by chemical etching with NH₃: H₂O₂ = 2:1 solution. After removing the Ag sheath, superconducting filaments from the tapes were wet-ground with acetone to powder-like form. The ground powder was mixed with acetone-diluted cellulose glue so as to decrease an effect of the preferred orientation from plate-like grains in the XRD

Table 1 Volume fraction (%) of phases in the precursor powder.

Bi2212	CaPbO ₄	(Sr,Ca) ₁₄ Cu ₂₄ O _x	(Ca,Sr) ₂ CuO ₃	(Sr,Ca) _{0.78} CuO _x	Pb3221
65.30	8.27	17.31	4.33	3.08	1.71

observation. Then the powder mixed with cellulose glue was vacuum-dried and ground again to make sample for the powder XRD measurement.

The powder XRD measurement was performed with RIGAKU RAD diffractometer in Bragg-Brentano geometry using Cu-K α radiation. A diffraction data was collected by θ -2 θ scan. The collected data were analyzed using the Rietveld method in order to identify the phases presented and refine their crystal parameters such as lattice parameter. The Rietveld analysis was carried out with RIETAN-2000 software [9].

3. RESULTS AND DISCUSSION

The phase component and the lattice parameter in the precursor powder were refined by the Rietveld analysis for the powder XRD data. The phase component is listed in Table 1. The lattice parameter of the Bi2212 phase was $a=5.595(2)$, $b=5.595(2)$ and $c=30.750(2)$.

Example of powder XRD pattern from superconducting filaments analyzed by the Rietveld method is shown in Fig.1. This XRD pattern was collected from the sample sintered for 108 ks at 1093 K. In Fig.1, the dots and the solid line indicate the experimental data and the calculated pattern from refined parameters, respectively. The six bands of markers at the bottom of the graph indicate the reflections from the six detected phases, that are (Bi,Pb)2223, Bi2212, Bi2201, (Sr,Ca)₁₄Cu₂₄O_x (14-24), (Ca,Sr)₂CuO₃ (2-1) and CuO from the top to the bottom respectively. It is

emphasized that AEC phases inside the filament such as 14-24 and 2-1 phase could be observed by conventional powder XRD measurement. The solid line at the bottom of the graph indicates an error between the experimental data and the calculated pattern. The R_{wp} , R_e and S factor showing reliability of the refinement and the volume fraction of the phases contained in the superconducting filaments are as listed in the graph.

Fig.2 shows the volume fraction change of the superconducting phases during sintering. As shown in Fig.2 (a), before the Bi2223 phase formation, an incubation period of about 36 ks was observed. The volume fraction of the Bi2212 phase remained almost constant throughout the incubation period. After the incubation, phase conversion from Bi2212 to (Bi,Pb)2223 was occurred and the volume fraction of Bi2212 decreased drastically. After sintering for 360 ks, the volume fraction of (Bi,Pb)2223 reached over 80 %.

After the incubation, small amount of the Bi2201 phase was also observed as shown in Fig.2 (b). The amount of Bi2201 increased with the Bi2212 to (Bi,Pb)2223 conversion, and decreased after the phase conversion saturated. It is said that, in the fastly cooled sample such as air-quenched, the Bi2201 phase crystallizes from the liquid phase present during sintering [3,4,8]. Therefore, the presence of Bi2201 indicated that the liquid phase was present during the phase conversion from Bi2212 to (Bi,Pb)2223 and

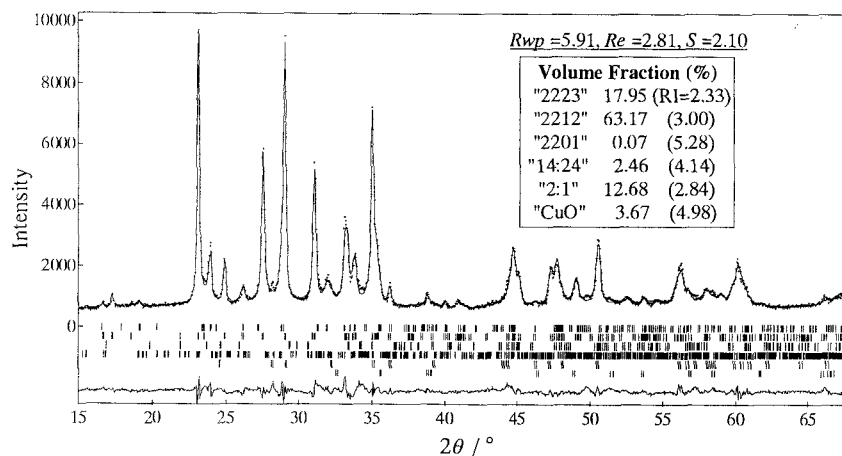


Fig.1 Example of powder XRD pattern analyzed by the Rietveld method for the sample sintered for 108 ks at 1093 K under 7.8% partial oxygen pressure. The dots and the solid line indicate the experimental data and the calculated pattern, respectively. Reliability of the refinement and volume fraction of the phases are shown in the figure.

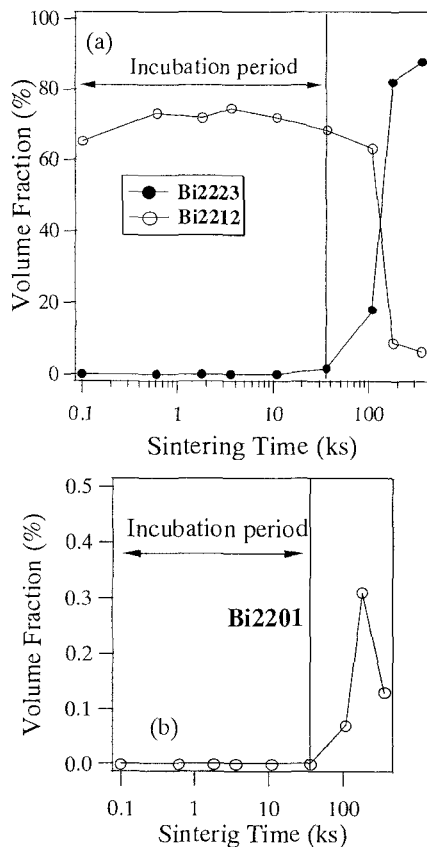


Fig.2 Sintering time dependence of volume fraction of superconducting phases, (a) Bi2223 and Bi2212, (b) Bi2201. Incubation period indicated in (a) and (b) corresponds to Bi2223 phase formation.

decreased at the end of the conversion.

Fig.3 shows refined lattice parameters of Bi2212 phase plotted as a function of sintering time. The tetragonal to orthorhombic structural change was clearly observed. As discussed in Refs.[10] and [11], the increasing addition of Pb leads to increase the separation of the lattice parameter of a- and b-axis of Bi2212, indicating that the modulation structure induced from lattice distortion in the Bi2212 crystal caused by excess oxygen [12] is relaxed by Pb substitution for Bi site in the Bi2212 structure. Considering that the Pb-rich phases such as CP and Pb3221 had disappeared at a very early stage in sintering as shown in Fig.4, this change resulted from the tetragonal Bi2212 to orthorhombic Pb-rich Bi2212 phase conversion occurred during sintering.

This phenomenon was similar as reported in Refs.[7]. However, there was a difference expected from different heat-treatment conditions such as a heating rate. In [7], the (Bi,Pb)2223 phase formation started as soon as the tetragonal to orthorhombic Bi2212 phase

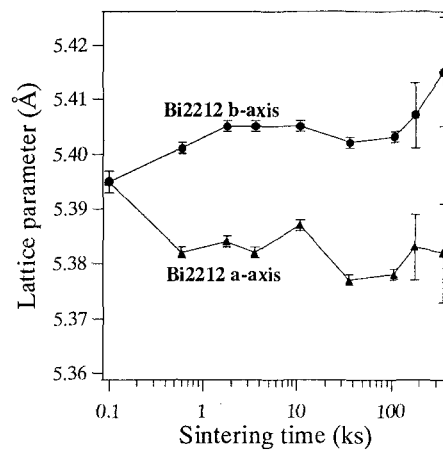


Fig.3 Lattice parameter change of Bi2212 phase during sintering.

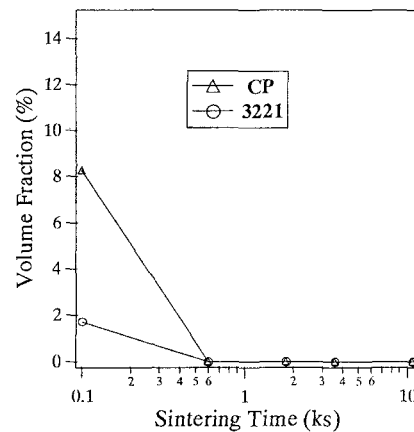


Fig.4 Volume fraction change of CP and Pb3221 phase containing Pb. These phases disappeared at very early stages in sintering.

conversion began after decomposition of the Pb-rich phases. Whereas, in this study, the incubation period required more than 30 ks before the beginning of the (Bi,Pb)2223 phase formation, although the tetragonal to orthorhombic Bi2212 phase conversion had started after 0.6 ks sintering.

A volume fraction change of secondary AEC and CuO phases was also observed as shown in Fig.5. The 1-1 phase ((Sr,Ca)_{0.78}CuO_x) disappeared at a very early stage of sintering. And the amount of the 14-24 phase ((Sr,Ca)₁₄Cu₂₄O_x) decreased monotonously and was no longer detected after 108 ks sintering. Whereas, the volume fraction of the 2-1 phase ((Ca,Sr)₂CuO₃) and CuO increased in the incubation for the (Bi,Pb)2223 formation and reached a maximum value at the end of the period. And once the (Bi,Pb)2223 phase formation had started, the amount of 2-1 and CuO decreased drastically to a small volume. These volume fraction

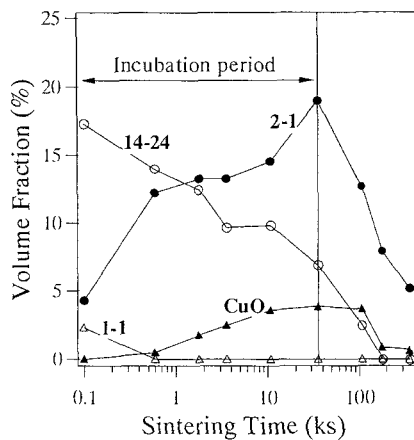


Fig.5 Sintering time dependence of volume fraction of AEC and CuO phases. Incubation period of the Bi2223 phase formation is also shown in the graph.

change after the incubation period was resulted from the decomposition of the secondary phases related to supplying cations used for the (Bi,Pb)2223 phase formation. However, the result in Fig.5 suggests that the gradual shift of preferable secondary phase in the incubation had been caused by different factors.

From some studies [13, 14], it can be said that a type of secondary cuprate phase strongly depends on oxygen partial pressure in calcining or sintering. In Refs.[13], the SEM observations revealed that the 14-24 and 2-1 phases were contained in the (Bi,Pb)2223 tapes fabricated under a high oxygen partial pressure, whereas the 2-1 and CuO phase were preferably contained under a low oxygen partial pressure. In the *in-situ* high-temperature neutron observation, the 14-24 phase had existed through sintering process under 20% partial oxygen pressure, even though the amount had decreased gradually [7]. Same tendency was observed even in calcining a precursor powder [14]. For the reasons mentioned above, in the incubation period for the (Bi,Pb)2223 formation, it is assumed that the volume fraction change of secondary phases was raised because the reaction path of the (Bi,Pb)2223 phase transformation had passed through a metastable state of the phase relation under 7.8% partial oxygen pressure before reaching a stable state consisting of mainly (Bi,Pb)2223. And that is suggested to be one of the reasons why the more than 30 ks incubation period was required before starting the (Bi,Pb)2223 phase transformation.

4. CONCLUSION

The phase transformation during sintering process had

been studied by the quantitative observations using the Rietveld analysis. The tetragonal to orthorhombic Bi2212 phase transition were observed, that resulted from Pb substitution for Bi site in the Bi2212 structure. And the more than 30 ks incubation period for the (Bi,Pb)2223 phase formation was observed. In this period, the preferable secondary phase were gradually shifted from the 14-24 phase to the 2-1 one. The reason was suggested that the reaction path had passed through a metastable state of the phase relation under 7.8% partial oxygen pressure before starting the (Bi,Pb)2223 transformation.

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