Reformation of (Bi, Pb)-2223 Superconducting Phase after Complete Peritectic Melting

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Abstract. Considerable fractions of (Bi, Pb)-2223 were recovered after the complete peritectic melting of that phase. The minimization of Pb-losses was a key-feature, so that only about 1.57 wt % of total Pb content was lost over the whole process. Therefore the system remained within the 2223 single-phase region. The new route employed here, including the participation of a stable liquid, should overcome some microstructural problems nowadays present in sintered 2223/Ag tapes, such as voids, cracks and bad grain connectivity. Further optimization of the complete melting-reformation process may reduce the fraction of secondary superconducting phases, which can act as weak-links.

1. Introduction
The synthesis of (Bi, Pb)-2223 by means of a melt-processing route could enhance the microstructure and performance of 2223/Ag tapes and bulk parts. It is, however, a challenging task, due to the narrow stability range and sluggish formation kinetics of that phase [1]. On the other hand, some works have shown the formation of 2223 out of a melt or in the presence of a melt [2-5]. By using high-temperature neutron diffraction, Giannini et al. [5] demonstrated the reversibility of the 2223 peritectic decomposition, after its partial decomposition into liquid and solid phases. Nonetheless, the reformation of 2223 after its complete peritectic decomposition has not been shown, so far.

Presented here are evidences of a successful reformation of 2223 phase after its complete peritectic decomposition (thereafter named as complete melting). These are preliminary results and the complete melting-reformation process has to be further optimized in order to beneﬁce of this new route for 2223 formation could fully appear.

2. Experimental
A powder with the nominal composition Bi₁.₈₄Pbₐ.₃₂Sr₁.₆₄Ca₁.₆₄Cu₃.₀₀O₁₀₊ₓ, possessing over 90%wt of 2223 phase, was synthesized through solid-state reaction starting from an homogenized mixture of oxides and carbonates. Composite samples were made by sealing the 2223 powder with a thin silver foil (0.025 mm, 99.9 %, Alfa Aesar) at the proportion of 30% vol. ceramic powder to 70% vol. silver. DTA of both the as-prepared powder and the 2223/Ag composite were preformed in static air with
heating rate of 10°C/min, in order to determine the influence of silver on the 2223 T\textsubscript{solidus}. TGA of the 2223/Ag composite was carried out in static air following a thermal schedule similar to the one used latter in the melting-reformation experiments (figure 1). Thus, a TGA 2223/Ag sample was heated up to 863°C, at 3°C/min, being then kept at 863 °C for 30 minutes and further slow cooled at 0.2 °C/min.

Figure 1 illustrates the thermal schedule applied on the complete melting-reformation process of 2223/Ag. Each arrow indicates a quenching procedure. No leak of liquid phase from the silver-sealed 2223 was observed in the samples treated by the complete melting-reformation process. The ceramic bodies were then withdrawn from the silver foil and ground. Ex-situ X-ray powder diffraction was carried out using a Siemens D-5000 diffractometer with CuKα radiation and a graphite monochromator.

2. Results and Discussion
By means of DTA the peritectic melting onset temperature (T\textsubscript{solidus}) was determined both for the as-prepared 2223 powder (T\textsubscript{solidus} = 864°C) and for the 2223/Ag composite (T\textsubscript{solidus} = 857°C). This effect of silver on T\textsubscript{solidus} was expected [6]. The TG curve of the 2223/Ag sample (figure 2) exhibits three different steps of mass loss with the total mass loss being about 0.55%. By heating up to about 200 °C, occurred a mass loss (~ 0.20 %) mostly due to the release of adsorbed water. Within the 650-800°C range, the mass loss can be mainly attributed to oxygen release, while at temperatures above 800°C the mass loss can be ascribed to both oxygen and lead losses. On the other hand, upon cooling down to 650°C the mass increased due to oxygen uptake (~ 0.25%). Still, it can be noticed that, at 650°C, the mass recuperation is not complete. Since one can not expect water adsorption to occur at 650°C, the mass difference between the heating and cooling cycles (about 0.1% at 650°C) can be attributed to the lack of Pb. This 0.1% weight loss corresponds to only 1.57 wt % of the total Pb content of the 2223 phase with the nominal composition used in the present work. If the 2223/Ag composite were heated to 10-20°C above T\textsubscript{solidus}, the Pb losses would increase, as already pointed out by Giannini et al. [5]. In this sense, the thermal schedule of the complete melting-reformation process (figure 1) has been designed to minimize Pb-losses, since the maximum temperature was 862°C +/- 1°C, i.e., only about 5°C above 2223 T\textsubscript{solidus}. In addition, the silver foil sealing was crucial to reduce Pb-loss. To assure a complete peritectic melting of 2223 phase at 862°C, the samples were maintained at this temperature for 1 hour.
Figure 2. TGA curve of the (Bi,Pb)-2223/Ag composite

Figure 3(A-D) shows XRD patterns of specimens quenched from 862°C, 850°C, 838°C and 400°C. After 1 hour at 862°C, 2223 decomposed completely into liquid, Pb-rich phase, Ca₂CuO₂ (2:1) and (Sr,Ca)₂Cu₂O₄ (14:24). On quenching the liquid crystallized and formed predominantly Bi-2201 and some Bi-2212 (figure 3A). By slow cooling from 862°C at 0.1°C/min it was possible to reform a considerable fraction of 2223 (figures 3B-D). The sample quenched from 850°C (figure 3B) had already a significant 2223 content, although 2212 was the most predominant phase and 2201 was also present in rather high fraction. The cuprate 2:1, which is one of the peritectic solid phases together with the cuprate 14:24, can also be detected in the diffraction pattern (figure 3B) as well as CuO and the plumbate Ca₂PbO₄, which appeared at this temperature. The specimen quenched from 850°C was also rich in an amorphous material, as it can be inferred from a very pronounced hump, extending from about 22° to 40° (figure 3B). At 838°C the phase ratios (figure 3C) are very different from that observed at 850°C. 2223 became the predominant phase at 838°C and the contents of the other two Bi-Sr-Ca-Cu-O phases (2212 and 2201) were significantly lower. At the same time, one can verify a strong decreasing of 2:1 content (see the diffraction line at 36.3°) and of the amorphous phase (the hump is much smaller) contents. Also, the fraction of Ca₂PbO₄ present at 838°C is lower than at higher temperatures (see the diffraction line at 17.9°). At 400°C (figure 3D), the 2223 phase content was higher than at 838°C. All other crystalline phases present at 838°C were also present at 400°C, but in smaller amounts.

3. Conclusions

The present work showed that it is possible to reform considerable fractions of (Bi,Pb)-2223 phase after the complete peritectic melting of this phase. The key detail in the complete melting-reformation process is the minimization of Pb-losses. If this condition is fulfilled the system does not migrate from the 2223 primary phase field. This new route of (Bi,Pb)-2223 synthesis within Ag environment may overcome microstructural problems still present in sintered 2223 that limit the performance of 2223 tapes and bulk parts. Materials defects found in sintered (Bi,Pb)-2223/Ag tapes such as voids and cracks could be significantly reduced through the complete melting-reformation process, enhancing thus the grain connectivity. Still, the complete melting-reformation process remains to be optimized, in order to eliminate the secondary superconducting phases (Bi-2212 and Bi-2201) due to theirs weak-link properties. By growing large (Bi,Pb)-2223 plates either directly from or in the presence of a melt, it might be also possible to diminish grain boundary problems.
Figure 3. XRD patterns of the specimens quenched from (A) 862 °C / 1 hour; (B) 850 °C; (C) 838 °C; (D) 400 °C. 1- 2201; 2- 2212; 3- 2223; 2:1- Ca$_2$CuO$_3$; 14:24- (Sr,Ca)$_{14}$Cu$_{24}$O$_{41}$; Pb- Ca$_2$PbO$_4$.

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