Influence of the oxygen partial pressure on the phase evolution during Bi-2212 wire melt processing

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***Abstract*—We have studied the influence of the oxygen partial pressure pO_2 up to 5.5 bar on the phase changes that occur during melt processing of a state-of-the-art Bi-2212 multifilamentary wire. Phase changes have been monitored *in situ* by high energy synchrotron X-ray diffraction (XRD). We found that the stability of Bi-2212 phase is reduced with increasing pO_2. For pO_2>1 bar a significant amount of Bi-2212 phase decomposes upon heating in the range 400 to 650 °C. The extent of decomposition strongly increases with increasing pO_2, and at pO_2=5.5 bar Bi-2212 decomposes completely in the solid state. Textured Bi-2212 can be formed during solidification when pO_2 is reduced to 0.45 bar when the precursor is molten. Since the formation of current limiting second phases is very sensitive to pO_2 when it exceeds 1 bar, we recommend to reduce the oxygen partial pressure below the commonly used pO_2=1 bar, in order to increase the pO_2 margins and to make the overpressure process more robust.**

***Index Terms*—Bi-2212, melt processing, XRD.**

I. Introduction

High critical current (J_c) densities in Powder-in-Tube (PIT) Bi-2212 wires are achieved after a heat treatment (HT) cycle that melts the precursor and leads to Bi-2212 recrystallization [1]. This enables the wind and react approach that can produce Bi-2212 conductors, cables and coils in more complex shapes than is possible with any other High Temperature Superconductor (HTS) material. Indeed, Bi-2212 is up to now the only HTS that can be produced in twisted multifilamentary round wire form, from which Rutherford cables can be made, making Bi2212 particularly attractive for high energy physics applications [2].

It is well known that during the Bi-2212 processing heat treatment (HT) an external oxygen supply through the oxygen permeable Ag wire matrix is needed in order to form Bi-2212. Oxygen is most conveniently supplied when the HT is performed in air at ambient pressure with an oxygen partial pressure (pO_2) of 0.21 bar. However, substantially higher critical current densities can be achieved when the same heat cycle is performed in a pO_2=1 bar.

Overpressure (OP) processing is a key for achieving homogeneous high critical currents in long lengths of Bi-2212 wires [3]. OP processing also enables varying pO_2 in a wide range above 1 bar. For the optimization of the processing procedure, as well as for the establishment of acceptable temperature and pressure margins, it is of interest to verify how pO_2 influences the phase sequence and the Bi-2212 precursor melting and recrystallization behaviors.

Since the development of high energy synchrotron beam lines it has become possible to directly observe the phase changes inside a superconducting wire that is placed inside a furnace. This enables non-destructive and time resolved *in situ* process studies with various experimental techniques [4]. High energy synchrotron X-ray diffraction is particularly useful to monitor phase changes during the processing of superconducting wires [5].

Previously we have reported on the formation of porosity and the phase changes occurring in a Bi-2212 wire during processing in pO_2=0.21 bar [6]. In this article we report for the first time the direct observation of the phase changes during heat cycles at $pO_2 \geq 1$ bar.

II. Experimental details

A. The samples

All experiments have been performed with 5 cm-long PIT type Bi-2212/Ag wires, which were produced by Oxford Superconducting Technology (OST) using Nexans precursor powder of $Bi_{2.17}Sr_{1.94}Ca_{0.89}Cu_{2.00}O_{8+\delta}$ composition (OST billet number PMM 100610, in the following referred to as W13). The as-drawn wire, with a nominal diameter of Ø=0.8 mm, has a 37×18 filament architecture and a Bi-2212 volume fraction of 25.8%. After standard 100 bar overpressure HT the volume fraction of Bi-2212 is 23.6%, and J_c at 4.2 K and 20 T of a W13 wire exceeds 2500 A/mm^2 using the densified cross section area [3]. The samples are identical to the straight Bi-2212/Ag wire samples that are often used for critical current (I_c) measurements.

B. X-ray diffraction

High energy synchrotron X-ray diffraction measurements were performed in the ID15B beamline of the European

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Synchrotron (ESRF). Diffraction patterns were acquired in transmission geometry using a high-efficiency high-readout-speed area detector. During the *in situ* HTs one pattern was acquired every 5 minutes. More details about the diffraction experiment can be found in [6].

For phase identification at a given temperature T, we have used room temperature XRD patterns (Table I) with shifts of d-spacing values estimated as $d(T)=d(RT)\times(1+\alpha T)$ with the isotropic thermal expansion coefficients either taken from the literature (for Ag, Bi-2212) or assumed to be $\alpha=10^{-5}$ K^{-1} for other compounds.

TABLE I
CRYSTALLOGRAPHIC DATA OF BI-SR-CA-CU-O COMPOUNDS USED IN THIS STUDY

Compound[a]	Space group	RT Lattice parameters (Å)	Sr/Ca
Bi-2212 [7]	*Pmmm*	a=b=5.405; c=30.805	1.94/0.89
Bi-2201 [8]	*Pnam*	a=b=5.385; c=24.547	1.8/0.4
2:4CF-HT [9]	*Pc*	a=11.209; b=5.915; c=19.943; β=101.64°	3:1
2:4CF-LT [10]	*P2₁/n*	a=8.397; b=5.999; c=5.900; β=89.99°	3:1
14:24AEC [11]	*CCC2*	a=11.395; b=13.055; c=27.413	10:4
1:1AEC	*Cmcm*	a=3.493; b=16.204; c=3.886	0.6/0.4
CuO [12]	*C12/C1*	a=4.685; b=3.426; c=5.130; β=99.55°	

[a] 2:4CF=$Bi_2(Sr_{4-y}Ca_y)O_7$ (CF=Copper-Free; LT and HT stand for low- and high-temperature modifications); 14:24AEC=$Sr_{14-z}Ca_zCu_{24}O_{38}$; 1:1AEC = $Sr_{1-x}Ca_xO_2$ (AEC = Alkaline Earth Cuprate).

C. Temperature and oxygen partial pressure control

Two furnaces have been used for the *in situ* XRD experiments. The HTs in inert gas and in ambient air have been performed under a continuous gas flow at ambient pressure in the ID15 tomography furnace, as described in [6].

HTs in pO_2>0.21 bar have been performed using a set-up that has been developed for combined *in situ* high energy XRD and mass spectrometry investigations during catalyzed gas/solid or liquid/solid reactions [13]. This set-up consists of a high pressure cell made of a single crystal sapphire tube, which is heated by a dedicated furnace. For the study of Bi-2212/Ag superconductors, the set-up was modified so that an S-type (Pt-Rh/Pt) thermocouple can be spot-welded onto the Ag matrix of the Bi-2212 wire for the temperature control up to 900 °C. The thermocouple is welded onto the wire about 2 mm from the X-ray beam position during XRD measurements. The estimated accuracy of the temperature measurement is better than ±10 °C. The temperature ramp rates during heating were 160 °C/h up to 820 °C, and then 50 °C/h up to the maximum temperature, similar to the rate during a typical Bi-2212 melt processing HT [6]. The wires were cooled from the peak temperature to room temperature within few hours, much faster than during a standard HT that lasts typically 3 days.

The partial pressure of O_2 was changed by changing the total pressure of industrial Air (Zero Air from Air Products Analytical Gases) from 1 bar to 100 bar. A small leak was added to the high pressure cell in order to have gas exchange during the HT cycle.

III. RESULTS

Below we present the phase sequences during Bi-2212 HT at different pO_2 ranging from pO_2=0.21 bar up to pO_2=5.5 bar.

A. Phase sequence during HT at pO_2=0.21 and 1.05 bar

Fig. 1 shows the evolution with temperature of XRD patterns that have been recorded during the pO_2=0.21 bar HT in ambient air. No major phase changes are observed prior to the Bi-2212 melting decomposition.

A phase with prominent diffractions peaks at Q=2.047, 2.078 and 2.108 $Å^{-1}$, tentatively identified as 2:4CF-HT, is formed when Bi-2212 melts around 880 °C. Minor diffraction peaks that occur at the same temperature could be characteristic for 1:1AEC phase. The Bi-2212 recrystallization and simultaneous 2:4CF-HT decomposition are detected on cooling at about 17 °C below the Bi-2212 decomposition and 2:4CF-HT crystallization temperatures. The Bi-2212 texture development can be seen by the increase of the Bi-2212 (020)(200) peak intensity with respect to that of the (117), (113) and (115) peaks.

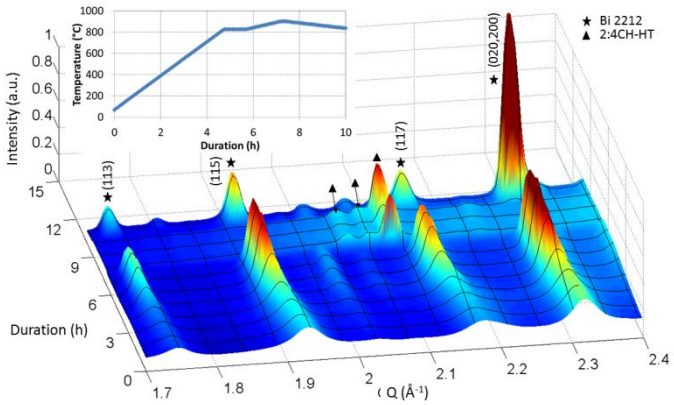

Fig. 1. Sequence of XRD patterns acquired during the HT in a flow of ambient air (pO_2=0.21 bar) with indexing of the major peaks. The temperature cycle is shown in the insert.

The appearance of a minor diffraction peak at Q≈2.11 $Å^{-1}$, probably characteristic of 2:4CF-LT, on heating at around 650 °C, may be an indication of some Bi-2212 phase instability.

XRD patterns upon heating in pO_2=1.05 bar are similar to those observed in pO_2=0.21 bar. Changes in the patterns that can be related to precipitation of a small amount of Bi-2201 and presumably 2:4CF-LT+CuO with subsequent reformation of Bi-2212 phase were observed on heating from 550 to 770 °C. In pO_2=1.05 bar, the Q≈2.11 $Å^{-1}$ peak (likely, the 2 1 -1 peak of 2:4CF-LT) to Bi-2212 (115) peak area ratio was roughly three times larger than it was in pO_2=0.21 bar.

B. Phase sequence in pO_2=5.5 bar (heating) and pO_2=0.45 bar (cooling)

In this experiment the oxygen partial pressure was kept constant at pO_2=5.5 bar during heating. At 869 °C, when the precursor was already molten it was reduced to pO_2=0.45 bar.

The sequence of XRD patterns acquired during this pressure and heat cycle are shown in Fig. 2.

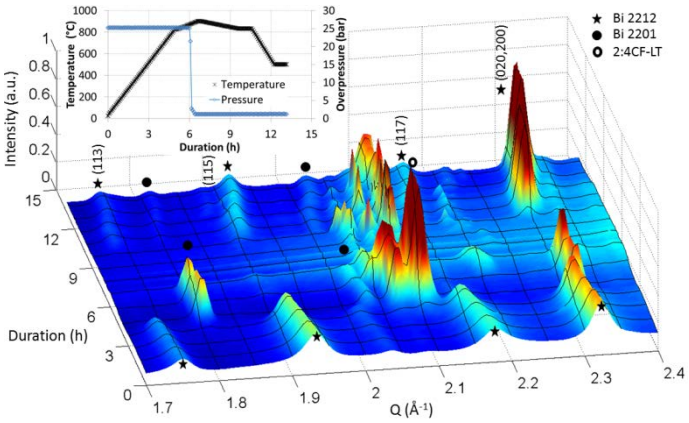

Fig. 2. Sequence of XRD patterns recorded during heating up at pO_2=5.5 bar and cooling down at pO_2=0.45 bar. The temperature and pressure cycles are shown in the inset.

In pO_2=5.5 bar Bi-2212 starts to decompose in the solid state above 450 °C, and disappears at 650 °C. As illustrated in Fig. 3, the Bi-2212 decomposition reaction has been identified as Bi-2212=>Bi-2201+2:4CF-LT+CuO. This phase assemblage remains until about 780 °C above which small amounts of new phases start to form, probably 2:4CF-HT and 14:24AEC.

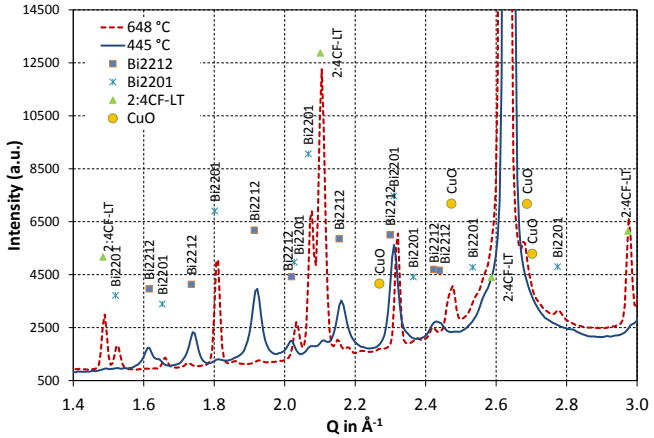

Fig. 3. Comparison of XRD patterns acquired at 445 and 648 °C upon heating in pO_2=5.5 bar with Bi-2212, Bi-2201, CuO and 2:4CF peaks from reference pattern (see Table I).

As it can be seen in Fig. 2, cooling in 0.45 bar O_2 resulted in recrystallization of the Bi-2212 phase starting at about 850 °C. The relatively stronger Bi-2212 (020)(200) peak intensity after recrystallization is due to the texturing of the Bi-2212 during recrystallization.

C. Influence of pO_2 on the Bi-2212 decomposition reaction

The Bi-2212 peak area evolutions during heating at different pO_2 are compared in Fig. 4. It is immediately obvious from the Bi-2212 area evolution that a large amount of Bi-2212 is transformed prior to precursor melting when heating is performed in pO_2=1.5 bar and 5.5 bar. We assume that the increase of the Bi-2212 peak area when the HT is performed at lower pO_2 is due to the crystallization of Bi-2212 from powder that was amorphous after the wire drawing process.

At pO_2=0.21 and 1.05 bar, Bi-2212 melting is completed at approximately 880 °C and at pO_2=1.5 bar precursor melting is completed at 860 °C. At pO_2=5.5 bar the Bi-2212 solid state transformation to Bi-2201+2:4CF-LT+CuO is completed at 650 °C.

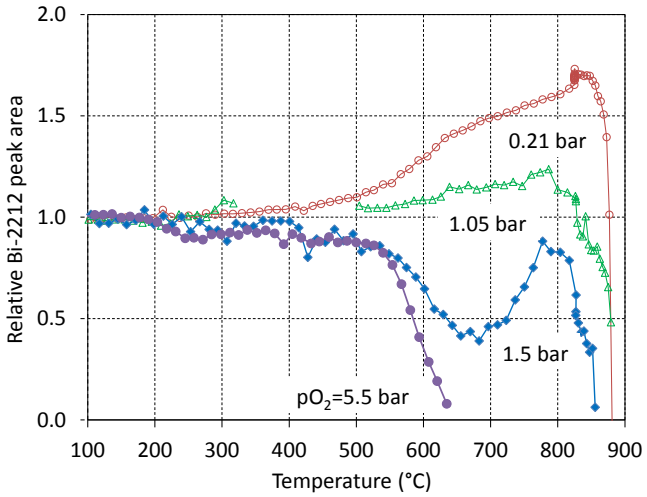

Fig. 4. Relative Bi-2212 peak area evolution during heating at different pO_2.

Only a tiny amount of Bi-2212 transforms into second phases when the HT is done in pO_2=0.21 bar. During heating at pO_2=1.05 bar, a slightly larger amount of second phase is formed. Increasing pO_2 further increases Bi-2212 instability.

In pO_2=1.5 bar Bi-2212 is unstable above 350 °C, and a significant amount of Bi-2212 decomposes to Bi-2201+2:4CF-LT+CuO, but partly reforms again from 670 to 820 °C. The strong influence of pO_2 changes above 1 bar on the amount of second phases formed is clearly seen in Fig. 5, which compares the evolution of prominent diffraction peaks of the main secondary phases, Bi-2201 and presumably 2:4CF-LT, during heating at pO_2=1.05, 1.5 and 5.5 bar.

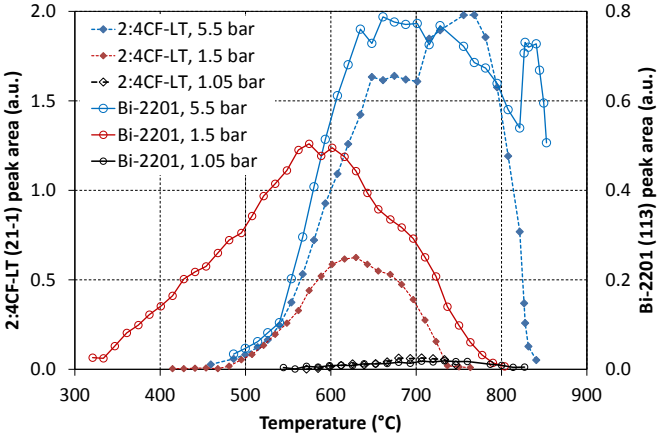

Fig. 5. Relative Bi-2201 and 2:4CF-LT peak area evolution during heating at pO_2=1.05, 1.5 and 5.5 bar.

IV. Discussion and Conclusion

Current limiting mechanisms in Bi-2212 PIT wires include obstructions of the current path by porosity [14] and second phase inclusions. An important goal of the Bi-2212 melt processing is therefore to minimize the formation of second phases while forming well-connected and textured Bi-2212 filaments.

Here we report for the first time a direct observation of the phase changes inside Bi-2212 round wires during processing at different oxygen partial pressures above ambient pressure. The 5 cm-long wire samples with closed ends that have been used in this XRD study are identical to the samples used for critical current measurements that are representative for long wires in magnet coils [15].

We found that in the range pO_2=0.21-1.05 bar only a small amount of Bi-2212 decomposes in the solid state prior to precursor melting, and there is only a relatively small influence of pO_2 on the phase sequence. However, further increasing pO_2 strongly changes the phase sequence. At pO_2=1.5 bar Bi-2212 decomposes partly prior to melting, and the precursor decomposition temperature is about 20 °C lower than it is at pO_2=1.05 bar. At pO_2=5.5 bar Bi-2212 decomposes at the very low temperature of about 630 °C. A similar decrease of the Bi-2212 decomposition temperature with increasing pO_2 has also been reported in [16,17]. In the study of thick Bi-2212 films the solid state Bi-2212 decomposition at pO_2=5 bar occurred at about 730 °C [16], which is about 100 °C higher than we observed the decomposition in the state-of-the-art multifilament Bi-2212 wire.

Since the stability boundary above which substantial Bi-2212 decomposition occurs prior to the precursor melting is close to pO_2=1 bar, reducing pO_2 below 1 bar, which is the commonly used oxygen partial pressure in Bi-2212 melt processing, would increase the pO_2 margin and could make the process more robust.

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