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# A STUDY OF PARAMETERS THAT INFLUENCE GROWTH AND STABILITY OF THE $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_y$ PHASE

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## ABSTRACT

The growth and stability of the $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_y$ (Bi-2223) phase contained in silver-sheathed wires has been investigated by a combination of x-ray diffraction, scanning electron microscopy, energy dispersive x-ray analysis, and transmission electron microscopy. Silver tubes loaded with Bi-2223 precursor powders were processed into filaments using established metallurgical techniques. The filaments were then heat-treated at selected temperatures (800 to 845°C) for a range of times (10 to 6000 min) in a 7.5% oxygen atmosphere. From these studies it has been possible to investigate the time-temperature-oxygen pressure domains wherein $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) + second phases transform to Bi-2223. Fractional conversion (Bi-2212 --> Bi-2223) versus time data show good conformance to the kinetic model for a diffusion-controlled reaction at the interface between thin sheets and a fine powder or a fluid. Quenching experiments also reveal that the Bi-2223 phase is stable in a limited temperature interval between 810 and 830°C.

## INTRODUCTION

(Bi,Pb)-Sr-Ca-Cu-O superconducting wires produced by the oxide-powder-in-tube (OPIT) method have demonstrated the ability to support large critical currents in high magnetic fields when the superconducting oxide is $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_{10}$ (Bi-2223) [1,2]. However, the preparation of single phase Bi-2223 is still difficult due to poor understanding of its complex phase diagram and melting behavior [3-5]. Moreover, the rate of formation of the Bi-2223 phase can be exceptionally sluggish, often requiring several hundred hours to achieve complete conversion [4,5]. In this paper, we report the results of an isothermal kinetics study of the formation of Bi-2223 in silver-sheathed wires. We show that the measured fractional conversion, C, versus time, t, curves fit a diffusion-controlled, two-dimensional, nucleation-growth equation, through comparisons of a series of measured (C, t) values and the various theoretical functions derived for different kinetic models. Finally, we present data that map the temperature interval of single-phase Bi-2223 stability and describe its decomposition behavior at higher and lower temperatures in 7.5 % oxygen.

## EXPERIMENTAL PROCEDURE

Precursor powders having a composition of $Bi_{1.7}Pb_{0.3}Sr_{1.9}Ca_{2.0}Cu_{3.0}O_y$ were loaded into silver tubes and processed into wires using established metallurgical forming techniques [6]. X-ray diffraction (XRD) measurements on the powders revealed that $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) was the major phase with no diffraction peaks due to Bi-2223. The tape samples used in the experiments were typically 8 mm wide, 0.25 mm thick, and ~25 mm long. They were heat-treated in a stainless steel chamber surrounded by a resistively-heated furnace with three independently programmable heating zones [7]. Temperatures were monitored using a calibrated Pt/Pt-Rh thermocouple positioned close to the samples and stabilized to within ± 1°C. Samples were initially kept in a cooled baffle above the hot zone at temperatures below 50°C, immersed into the preheated furnace, equilibrated at the chosen temperature for a fixed time, and quenched in a silicone oil bath held at room temperature. All experiments were carried out in 7.5% oxygen (the balance being nitrogen).

XRD measurements were made on peeled sections of each quenched tape sample using a Philips diffractometer with Cu Kα radiation. The fractional conversion, C, of the Bi-2223 phase was calculated on the basis of the XRD intensity ratios of the $(0010)_{2223}$ and $(008)_{2212}$ peaks [8]. The resulting samples were examined by scanning electron microscopy (SEM) on a JEOL 35U equipped with an energy-dispersive x-ray analyzer (EDX). Transmission electron microscopy (TEM) was carried out on a Philips CM30 analytical microscope. Specimens were prepared from slides by mechanical polishing and dimpling to ~20 µm thickness, followed by argon ion milling at 5 kV with a gun current of ~1 mA.

## RESULTS AND DISCUSSION

Figure 1 shows a typical C-t plot summarizing characteristic kinetic behavior observed for isothermal formation of the Bi-2223 phase from Bi-2212 + second phases at 825°C in 7.5% $O_2$. Evidence for the onset of formation of the Bi-2223 phase typically appeared after an initial induction period of ~100 minutes. Once the reaction started, the C-t curve followed an S-shaped profile that plateaued in $\leq$ ~5300 minutes. The presence of an induction period indicates a slow process preceding establishment of the main transformation, which may be due to either the development of stable Bi-2223 nuclei in the system or some chemical reorganization of the second phases. It should be pointed out that the growth behavior is very sensitive to a number of processing conditions, most notably the nature of any heat-treatment procedures used on the precursor powder [8].

In order to obtain information concerning the reaction mechanism, the experimental data were compared with theoretical functions derived for kinetic models based on various reaction interface geometries and rate-limiting phenomena. A summary of such models has been provided by Hulbert [9] for solid-state reactions limited by different mechanisms, including nuclei growth (NG), diffusion (D), and phase boundary (PB) reactions. It was found that the fractional conversion data could be fitted well with a simple two-dimensional (2D), diffusion-controlled, nucleation-growth equation (Fig. 2), which can be expressed [9] as

$$\{-\ln(1-C)\}^{1/n} = k_0\, t \exp(-E/RT)$$

where $k_0 = 1.71 \times 10^{-22}$ is the rate constant, E is the activation energy, R is the universal gas constant, T is the annealing temperature in degrees Kelvin, t is the annealing time, and n is an exponent parameter which is dependent on the nature of the reaction mechanism, the nucleation rate, and the geometry of the nuclei (for this work we chose n = 1, corresponding to a constant and/or deceleratory nucleation).

TEM observations strongly support a two-dimensional reaction model. Side-view micrographs taken from the direction parallel to the wire surface (i.e., beam direction perpendicular to the rolling force direction) show partially converted zones of Bi-2223 within 2212 grains (Fig. 3). Projection of the reacting zone to the observation plane reveals a needle-like shape (see Fig. 3) which corresponds to a thin plate or a thin sheet in the full grain. This indicates that the reaction zone is indeed two-dimensional, presumably because the growth of the product in another dimension is limited by the platelike microstructure of its precursor, i.e., the 2212 phase. The product is undoubtedly the Bi-2223 phase, as evidenced by its larger interplanar spacing (~1.85 nm) compared with the smaller spacing (~1.5 nm) of the surrounding 2212 phase [8].

The reaction appears to start at the grain boundary (where an amorphous phase is observed by TEM) and gradually extend into the 2212 precursor grain by diffusion of the required $Ca^{2+}$ and $Cu^{2+}$ into the reactant interface to form the Bi-2223 phase (see Fig. 3). The extra $Ca^{2+}$ and $Cu^{2+}$ are transported from Ca- and/or Cu-rich phases, such as $Ca_2CuO_3$ and CuO, through grain boundaries. It is clear that the presence of a liquid phase would enhance significantly the diffusion of $Ca^{2+}$ and $Cu^{2+}$ due to the absence of the stabilizing influence of the regular lattice. However, even if interdiffusion is dramatically accelerated by a liquid phase, the formation of the Bi-2223 could still be sluggish due to the slow solid-state diffusion of extra $Ca^{2+}$ and $Cu^{2+}$ from grain boundaries to the reactant surface. In this sense, reduction of the initial reactant grain size should be helpful in promoting Bi-2223 formation, as has been the case for samples that were subjected to intermediate grinding [10].

The activation energy, E, is derived from the slope of the plot ln(-ln(1-C)) against 1/T (Fig. 4). The data appear to fall on a pair of intersecting lines, with the line in the lower temperature sector having a steeper slope that evidences a higher activation energy than the line in the higher temperature sector. One possible interpretation of this result is that the conversion rate in the temperature sector below the crossing point (~819°C) is controlled by a solid-state reaction (thus a high diffusional activation energy), while the rate at temperatures above the intersection point is controlled by a liquid phase reaction having a much lower diffusional activation energy.

Finally, we have determined the stability range of single phase Bi-2223 and studied its decomposition behavior. In this case, samples were subjected to a two-step heat treatment. They were first immersed and annealed at 825°C (i.e., to convert the precursor powder to single phase Bi-2223), stepped to lower (810°C, 800°C) or higher (840°C, 845°C) temperatures, and held for 3000 minutes before quenching. After these treatments, XRD revealed that non-2223 peaks, which were mainly due to 2212, appeared for the sample annealed at 800°C (Fig. 5). For samples annealed at 840 and 845°C, peaks located at $2\theta = 21.9°$ and $29.3°$, corresponding to the (006) and (008) reflections of the $Bi_2Sr_2CuO_6$ (2201) phase, were clearly present (Fig. 5). It can be concluded from these observations that the Bi-2223 phase in silver-sheathed wires has a limited thermostability range with a lower boundary between 800 and 810°C and an upper boundary between 830 and 840°C in 7.5% oxygen.

## ACKNOWLEDGEMENT

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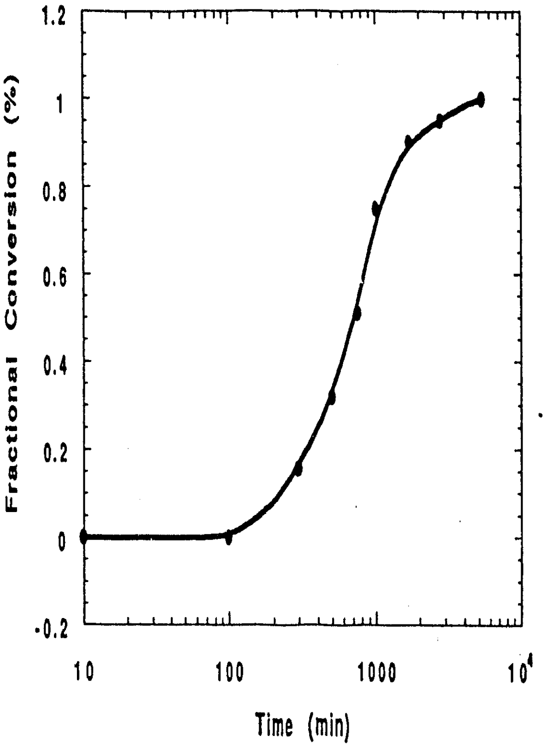

Figure 1. C-t plot of as-processed sample.

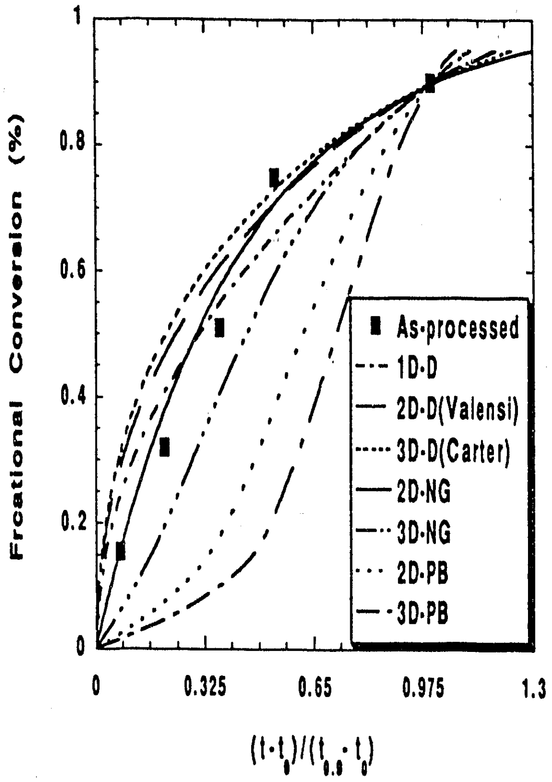

Figure 2. The comparison of reduced time ($t_r=t/t_{0.9}$) plots.

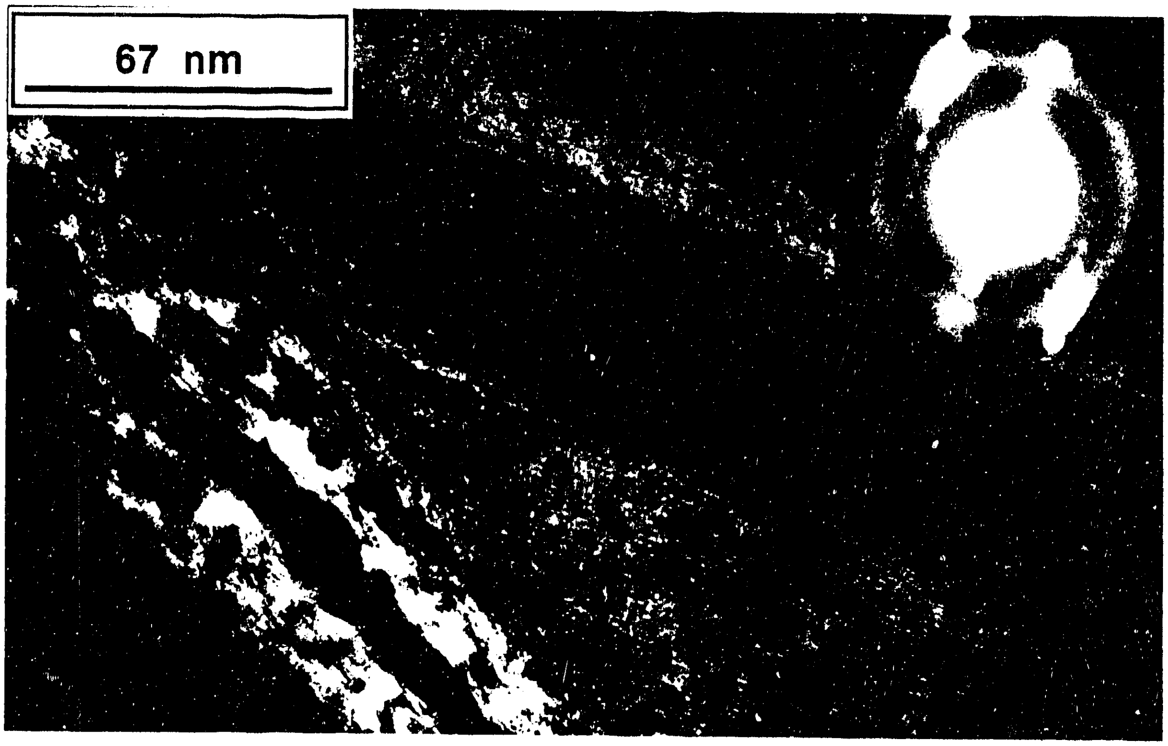

Figure 3. TEM image of a partially reacted zone.

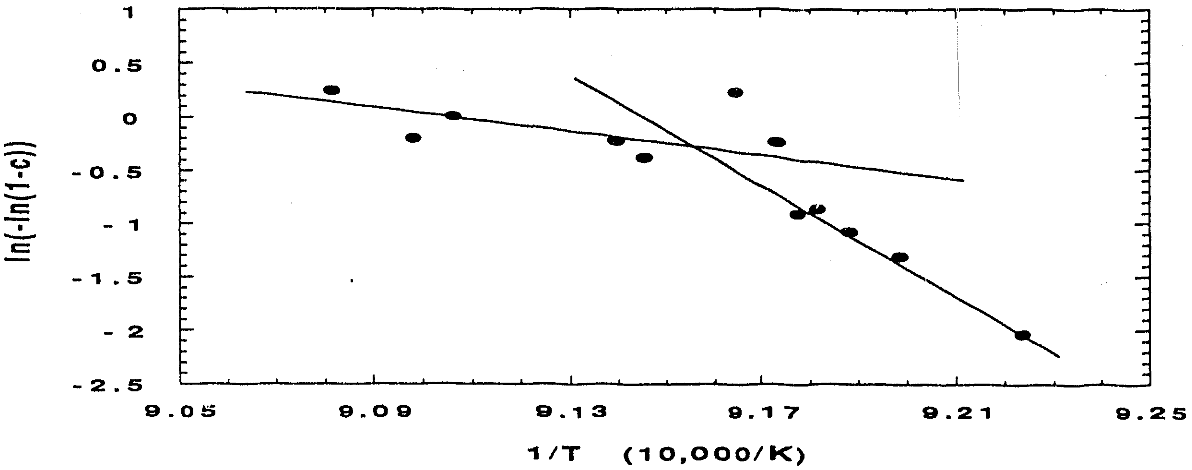

Figure 4. Ln(-ln(1-C)) against 1/T for various temperatures using a fixed equilibration time of 1000 min.

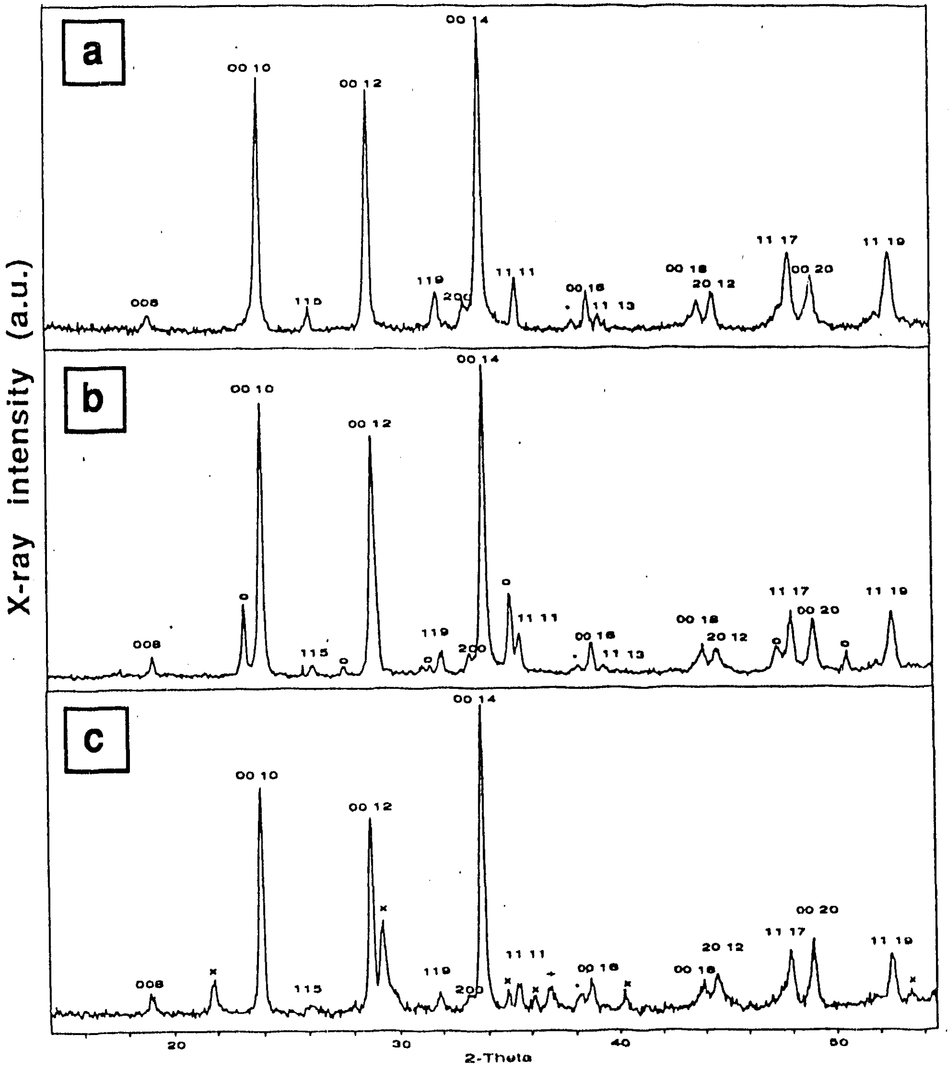

Figure 5. X-ray diffraction patterns (Cu Kα radiation) of (a) the sample annealed at 825°C, (b) the sample annealed first at 825 and then at 800°C, and (c) the sample annealed first at 825 and then at 845°C. Peaks due to 2212, 2201, and Ag are indicated by (o), (x), and (*).

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