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INTERGRANULAR PHASES IN CYCLICALLY ANNEALED $YBa_2Cu_3O_{7-x}$ AND THEIR IMPLICATIONS FOR CRITICAL CURRENT DENSITIES

by

Andrew P. Clarke

A thesis submitted in partial fulfillment
of requirements for the degree

of

MASTER OF SCIENCE

in

Physics

Approved:

_____	_____
Wilford Hansen Major Professor	Jan J. Sojka Committee Member
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J. R. Dennison Committee Member	Byron R. Burnham Dean of Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah

2008

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ABSTRACT

Intergranular Phases in Cyclically Annealed $YBa_2Cu_3O_{7-x}$

and Their Implications for Critical Current Densities

by

Andrew P. Clarke, Master of Science

Utah State University, 2008

Major Professor: Dr. Wilford N. Hansen
Department: Physics

We report changes in the intergranular material and grain morphology of $YBa_2Cu_3O_{7-x}$ during cyclic anneals between 780 and 980 ºC in oxygen at atmospheric pressure. Two endothermic reactions were detected: (a) the eutectic reaction of $YBa_2Cu_3O_{7-x}$ with CuO and $BaCuO_2$ at 900 ºC (enthalpy ΔH_a) and (b) the peritectic reaction of $YBa_2Cu_3O_{7-x}$ with CuO at 950 ºC (ΔH_b). During the first anneal, only reaction (b) is detected, and although it should only occur if there is an excess of CuO, its signature is present in all published data. Cyclic annealing causes a monotonic decrease in ΔH_b and an increase in ΔH_a, larger average grain sizes, and greater volume fraction of the superconducting phase. A steady state is reached after 10 cycles at which point $\Delta H_b = 0$. We propose a model that explains the origin of the intergranular CuO and the changes in the intergranular material composition with cyclic annealing.

(45 pages)

ACKNOWLEDGMENTS

This work was supported by the United States Department of Energy, Office of Basic Energy Science, Division of Material Sciences and a grant from the Associated Western Universities, Inc. I would like to express my deep gratitude to Dr. Ricardo B. Schwarz for his guidance, support, and supervision of this work during my time at Los Alamos, and his continued moral support and friendship since. I also thank Joseph D. Thompson for his measurements and interpretations, editing contributions, and many helpful discussions. I am also indebted to Philip Nash, Martin Maley, and Jeff Willis for their many helpful discussions.

The final presentation of this work as a thesis, long after it was finished, was made possible by of the patience and support of my thesis committee: Professors Wilford Hansen, Jan Sojka, and JR Dennison.

I give special thanks to my wife, Leanne, who always supports my dreams and my efforts to make them real.

Andrew P. Clarke

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CHAPTER I

INTRODUCTION

Among the requirements for a useable superconductor are high critical current density, J_c, and high critical magnetic field, H_{c2}. Under both these requirements, polycrystalline compacts of $YBa_2Cu_3O_{7-x}$ have not performed as well as oriented thin films. So far, the best bulk specimens have been highly-textured, large-grained samples prepared by the melt-textured-growth process [1, 2], but even in these samples J_c is only approximately 1% of the J_c in oriented thin films [3]. Several authors [4-8] have compared the measured J_c with that deduced from magnetic hysteresis measurements using the Bean Model [9-12]. These comparisons show that the intergranular J_c in bulk $YBa_2Cu_3O_{7-x}$ is at least as large as that measured in thin films. Theoretical models [13] have been developed to explain the measured transport properties in bulk $YBa_2Cu_3O_{7-x}$ in terms of superconducting grains connected by superconducting "weak links," and calculations based on these models explain both the low measured critical current density and the further decrease in this current under relatively weak applied magnetic fields.

Although investigators now agree that the relatively low J_c in bulk $YBa_2Cu_3O_{7-x}$ is mainly caused by second-phase intergranular material, our understanding of these phases is still limited. In this paper we study intergranular reactions that take place when annealing these materials in oxygen at temperatures close to 900 ºC. We further study the evolution of the intergranular material under cyclic annealing in oxygen between 780 ºC and 980 ºC.

CHAPTER II

PREVIOUS WORK—LITERATURE REVIEW

The phenomenon of superconductivity was first reported in 1911 by Onnes [14], who detected it in mercury at critical temperature, T_c , equal to 4.12 K. The discovery of other superconductors soon followed, with lead (Pb) at T_c = 7 K and niobium nitride (NbN) at 16 K.

The expulsion of static magnetic fields by superconductors was first reported by Meissner and Ochsenfeld [15] in 1933. The Meissner Effect differed from the classical effect described by Lenz's Law, in that Lenz's Law only predicts the expulsion of *changing* magnetic fields due to classical diamagnetism, whereas superconductors expel even *static* magnetic fields. This discovery allowed researchers to discern between true superconducting behavior and simple low resistivity in mixed-phase samples, and in samples through which electrical current could not be easily passed. London and London [16] showed, in 1935, that the Meissner Effect was caused by the minimization of the electromagnetic free energy of the current-carrying superconductor, and was continuous at a surface boundary, with a characteristic penetration into the superconductor called the London Penetration Depth.

In 1957, Abrikosov [17] published a paper proposing the existence of two classes of superconductor, now known as Type I and Type II, based on the Ginsburg-Landau theory of superconductivity [18]. Type I describes materials with discrete transition field strength, H_c, above which superconductivity ceases, and the latter materials (Type II) that exhibit a mixed-phase transition regime bounded by first and second discrete critical field

strengths, H_{c1} and H_{c2}. This gave researchers insight into so-called “spin glass” (Type II) materials that pin quanta of magnetic field (fluxons). This had later significance in understanding the mechanisms involved in high-T_c superconductors.

In 1962, Josephson [19] predicted the tunneling of Cooper pairs, the basic current carriers in the superconducting theory of Bardeen, Cooper, and Schrieffer [20], across thin insulating barriers. The Josephson Effect would later help explain the disparity between the measured critical current density, J_c, at which superconductivity ceases, and the value predicted from measurements of Hc, using the Bean model [9-12], in mixed-phase superconductors. Significantly, the Josephson Effect became the basis for a new ultra-sensitive Superconducting Quantum Interference Device (SQUID) magnetometer that allowed researchers to detect superconducting behavior in small fractions of mixed-phase samples.

In 1986, Bednorz and Muller [21] first reported the onset of superconducting behavior in mixed phase BaLaCuO powders. They analyzed their samples using powder x-ray diffractometry and isolated the superconducting phase Ba:La2Cu3Ox, where Ba represented only a few atomic percent. Once isolated as the superconducting phase, exact mixtures were made and single phase samples could be examined. SQUID magnetometer studies indicated a transition to superconductivity at T_c = 36K, roughly twice the critical temperature of any previously reported superconductors.

These *cuprate perovskite* materials were studied further, and in 1987 Wu et al. [22] reported a superconducting phase within the YBaCuO system at $YBa_2Cu_3O_{7-x}$ with a T_c = 93K. This caused much excitement and an explosion of research into these high-T_c superconductors, or HTSC.

Further development of the new HTSC materials would be required if they were to become useable, for though these brittle ceramics expelled magnetic fields as strong Type II superconductors, they could carry very little superconducting current [23-25]. In the research community there were reports [26-28] of thin films of $YBa_2Cu_3O_{7-x}$ that exhibited two orders of magnitude higher critical current densities than the best bulk samples measured, and no one was sure why. With similar H_c values, this difference inferred that the bulk samples consisted of superconducting grains separated by layers of insulating second phase materials, and that current densities were therefore limited by Josephson Effect tunneling across these intergranular "weak links."

We undertook the research reported here with the goal of determining the compositional and thermodynamic pathways taken by an amorphous powder of Y, Ba, Cu, and oxygen on its way to becoming $YBa_2Cu_3O_{7-x}$ crystalline. In doing this, we hoped to discover the processes that lead to the formation of the intergranular material limiting J_c, and perhaps uncover a remedy to its formation.

CHAPTER III

EXPERIMENTAL PROCEDURE

We mixed BaO_2, CuO, and Y_2O_3 inside an argon-atmosphere glovebox (O_2 and H_2O content less than 1 ppm) to make powder samples with the composition $YBa_2Cu_3O_x$. The BaO_2 was reagent grade from J. T. Baker Chemical Co. (Phillipsburg, NJ 08865) with an assay of 98 wt.% min. (major impurity $BaCO_3$ with less than 0.002 wt.% lead and less than 0.03 wt.% iron). The CuO was 99.999 wt.% from Aesar/Johnson-Matthey (Seabrook, NH 03874). The Y_2O_3 was 99.999 wt.% from Research Chemicals (Phoenix, AZ 85063). The CuO and Y_2O_3 powders were baked inside the glovebox for 1 h at 750 ^oC to remove absorbed water.

We used a high-energy Spex model 8000 mixer located inside the glovebox to mechanically alloy 6 g of powder using a hardened steel vial and hardened steel balls. Mechanical alloying (MA) is a high-energy ball-milling process originally developed to prepare nickel-based precipitation-hardened alloy powders [29]. Recently, researchers have also applied MA to the synthesis of amorphous metallic alloy powders [30]. During MA, the powder particles trapped between colliding balls are repeatedly fractured and cold-welded. This refines the powder structure, and for sufficiently long MA time, it leads to the formation of a true alloy. With MA there is always the danger that the milling may erode the vial and/or the balls and introduce impurities into the powder. By using a hardened steel vial and hardened steel balls, we minimized or eliminated this source of contamination. The weight of the vial and the balls after 10 successive MA experiments was the same within the 0.01 g accuracy of our balance. From this we estimate that if

impurities were introduced into the powder during MA, these amounted to less than 0.016 wt.%. We detected no iron by energy-dispersive X-ray analysis in a scanning electron microscope, which indicated that the iron content was below the 1 at.% resolution of the detector.

We used X-ray diffraction (Cu Kα radiation) and differential scanning calorimetry (DSC) to study structural transformations in the as-ball-milled powder during the first oxygen anneal, as well as during the subsequent cyclic anneals. All anneals were done in flowing oxygen using cooling and heating rates of 10 ºC min^{-1} except the final cooling from 780 ºC, which was done at 2 ºC min^{-1}. We prepared six loose-powder samples, 100 mg each, in this manner to study the effect of 1, 2, 4, 8, 14, and 20 cyclic anneals. Following the anneals in the DSC, the powder samples had sintered into compacts that were easily removed by tilting the alumina DSC cups. There was no reaction with the alumina cups. We cyclically annealed a seventh sample, made from a pressed rod, 67 times in an oxygen-purged tube-furnace using the same heating and cooling rates.

The superconducting properties of the samples were measured by magnetic susceptometry using a Quantum Design (San Diego, CA) SQUID magnetometer.

We used scanning electron microscopy (SEM) to measure grain size and to identify phases in samples that had been studied in the DSC and had undergone susceptometry measurements. For the SEM studies, we broke the sintered samples in half. One half of each was polished using an oil-based diamond paste, and both were mounted onto aluminum holders using colloidal graphite solution. We made composition determinations on the polished samples using energy-dispersive X-ray (EDX) analysis.

The deconvolution of the EDX spectra was done with a Kevex Analyst 8000 hardware and standard-less software. Although this technique can determine the relative amounts of metallic elements in alloys such as $YBa_2Cu_3O_{7-x}$ to an accuracy no better than ± 5 at.%, this accuracy is sufficient to discern between phases such as $YBa_2Cu_3O_7$, Y_2BaCuO_5, BaCuO2 and CuO. The EDX detector did not allow us to detect elements with atomic number below 11.

CHAPTER IV

RESULTS

Phase Transformations During the Synthesis of $YBa_2Cu_3O_{7-x}$

Figure 1 shows X-ray diffraction patterns of the mixed powder after 3 and 10 h of MA. After 3 h of MA the powder still has most of the Bragg peaks of the initial oxides. After 10 h of MA these peaks have disappeared and the diffraction pattern now has broad maxima and a few new Bragg peaks. The broad diffraction maxima indicate that the bulk of the powder is an amorphous oxide. Some of the new Bragg peaks belong to a cubic perovskite with lattice parameter close to the *a*-lattice parameter of $YBa_2Cu_3O_7$. In the figure the Bragg peaks of the cubic perovskite have been indexed in the notation of the tetragonal perovskite with $c \approx 3a$. The conclusion that the perovskite is cubic, rather than tetragonal, follows from the observation that the Bragg peaks such as (104) and (214), present in $YBa_2Cu_3O_{7-x}$, are absent in the mechanically alloyed powder. It is probable that these peaks are absent because the yttrium and barium atoms are disordered rather than arranged on the (00z) planes, alternating in the form …Ba-Ba-Y-Ba-Ba-Y-…, as required for the tetragonal form. A few Bragg peaks in curve (b) belong to phases we could not identify. During MA the powder loses oxygen; by weighing the vial and its contents before and after MA we deduce that the oxygen stoichiometry per YBa_2Cu_3 unit decreases from 8.5 in the as-mixed oxides to 7.9 ± 0.2 after 10 h of MA.

Figure 2 is a DSC trace typical of the first oxygen anneal of the as-mechanically-alloyed $YBa_2Cu_3O_x$ powder. The transformations labeled A, B1, B2 and C are

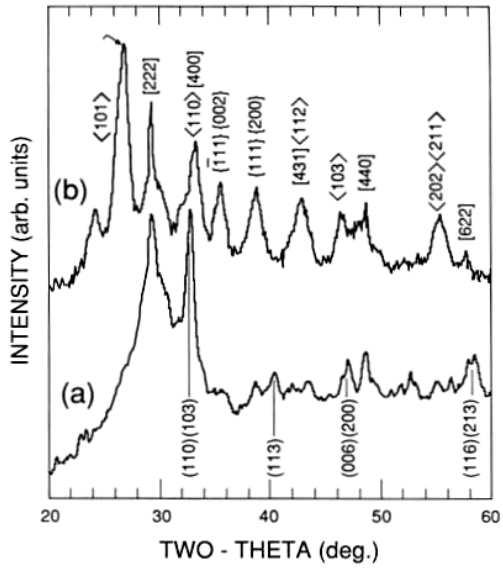


Fig. 1. X-ray diffraction patterns of mixed oxide powders after mechanical alloying for 3 h (top) and 10 h (bottom). The Bragg indices for the various compounds present are identified by bracket type: ($YBa_2Cu_3O_{7-x}$), [Y2O3], ⟨BaO2⟩ and {CuO}.

irreversible, and the subsequent heating DSC traces show only a smooth baseline curve from 100 to 890 C. In a separate study [31] we used X-ray diffraction and thermogravimetry to identify the crystalline phases present in samples rapidly cooled from temperatures below and above peaks A, B1 and B2. These measurements enabled us to identify the transformations giving rise to these peaks. Peak A (exothermic) results from the formation of two intermediate crystalline phases: Y_2O_3 and $BaCuO_2$. Peak B1 (endothermic) is accompanied by severe oxygen loss, as evidenced by thermogravimetry [31]. This loss is immediately followed by the crystallization of the tetragonal form $YBa_2Cu_3O_{7-x}$, which gives endothermic peak B2. The small transformation labeled C only occurs during an oxygen anneal (it is absent when annealing in air) and has not yet been identified. Using the ternary Y_2O_3 – BaO_2 – CuO equilibrium phase diagram proposed by Aselage and Keefer [32] we attribute endothermic peaks D and E to the

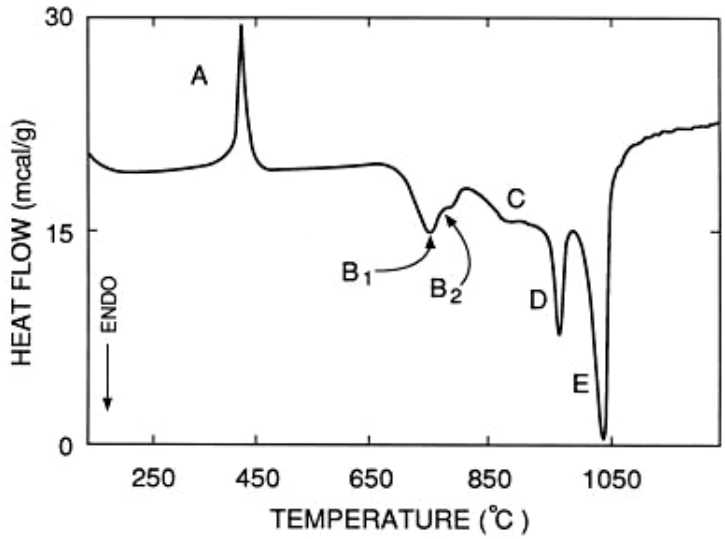


Fig. 2. DSC trace for the first oxygen anneal of the mixed alloy powders mechanically alloyed for 10 h. Sample weight = 60.80 mg.

following reactions involving the formation of melts:

$$(950\ ^{o}C) \qquad YBa_2Cu_3O_{7-x} + CuO \rightarrow Y_2BaCuO_5 + L(p_1) \qquad (1)$$

$$(1015\ ^{o}C) \qquad YBa_2Cu_3O_{7-x} \rightarrow Y_2BaCuO_5 + L(p_2) \qquad (2)$$

The large endothermic peak E in Fig. 2 is caused by the incongruent melting of $YBa_2Cu_3O_{7-x}$ into Y_2BaCuO_5 and the peritectic liquid $L(p_2)$. Because this melt reacts with the alumina cup in the DSC, we avoided reaching this temperature in all subsequent studies.

During a DSC study involving cyclic anneals between 800 and 980 ºC, we noted a continuous decrease in the enthalpy of transformation D. Figure 3 shows an overlay of DSC traces during the heating part of the first five cyclic anneals between 780 and 980 ºC. The enthalpy of transformation D decreases with each cyclic anneal, whereas a new transformation at 900 ºC, labeled F, appears after the sample has been cycled once. The

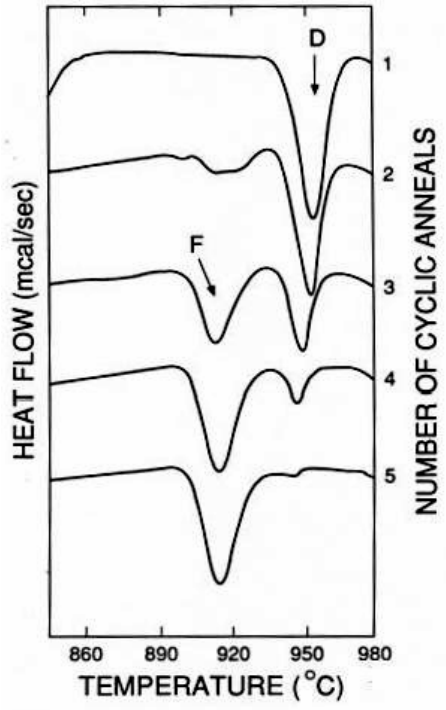


Fig. 3. DSC traces for five consecutive cyclic oxygen anneals.

area of transformation F increases with cycling, until, after 10 cycles, peak D is absent, peak F is stable, and the DSC trace is completely reversible. The enthalpies of transformations D and F are plotted as functions of the number of cyclic anneals in Fig. 4, showing the smooth, continuous nature of these changes.

To ensure that the change from peak D to peak F with cyclic anneal was not caused by a reaction between the powder and alumina in the calorimeter cups, we re-ground a sample that had been cyclically annealed four times (see curve 4 in Fig. 3) and repeated the thermal treatment in the same alumina cup. The DSC trace after re-grinding was very similar to curve 2 in Fig. 3, indicating that the transition from peak D to peak F results from reactions within the powder.

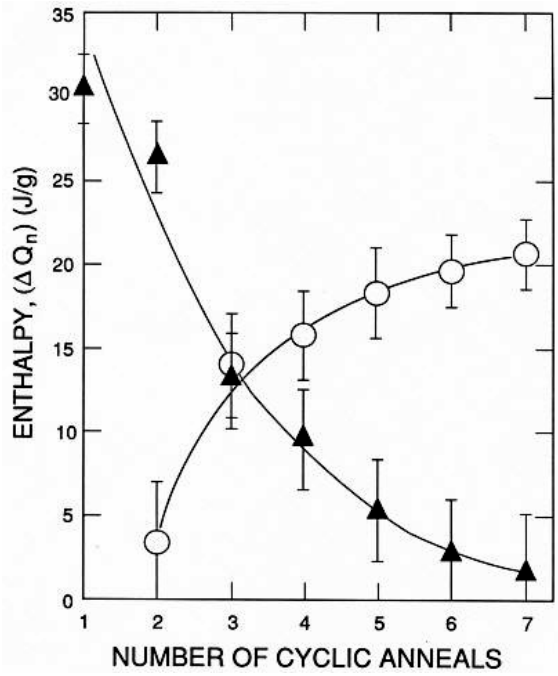


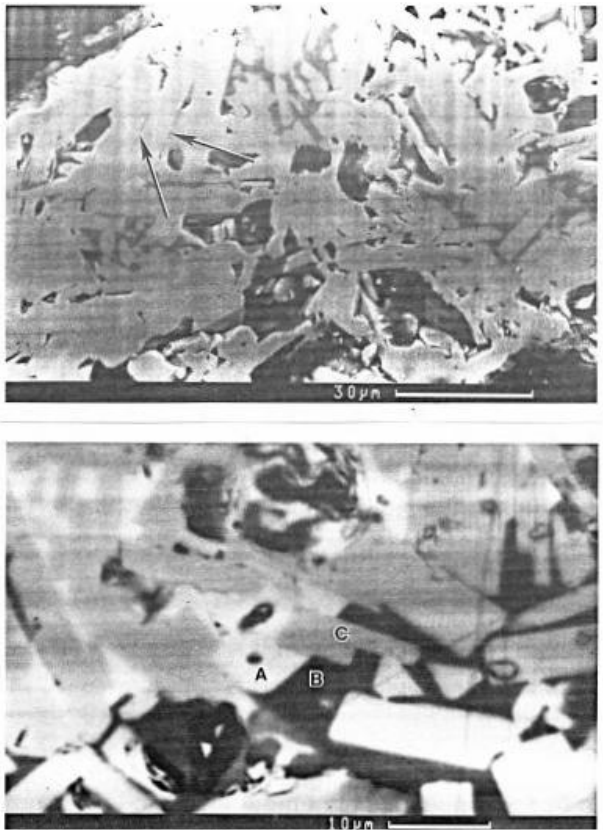
Fig. 4. Area under the DSC peaks D (filled triangles) and F (open circles) *vs*. number of cyclic oxygen anneals.

The ternary $Y_2O_3 – BaO_2 – CuO$ equilibrium phase diagram reported by Aselage and Keefer [32] enabled us to identify the reaction giving rise to peak F in the DSC traces as the following:

$$(900\ ^oC) \qquad YBa_2Cu_3O_{7-x} + BaCuO_2 + CuO \rightarrow L(e_1) \qquad (3)$$

Chemistry of the Intergranular Material

We used SEM and EDX analysis to study the intergranular material in samples cyclically annealed once and 14 times. Figure 5(a) shows the backscattered electron image of a sample heated to 980 ºC in flowing oxygen (i.e., above peak D in Fig. 2) and cooled to room temperature at 150 ºC min^{-1}. We observed two phases. For the major light phase, EDX revealed yttrium, barium and copper in atomic ratio close to 1:2:3. The



(a)

(b)

Fig. 5. Scanning electron micrographs of samples polished after 1 (a) and 14 (b) cyclic oxygen anneals. In (b), the components of the triple-point eutectic solidification are A = $BaCuO_2$, B = CuO and C = $YBa_2Cu_3O_{7-x}$.

minor dark phase had only copper. The two phases present, $YBa_2Cu_3O_{7-x}$ and CuO, are those on the left hand side of eqn. (1). Notice that thin layers of CuO, indicated by the arrows, surround several $YBa_2Cu_3O_{7-x}$ crystals. We believe that, at a temperature close to 950 ºC but before the peritectic liquid forms for the first time, CuO is distributed uniformly throughout the sample surrounding each of the $YBa_2Cu_3O_{7-x}$ crystals. Following the reaction at 950 ºC, most of the CuO appears concentrated at discrete regions, which, as seen in Fig. 5(a), contain small $YBa_2Cu_3O_{7-x}$ crystallites. This agglomeration could only have resulted from the migration of the peritectic liquid L(p1),

toward the more porous regions of the sample. The solidification of this liquid leads to the formation of small $YBa_2Cu_3O_{7-x}$ crystals, according to eqn. (1). We should note that Fig. 5(a) shows a region of the sample particularly rich in CuO which is not typical of the average.

The DSC trace for samples annealed 14 times shows only peak F, the 900 ºC endotherm. The backscattered electron image of such a sample, shown in Fig. 5(b), reveals three phases that appear as white, light-gray, and dark-gray, labeled A, B, and C. EDX analysis reveals that A is close to a 1:1 mixture of barium and copper, phase B is yttrium, barium and copper in atomic ratio close to 1:2:3; and the dark phase C has, again, only copper. We conclude that these three phases are $BaCuO_2$, $YBa_2Cu_3O_{7-x}$ and CuO, respectively. Notice in Fig. 5(b) that the three phases coexist at triple-points as required by the eutectic crystallization in eqn. (3).

Changes in the intergranular material composition are also detected by X-ray diffraction. Figure 6 shows X-ray diffraction patterns taken from samples annealed once and 20 times. The vertical scale has been enlarged. In the sample annealed once, the only Bragg peak clearly present besides those of $YBa_2Cu_3O_{7-x}$ is the (111) peak of CuO, whereas the sample cyclically annealed 20 times clearly contains $YBa_2Cu_3O_{7-x}$, CuO, Y_2BaCuO_5, and $BaCuO_2$. The presence of these phases is explained with the model discussed in Section 4.

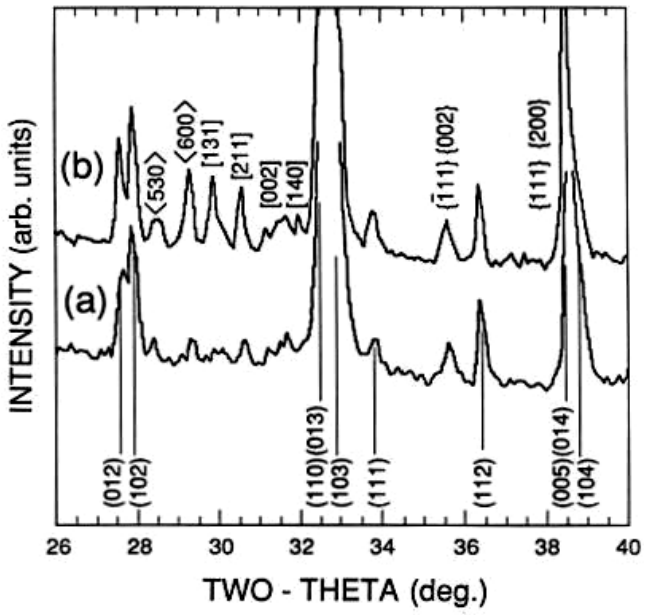
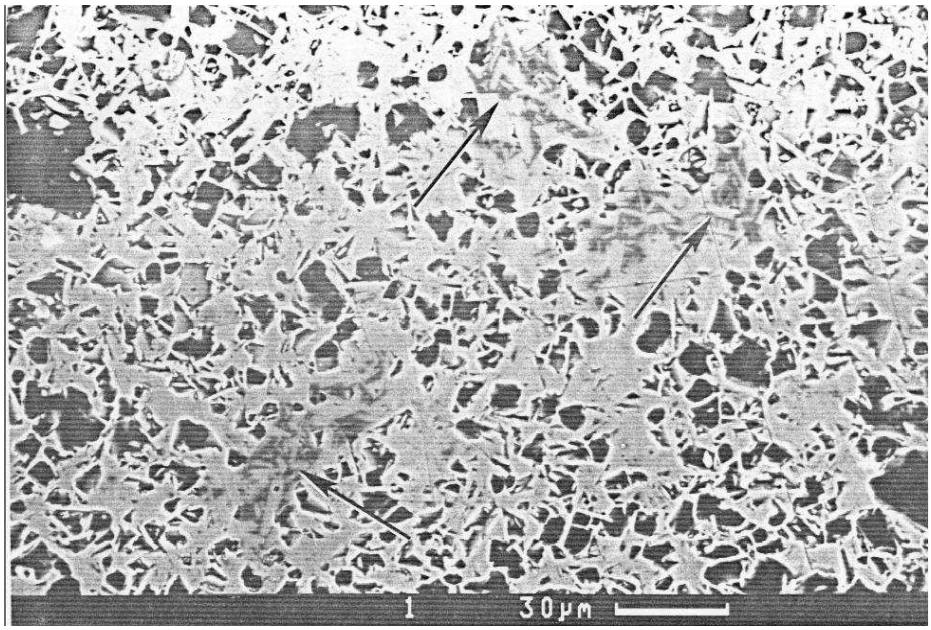


Fig. 6. X-ray diffraction patterns of YBa2Cu3O7-x cyclically annealed once (a) and 20 (b) times. The Bragg indices for the various compounds present are identified by bracket type: ($YBa_2Cu_3O_{7-x}$), [Y_2O_3], ⟨BaO_2⟩ and {CuO}. Note the increased splitting between the (012) and (102) reflections after 20 cyclic oxygen anneals.

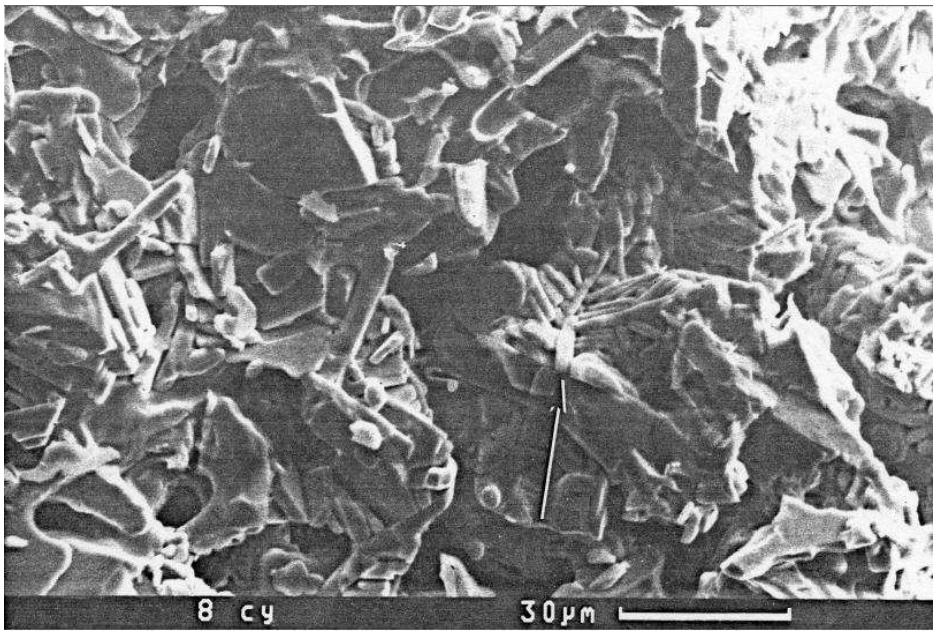
Grain Growth During Cyclic Annealing

During the cyclic anneal the average grain size increases monotonically, causing interesting changes to take place not only with regard to the grains themselves, but also in the morphology of the intergranular melts. In Figure 7 we illustrate these changes by comparing scanning electron micrographs of samples cyclically annealed 1, 8 and 67 times. The polished cross-section of a sample cyclically annealed once (Fig. 7(a)) shows the segregation and "pooling" behavior of the peritectic melt, which, upon solidifying, forms small $YBa_2Cu_3O_{7-x}$ crystals imbedded in CuO. The fracture surface of a sample cyclically annealed eight times (Fig. 7(b)) shows "feather" patterns of small $YBa_2Cu_3O_{7-x}$ crystals in the spaces between much larger crystals of $YBa_2Cu_3O_{7-x}$. This "feather"

morphology is typical of crystallization requiring phase separation during the directional freezing of liquids. The sample cyclically annealed 67 times (Fig. 7(c)) is very different;

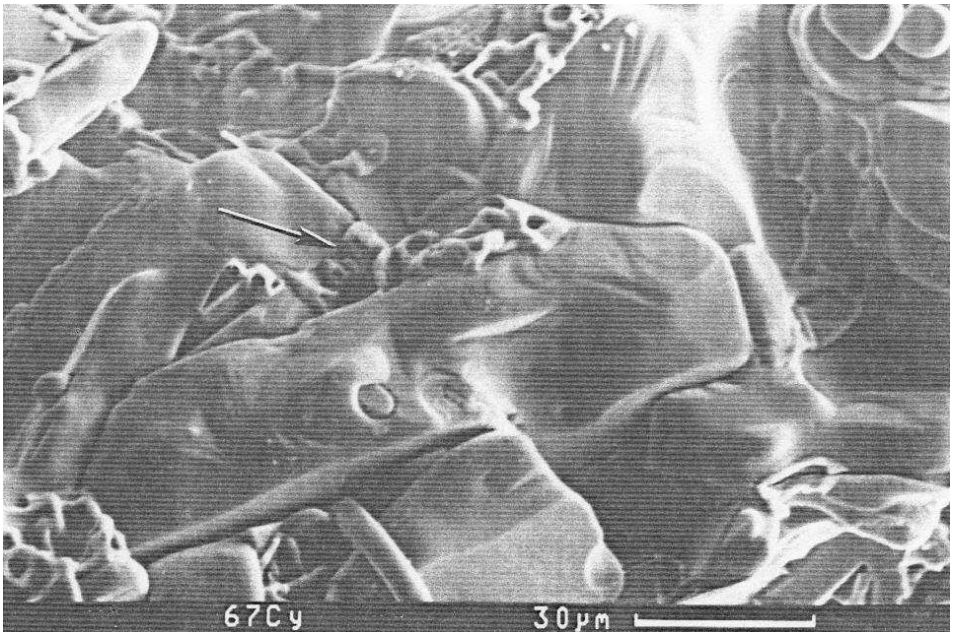


(a)



(b)

Fig. 7. Scanning electron micrograph of samples cyclically annealed 1 (a), 8 (b), and 67 (c) times. The magnification is approximately the same for all samples. Image (a) is a backscattered electron image of a polished surface, (b) and (c) are secondary electron images of fractured surfaces.



(c)

Fig. 7. (*continued*).

the feather patterns of small $YBa_2Cu_3O_{7-x}$ crystals are no longer in evidence. Instead, the intergranular material now appears as thin sheets of "lacy" material in spaces between large $YBa_2Cu_3O_{7-x}$ crystals. In addition, the surfaces of the large $YBa_2Cu_3O_{7-x}$ crystals show a layered morphology indicating that these crystals grew epitaxially at each thermal cycle.

Typically, $YBa_2Cu_3O_{7-x}$ crystals grow as rectangular plates with the *c*-axis normal to the plates, as shown in the inset of Fig. 8. This allows us to identify the *c*-axis by a visual inspection of SEM micrographs and to measure the dimensions of the grains. Figure 8 shows the average of crystal dimensions measured from scaled SEM photographs of fractured samples. We made no distinction between the (*a*) and (*b*) direction. Although these results only give an approximate measure of grain size, it is clear from Fig. 8 that grain size is a monotonically increasing function of the number of

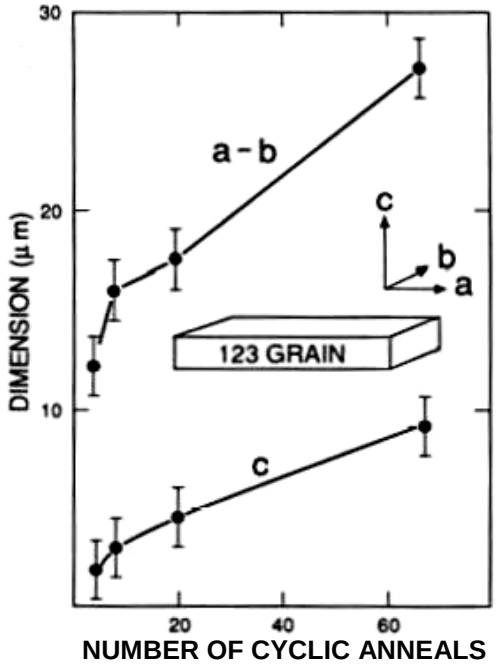


Fig. 8. Average size of the $YBa_2Cu_3O_{7-x}$ crystals *vs*. number of cyclic oxygen anneals.

cyclic anneals.

Besides the increase in average grain sizes, we have observed the almost complete disappearance of small (1-10 μm) $YBa_2Cu_3O_{7-x}$ grains in samples cyclically annealed more than 20 times. It became clear from examining a number of scanning electron micrographs that grain growth was accompanied by an overall narrowing of the crystal size distribution. We believe that this is caused by two phenomena:

1. Small grains of $YBa_2Cu_3O_{7-x}$ are preferentially consumed during the heating part of the cycles (formation of peritectic melt according to eqn. (1)); and
2. The surface of the large crystals is a preferred site for the nucleation of $YBa_2Cu_3O_{7-x}$ during the solidification of the peritectic melt.

Indeed, the surface of the large $YBa_2Cu_3O_{7-x}$ crystal in the center of Fig. 7(c) (sample cyclically annealed 67 times) is layered, indicating that this crystal grew in size

at each consecutive cycle by epitaxial growth from a liquid phase.

The degree of orthorhombicity, $(b\text{-}a)/a$, also increases with the number of cyclic anneals. For a sample cyclically annealed 20 times, $(b\text{-}a)/a = 1.0175 \pm 0.0005$. A sample cyclically annealed once shows only 90% of this splitting, despite an identical slow cool in flowing oxygen.

Changes in the Volume Fraction of Superconducting Phase

We determined superconducting transition temperatures (T_c) from the onset of diamagnetism in samples warmed in a d.c. magnetic field of 100 G, after zero field cooling to 7 K from room temperature. The seven samples cyclically annealed to different numbers of cycles all had T_c of 91 ± 1 K. We made magnetic susceptibility measurements at 7 K in a d.c. magnetic field of 100 G, which is lower than H_{c1}. Although the demagnetizing factor is difficult to calculate accurately, we take advantage of the fact that our samples are all of the same mass (100 mg) and external shape (that of the interior of the alumina calorimeter cup). This enables us to compare the susceptibilities and to deduce the relative fractions of superconducting phase. In Fig. 9 we have plotted susceptibility *vs*. number of cycles, and it is clear that the superconducting fraction increases with cyclic annealing.

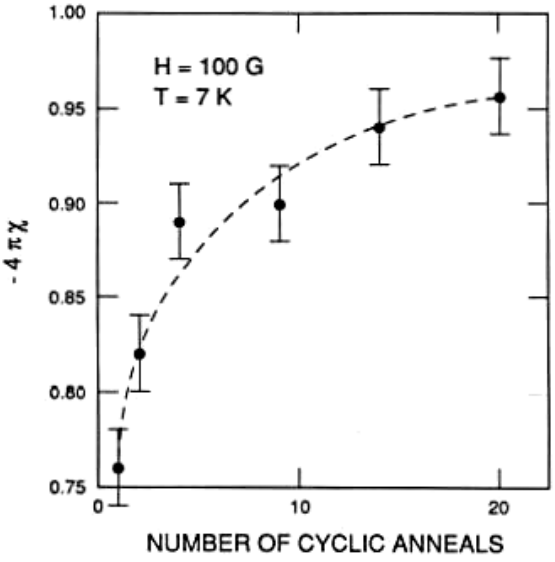


Fig. 9. Magnetic susceptibility of $YBa_2Cu_3O_{7-x}$ *vs*. number of cyclic oxygen anneals.

CHAPTER V

DISCUSSION

Presence of CuO at the Surface of $YBa_2Cu_3O_{7-x}$ Grains

According to the equilibrium phase diagram [32], single-phase $YBa_2Cu_3O_{7-x}$ undergoes no phase transition until melting at 1015 ºC. Because the reaction giving rise to peak D in the DSC trace requires the presence of CuO, the detection of this peak indicates that at 950 ºC the sample has free CuO. We clearly observe CuO by SEM and X-ray diffraction in samples that were heated once to 980 ºC and rapidly cooled by dropping them from the inside of a small furnace onto a copper block at room temperature. The possibility that CuO is present because of an excess of CuO in the starting mixture of oxides must be ruled out because we also observed peak D in DSC traces of samples we synthesized with deliberate copper deficiencies of 6 and 10 at.%. It might be argued that CuO forms to balance the crystallization of other copper-deficient phases such as Y_2O_3, but we have not detected any phases other than $YBa_2Cu_3O_{7-x}$ and CuO in X-ray diffraction patterns of samples annealed once to 980 ºC (Fig. 6, curve (a)). Finally, it may be argued that our intergranular material was rich in metallic impurities, as sometimes observed [33], but the EDX analysis of the dark phase in Fig. 5(a) revealed only copper (oxygen is not detected by our EDX).

We have also observed peak D in the DSC traces of $YBa_2Cu_3O_x$ prepared by other techniques. In refs. 34 and 35 we reported the synthesis of $YBa_2Cu_3O_x$ by the slow oxidation of YBa_2Cu_3 powder in both ^{18}O and ^{16}O. Peak D is clearly seen in the DSC

traces during the first heating to 980 ºC in both oxygen isotopes. We have also seen peak D when analyzing in our DSC the $YBa_2Cu_3O_x$ samples prepared by other researchers [36] starting from Y2O3, BaCO3 and CuO.

The presence of CuO in nominally pure $YBa_2Cu_3O_{7-x}$ crystal at 950 ºC appears to be a ubiquitous phenomenon. In fact, all DSC traces we have found in the literature [32,34,35,37-39], which span the temperature range 900 to 1000 ºC show the presence of peak D. We propose tentatively that a CuO phase forms at the surface of large $YBa_2Cu_3O_x$ crystals when these are heated in air or oxygen to elevated temperatures. This phase presumably forms when copper atoms diffuse from the bulk, leaving behind constitutional vacancies and lowering the alloy's free energy. Similarly, in $YBa_2Cu_3O_x$ powder heated to high temperatures, copper would segregate at the particle surfaces. In porous aggregates, copper would segregate at the surface of interior cavities as well as exterior surfaces. From Fig. 5(a) it is apparent that grain boundaries are also effective sinks for the copper segregation.

In powder aggregates, the presence of CuO should be more noticeable in the larger particles. Suppose that at 950 ºC, a fraction ε of the copper atoms in $YBa_2Cu_3O_{7-x}$ migrates to the surface of the particles. It is easy to deduce that the formation of a monolayer of CuO surrounding a spherical $YBa_2Cu_3O_{7-x}$ particle of radius r requires

$$r > 4V_y/[\varepsilon (V_c)^{2/3}] \qquad (4)$$

where V_y and V_c are the volumes of the $YBa_2Cu_3O_7$ and CuO unit cells with three and four copper atoms, respectively. We have not found values for the enthalpies of vacancy formation at copper sites in bulk $YBa_2Cu_3O_x$, which would allow us to estimate ε at 950

ºC. If we assume, for the sake of discussion, that $\varepsilon = 10^{-3}$, and with $V_y = 1.73 \times 10^{-28}$ m^3 and $V_c = 8.2 \times 10^{-29}$ m^3, we deduce from eqn. (4) that the formation of a monolayer of CuO requires particle sizes with r > 3.7 μm. This simple argument suggests that there is a critical particle size below which the peritectic reaction of eqn. (1) does not occur simply because there is an insufficient density of copper atoms to form a CuO phase. In this case the copper atoms that migrate to the surface of the particles heated to 950 ºC would diffuse back into the bulk when they are cooled to lower temperatures. The same reversible diffusion should occur in thin films below a certain critical film thickness.

The measurement by Kuwabara and Shimooka [40] of the dependence of J_c on grain size in $YBa_2Cu_3O_x$ seem to support the model presented above. They prepared bulk samples of different average grain size *d* by sintering fine $YBa_2Cu_3O_x$ powder at temperatures between 920 and 950 ºC for 3 to 10 h, and measured J_c in rods cut from these specimens. For $d > 2.0$ μm, J_c is independent of *d* and is close to 100 A cm^{-2}. However, $1 < d \leq 2.0$ μm, J_c goes through a sharp maximum, reaching values in excess of 800 A cm^{-2}. The authors attribute the increase in J_c for $1 < d \leq 1.2$ μm to the increase in the density of the samples, which they also measure. They tentatively attribute the decrease in Jc for $1.2 < d \leq 2.0$ μm to "residual stresses" in the samples. They also note that the decrease in J_c is accompanied by a decrease in the tensile strength of the samples. We propose as an alternative explanation for the abrupt decrease in J_c that the critical *d*-value for the formation of a CuO phase at the grain boundaries and at the surfaces of cavities in their $YBa_2Cu_3O_x$ samples, as defined by eqn. (4), was close to 1.2 μm. Then, for $d > 1.2$ μm, intergranular phases would have formed by the reaction of CuO with

$YBa_2Cu_3O_x$ as explained in ref. 32. This mechanism would also explain the observed decrease in tensile strength if the intergranular phases formed by the reaction in eqn. (1) decrease the interparticle cohesion strength. For grain sizes smaller than 1.2 μm, the density of copper atoms segregated at grain boundaries and particle surfaces is lower than that needed to form a CuO phase. On slow cooling these fine-grain samples, the copper would diffuse back into the particles, allowing the grain boundaries to remain free of second phases. Certainly, further experiments are needed to verify this model.

The foregoing discussion suggests that (a) high J_c values may be obtained in dense compacts of small grain size, as also suggested by the measurements in ref. 25; and (b) to avoid the formation of intergranular phases the sample must be sintered at temperatures below 950 ºC. However, if segregated copper atoms are able to diffuse over long distances by either grain boundary or surface diffusion, then the formation of a CuO phase at high temperatures may occur even for fine grain materials and for annealing temperatures below 950 ºC. Extremely slow cooling rates would then be required to allow for the copper to return to the bulk. This reverse copper migration would be facilitated by an excess of oxygen vacancies, suggesting that cooling from the sintering temperature to a temperature in the vicinity of 500 ºC be made in a reduced oxygen partial pressure. Full oxygenation to reach the seven oxygens per YBa_2Cu_3 formula could be achieved by annealing in pure oxygen at 450 ºC. Empirically it has been found [41] that sintering in a reduced oxygen partial pressure results in samples with large J_c.

Changes in the Intergranular Material Composition with Cyclic Annealing

We explain the progressive transition in the DSC traces from peak D to peak F on cyclic annealing with a model in which the peritectic reaction of eqn. (1) is irreversible. The main features of the model are explained with the help of Fig. 10. This figure shows, schematically, two isothermal sections of the ternary phase diagram for Y_2O_3 – CuO – BaO shown in Fig. 5 of ref. 32. These sections are for the temperature T_1 = 900 ºC (just above the ternary eutectic reaction temperature of eqn. (3)) and T_2 = 960 ºC (just above the peritectic reaction temperature of eqn. (1)). In this figure and in the following discussion we denote a $Y_xBa_yCu_zO_p$ phase simply by (*xyz*). Further details of the ternary phase diagram are shown in Fig. 5 in [32], including the position of the invariant points e_1 and p_1 inside the (011) – (001) – (123) triangle.

We proposed in the previous section that when (123) is heated to temperatures close to 900 ºC, the generation of constitutional vacancies at copper sites causes the formation of a small volume fraction of (001) at grain boundaries and at free surfaces. Thus, the initial alloy composition is represented by point *a* in Fig. 10, located along the two-phase (123) – (001) tie-line. For the sake of clarity, in Fig. 10 we have exaggerated the volume fraction of (001) present and we have drawn point *a* farther away from point (123) than in reality. The shaded areas in Fig. 10(a) and 10(b) represent liquid. In agreement with the DSC measurements, no reaction occurs upon heating the alloy to 900 ºC for the first time because point *a* is on the (123) – (001) tie-line. However, at 950 ºC (123) reacts with (001) forming L(p_1) and (211), according to eqn. (1). Figure 10(b)

shows that at 960 ºC the sample (point *a*) is now a three-phase mixture of (123), (211) and liquid. Morphologically, (123) is the majority phase, with the (211) and liquid phases being located at the grain boundaries.

We propose that, on cooling, the (reverse) peritectic reaction of eqn. (1) is incomplete. $L(p_1)$ and (211) are not totally consumed because of a deficiency of (211) at the reaction zones. The $L(p_1)$ formed on heating migrates under capillary action and/or gravitational force, becoming separated from the (211). This separation of $L(p_1)$ and (211) can also be attributed to fractional crystallization [32], whereby (123) formed at the onset of the solidification effectively encloses the still unreacted (211) and prevents a complete reaction. The (211) left behind by the migrating peritectic liquid is no longer of consequence because no reactions occur between (211) and (123) in the temperature regime of the cyclic anneal. Removing part of the (211) phase from the reaction is equivalent to moving the alloy composition from point *a* to point *b*, as shown in Fig. 10. On cooling from 960 to 950 ºC, part of the liquid solidifies into (123) and (211). On further cooling to 900 ºC, part of the liquid solidifies into (123) and (001), and the remaining liquid shifts in composition toward the shaded area in Fig. 10(a). The last fraction of liquid to solidify has the eutectic composition of eqn. (3). This eutectic liquid freezes into triple-points consisting of $YBa_2Cu_3O_{7-x}$, $BaCuO_2$, and CuO, which were clearly seen in the scanning electron micrograph of Fig. 5(b). The reactions just described repeat with every thermal cycle.

At each cycle, an additional fraction of (211) becomes separated from the liquid, causing the alloy composition to stepwise move away from point (211) along the line joining points (211) and *a*. The change in the intergranular composition ceases when the

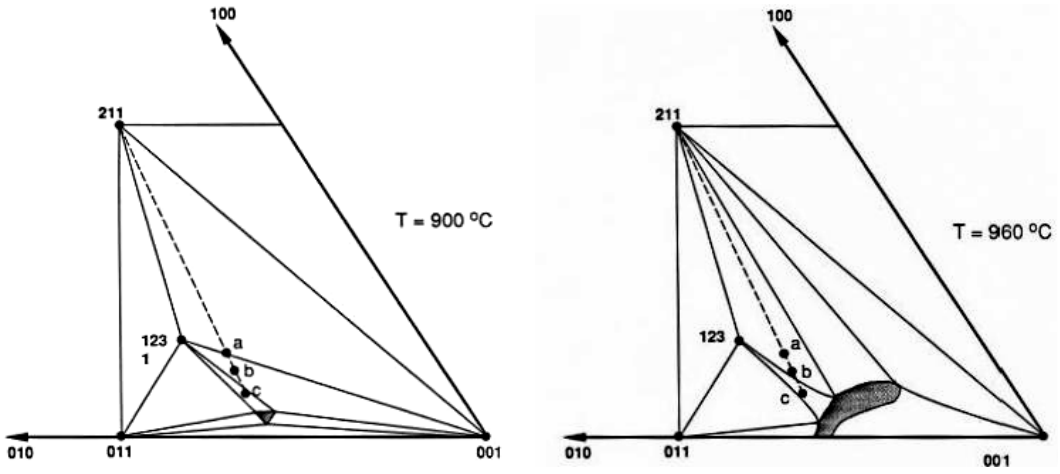


Fig. 10. Schematic isothermal sections of the ternary Y_2O_3 – CuO – BaO phase diagram of Aselage and Keefer [32].

composition reaches the two-phase region (123) – L(e_1), shown as point *c* in Fig. 10(a). Then the composition of the liquid phase remains constant for 900 < T < 960 ºC and no further changes are detected in the DSC curves during cyclic annealing. In summary, the formation of nonreacting (211) at each thermal cycle causes a decrease in the volume fraction of CuO in the intergranular material. At point *c*, all the CuO is tied up in the eutectic liquid and no CuO is available for the peritectic reaction that occurs on heating to 950 ºC.

The model proposed here can explain quantitatively the changes in the areas under peaks D and F in the DSC traces. These areas measure the enthalpies of reaction in eqn. (1) and (3), respectively. The enthalpy of reaction D measured during the heating part of the *n*th cyclic anneal is proportional to the amount of CuO available at 950 ºC, at the onset of the peritectic reaction of eqn. (1). As we have seen, the CuO decreases with each cycle because a fraction of the (211) does not react reversibly. If we assume that at

each cycle the CuO decreases by a fraction α, then the enthalpy of reaction D should decrease with the number of cycles, n, according to the following equation:

$$\Delta Q_{D(n)} = (1 - \alpha)^{n-1} \Delta Q_{D(1)} \qquad (5)$$

Equation (5) suggests a linear plot of $\ln[\Delta Q_{D(n)}]$ *vs.* n. Figure 11 is such a plot, showing a linear fit for $n > 3$.

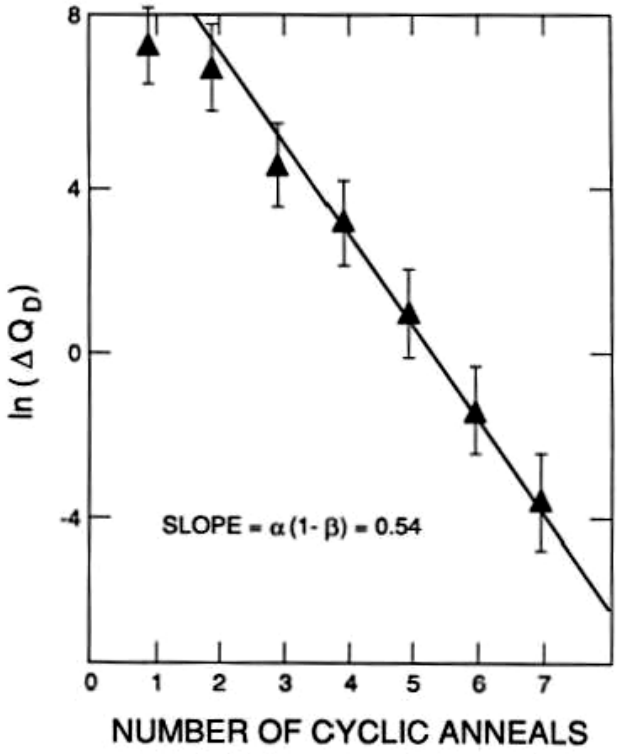


Fig. 11. Semi-log plot of the enthalpy of peak D *vs*. number of cyclic oxygen anneals.

CHAPTER VI

CONCLUSIONS

We propose that, when bulk $YBa_2Cu_3O_{7-x}$ is heated to near 900 ºC, constitutional vacancies form at copper sites. Copper atoms segregate to gain boundaries and surfaces driven by a lowering in the crystal's free energy. The surface density of copper atoms increases with increasing grain size due to the increase in the volume-to-surface ratio. In large-grain $YBa_2Cu_3O_{7-x}$, the amount of copper is sufficient to form a CuO at grain boundaries, grain surfaces, and cavities. A CuO phase can also form in the fine-grain $YBa_2Cu_3O_{7-x}$ if the copper atoms diffuse and segregate.

Heating $YBa_2Cu_3O_{7-x}$, to 950 ºC causes the reaction of $YBa_2Cu_3O_{7-x}$ with CuO to form Y_2BaCuO_5 and liquid. On cooling, the reaction is not fully reversible because part of the liquid migrates and becomes separated from the Y_2BaCuO_5.

The cyclic anneal of bulk $YBa_2Cu_3O_{7-x}$, between 780 and 980 ºC causes the formation of increasing amounts of Y_2BaCuO_5 at grain boundaries and voids. The volume fraction of Y_2BaCuO_5 formed this way saturates when the composition of the intergranular melt equals that of the ternary eutectic of $YBa_2Cu_3O_{7-x}$ + $BaCuO_2$ + CuO.

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APPENDIX

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