IS-T 1773

Recrystallization of High Temperature Superconductors

by

Kouzoudis, Dimitris

MS Thesis submitted to Iowa State University

Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

Date Transmitted: May 9, 1996

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. W-7405-Eng-82.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

AVAILABILITY:

To DOE and DOE contractors: Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

prices available from: (615) 576-8401
FTS: 626-8401

To the public: National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

TABLE OF CONTENTS

ACKNOWLEDGMENTS	vi
CHAPTER 1. INTRODUCTION	1
CHAPTER 2. HISTORICAL SURVEY	3
Grain Boundary Problem	3
Sheathing problem	4
Multiple phase problem	4
Success of the PIT technique	5
X-ray and SEM studies	6
Simulation of the PIT process	7
CHAPTER 3. EXPERIMENTAL TECHNIQUES AND CONDI- TIONS	8
CHAPTER 4. EXPERIMENTAL RESULTS AND DISCUSSIONS	14
Growth of a new phase	14
Chemical analysis of the new phase	20
Onset of growth	52
CHAPTER 5. CONCLUSIONS	60
BIBLIOGRAPHY	61

LIST OF FIGURES

Figure 3.1:	Experimental setup for heat treatment	9
Figure 3.2:	SEM contrast due to surface topography	11
Figure 3.3:	SEM imaging of the Ag/BSCCO interface	12
Figure 3.4:	X-ray production and detection	13
Figure 4.1:	Uncoated BSCCO grains at 601°C.	15
Figure 4.2:	Growth of nucleation cites on the Ag/BSCCO interface at 601°C.	16
Figure 4.3:	Uncoated side of the starting BSCCO pellet	17
Figure 4.4:	Silver coated side of the starting BSCCO pellet	18
Figure 4.5:	Ag/BSCCO interface at 420°C.	20
Figure 4.6:	EDS spectrum of Fig. 4.5	21
Figure 4.7:	Ag/BSCCO interface at 518°C.	22
Figure 4.8:	EDS spectrum of Fig. 4.7	23
Figure 4.9:	Ag/BSCCO interface at 601°C.	24
Figure 4.10:	EDS spectrum of area A of Fig. 4.9	25
Figure 4.11:	EDS spectrum of area B of Fig. 4.9	26
Figure 4.12:	EDS spectrum of area C of Fig. 4.9	27
Figure 4.13:	Ag/BSCCO interface at 654°C.	28

Figure 4.14: EDS spectrum of area A of Fig. 4.13	29
Figure 4.15: EDS spectrum of point B of Fig. 4.13	30
Figure 4.16: Ag/BSCCO interface at 701°C.	31
Figure 4.17: EDS spectrum of area A of Fig. 4.16	32
Figure 4.18: Ag/BSCCO interface at 755°C.	33
Figure 4.19: EDS spectrum of area A of Fig. 4.18	34
Figure 4.20: Ratio of the net area of the Bi and Sr peaks with respect to the Ag peak for different annealing temperatures	35
Figure 4.21: Standard Bi EDS lines	37
Figure 4.22: Standard Ca EDS lines	38
Figure 4.23: X-ray diffraction data for the sample annealed at 420°C , silver coated side	39
Figure 4.24: X-ray diffraction data for the sample annealed at 420°C , un- coated side	40
Figure 4.25: X-ray diffraction data for the sample annealed at 755°C , silver coated side	41
Figure 4.26: X-ray diffraction data for the sample annealed at 755°C , un- coated side	42
Figure 4.27: Pore on the Ag coating at 601°C	43
Figure 4.28: Pore on the Ag coating at 654°C	44
Figure 4.29: Pore on the Ag coating at 701°C	45
Figure 4.30: Pore on the Ag coating at 755°C	46
Figure 4.31: EDS spectrum of the pore of Fig. 4.27	47
Figure 4.32: EDS spectrum of the pore of Fig. 4.28	48

Figure 4.33: EDS spectrum of the pore of Fig. 4.29	49
Figure 4.34: EDS spectrum of the pore of Fig. 4.30	50
Figure 4.35: Temperature dependence of the Cu lines at the pores	51
Figure 4.36: Etched area of the sample of Fig. 4.18 , uncoated side	53
Figure 4.37: EDS spectrum of area A of Fig. 4.36	54
Figure 4.38: EDS spectrum of area B of Fig. 4.36	55
Figure 4.39: EDS spectrum of area C of Fig. 4.36	56
Figure 4.40: Hillocks growth around the pores on the 601° sample	57
Figure 4.41: Hillocks growth anywhere on the 601° sample	58
Figure 4.42: High magnification picture of Fig. 4.41	59

ACKNOWLEDGMENTS

The author wishes to express deep appreciation to his advisor Dr. D. K. Finnemore for his guidance and encouragement throughout the course of this research; to Mr. J. E. Ostenson for his invaluable assistance concerning laboratory techniques; to Mr. G. Steininger for his technical advice and help on machine shop constructions; and finally to his parents for their endless moral support and concern.

This work was performed at Ames Laboratory under Contract No. W-7405-Eng-82 with the U.S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1773 to this thesis.

CHAPTER 1. INTRODUCTION

Since the discovery of high-critical-temperature (high T_c) superconductivity in 1986, a considerable amount of work has been done to develop commercial products. Applications such as power transmission, power generation, motors, magnetic energy storage, transportation, new electronic circuits appear to be feasible because the high temperatures permit simplified cryostats and higher heat fluxes.

In the electric power field the key barrier to commercialization, at present, is the development of a low cost conductor for magnets. Major problems that need to be solved in this direction are the low critical current density (J_c) and the poor mechanical properties of high T_c materials. The latter problem has to do with the fact that most of the high T_c superconductors are ceramics which means that they are relatively brittle and thus difficult to handle and process. Both intrinsic and material properties are responsible for the former problem and considerable work has been done towards this direction.

Currently one of the the most widely used materials is the Bi-based compounds $Bi_2Sr_2CaCu_2O_z$ and $Bi_2Sr_2Ca_2Cu_3O_z$ (known as BSCCO 2212 and 2223 compounds) with T_c values of about 85 K and 110 K respectively. Lengths of high performance conductors ranging from 100 to 1000 m long are routinely fabricated and some test magnets have been wound. An additional difficulty here is that al-

though Bi-2212 and Bi-2223 phases exist over a wide range of stoichiometries, neither has been prepared in phase-pure form.

So far the most successful method of constructing reliable and robust wires or tapes is the so called powder-in-tube (PIT) technique [1, 2, 3, 4, 5, 6, 7] in which oxide powder of the appropriate stoichiometry and phase content is placed inside a metal tube, deformed into the desired geometry (round wire or flat tape), and annealed to produce the desired superconducting properties. Intermediate anneals are often incorporated between successive deformation steps. Silver is the metal used in this process because it is the most compatible with the reacting phase.

In all of the commercial processes for BSCCO, Ag seems to play a special catalytic role promoting the growth of high performance aligned grains that grow in the first few micrometers near the Ag/BSCCO interface. Adjacent to the Ag, the grain alignment is more perfect and the current density is higher than in the center of the tape. It is known that Ag lowers the melting point of several of the phases but the detailed mechanism for growth of these high performance grains is not clearly understood. The purpose of this work is to study the nucleation and growth of the high performance material at this interface.

CHAPTER 2. HISTORICAL SURVEY

Grain Boundary Problem

Despite the high Critical temperature T_c and critical magnetic field H_{c2} values, BSCCO has been of limited commercial value because the critical current, J_c , is relatively low. These materials have: (i) a localized covalent ionic chemical bonding at grain boundaries that results in NIN (Normal-Insulating-Normal metal) junctions; (ii) a very short coherence length ξ so that local defects can have a large effect; and (iii) a high anisotropy in the superconducting wave function that gives pancake vortices rather than columnar vortices [8, 9]. These features make these ceramic materials particularly difficult to prepare with sufficient uniformity to give high performance J_c characteristics. The weak links at the grain boundaries lead to low intergrain current densities because they act as easy paths for Josephson vortices. In fact most of the high- T_c compounds have these weak links and there is rapid magnetic flux line creep along them. It should be mentioned that flux creep is more profound in BSCCO than in YBCO ($YBa_2Cu_3O_{7-x}$) [10] due to a higher anisotropy. BSCCO exhibits a wide reversible regime [11] and low melting temperature of the Abrikosov lattice [12]. Pinning is needed also to hold the flux line lattice in the intrinsic superconducting regions. Strong pinning is difficult to achieve in practice because the imperfections have to be of the order of ξ , ie., few Angstroms. From the above it is clear that grain

alignment and strong grain to grain coupling are desirable in these compounds.

Sheathing problem

The material used as the tube in the PIT process, must be compatible with the processing of the BSCCO core and Ag or Ag alloys have been the only successful jacket material to date. [23, 24]. Silver has relatively high oxygen diffusivity and low reactivity with BSCCO compounds at the processing temperature, and good thermal conductivity at 77 K which provides a means of thermal dissipation, thus stabilizing the superconductor's environment. The stabilizing effect is of fundamental importance for type II superconductors, in which undesirable large local rises in temperature can develop through flux jumping in the mixed state [25]. In addition Ag protects the oxide core from chemical corrosion and mechanical abrasion. Furthermore, reliable, low-resistivity external connections can easily be made by preparing contacts to the metallic sheath.

Multiple phase problem

The chemistry of these materials also is a major problem in producing the superconducting phases out of precursor powders. To date, it has been impossible to produce a pure 2223 phase. Long sintering times as well as close temperature control are required in order to establish it as the major phase. Generally it is easier to form the 2212 phase but it is desirable to have the 2223 one due to its higher transition temperature. The kinetics of the reaction and the limited range of the stability of Bi-2223 seem to complicate its development [26, 27, 28, 29, 30, 31]. It is believed [32, 33, 34] that partial substitution of bismuth with lead both stabilizes and

accelerates the formation of the 2223 phase. Different processes such as solid-state reaction, freeze drying, co-precipitation, etc. have been tried towards this direction [35, 36, 37]. Typically large segregated particles of $Sr - Ca - Cu - O$, $Ca - Cu - O$, and $Cu - O$ phases coexist with the 2223 during the process. Carbonates also might be present and it was found [38] that they suppress J_c because they possibly result in poor grain connectivity and high porosity. Y. Ikeda et al [39] give a comprehensive overview of various phases formed when mixtures of Bi_2O_3 , $SrCO_3$, $CaCO_3$, and CuO are heated in air.

Success of the PIT technique

The powder-in-tube technique seems to deal successfully with most of the above difficulties. A significant improvement in the critical current density J_c and flexibility has been achieved in Ag-clad $Bi_2Sr_2CaCu_2O_{8+x}$ [13, 14, 15] and Ag-clad $Bi_2Sr_2Ca_2Cu_3O_{10+x}$ [23, 24, 16, 17]. Major success has been achieved in producing nearly magnetic field independent J_c 's which are already comparable or even superior than the ones in conventional superconductors, especially at fields above 20 T [18]. Critical current densities as high as $10^4 A/cm^2$ at 77K have been reported [19, 20, 21, 22].

The improved J_c and $J_c - B$ behavior has been attributed to the improvement of grain alignment, to the decrease of the non-superconducting phases and to the role of some of phases as effective pinning centers. It should be emphasized that BSCCO has very clean grain boundaries and has plate-like grains so alignment seems to be the major contributing factor. Alignment can be achieved by: (i) mechanical deformation during the process which takes advantage of the textured shape of these

grains; (ii) annealing [23, 24, 40, 41]; (iii) liquid phase sintering due to partial melting of the powder [42]; and (iv) Ag-sheath-induced texture [17, 43]. Scanning electron microscope pictures show that the degree of texturing decreases as the probe moves from the Ag/BSCCO interface towards the center of the oxide layer. Additionally silver has been reported to have a relatively strong effect on pinning [17, 44, 45], and also on the acceleration of the formation of the 2223 phase.

X-ray and SEM studies

Although there is a clear picture about grain alignment and texturing, there is a great deal of uncertainty about details of phase formation, especially at the Ag/BSCCO interface. J. Polonka et. al. [46] have studied the different phases that grow during ramp up to the melting temperature and cooling down again, by using a real time analysis x-ray diffraction set up. Ming Xu et. al. [47, 48] examined also the stability of these phases versus time using the same technique. They observed that the major 2212 lines diminish at about 300 K and appear back again at around 700 K, depending on the details of the temperature-time sequence. At the same time 2223 lines started to grow. Since x-rays penetrate about 1 micron, surface kinetics and chemistry should be responsible for these results. Environmental scanning electron microscope studies revealed that the Ag coated grains develop a texture at the interface in the form of a dense array of hillocks that looks like "chicken pox" [49]. These hillocks grow at about 700 K.

Simulation of the PIT process

In the experiments of this thesis, we simulate the PIT process by pressing a pellet of the powder, by coating the pellet with a thin layer of silver, by annealing at different temperatures, and by systematically following the growth of various phases with microanalytical tools.

CHAPTER 3. EXPERIMENTAL TECHNIQUES AND CONDITIONS

The starting materials were mixed powders of Pb-doped 2212 plus $Ca_2Cu_1O_3$ plus CuO with an average $Bi_2Sr_2Ca_2Cu_3$ stoichiometry. This mixture powder was labeled "AI 37375 92 Pb: BSCCO NEIL" and it was produced at Argonne National Lab according to a commercial process used by Intermagnetics General Corporation. The mixed powders were then pressed into a disk pellet with diameter and height of 6 and 0.5 mm correspondingly, under a pressure of about 82,000 psi. The mass of each pellet was around 80 mg.

The next step is the deposition of Ag. Investigation of the Ag on BSCCO in the scanning electron microscope (SEM) revealed that unless some care is taken in cleaning the silver before putting it in the evaporator, the Ag coating could be uneven. We tried various cleaning procedures and the most successful one was the following: (i) High purity Ag in the form of thin wire is passed through a lighter's flame in order to oxidize foreign elements on the surface; (ii) nitric acid is used to remove these oxides as well as any possible carbonates; (iii) the acid is flushed out by plenty of de-ionized water; (iv) the wire is put in an ultrasonic cleaner for 10 min to eliminate possible fingerprint and other organic materials; (v) it is then wrapped around the evaporation filament and put inside a vacuum system (a typical bell jar) and (v) a deposition is performed for 20 min without the sample present in order to

Figure 3.1: Experimental setup for heat treatment

get rid of the first few surface monolayers.

Typically eight to ten pellets are put together in the bell jar in order to make sure that they have identical deposition conditions. The distance between silver and pellets is around 5 cm. When the vacuum level is of the order of 10^{-6} Torr, deposition begins with a rate of 0.02 nm/sec until the thickness monitor reads 235 nm. Silver was deposited on one side of the pellets only in order to be able to observe reactions in both Ag coated and uncoated BSCCO.

The experimental set up of Fig. 3.1 was used for heat treatment. The pellet was inserted inside an alumina boat with the Ag coated face up in order to avoid any possible contamination from the boat. After the tube was pumped down to

the 1-5 mTorr range, oxygen gas was inserted and the pressure regulator maintained the pressure to 50 Torr. The same pressure was used for all experiments. The temperature then was ramped at a rate of $13^{\circ}\text{C}/\text{min}$ to the desired temperature and held constant for 1 hour. Finally the tube was brought out of the furnace and into the air in order to quench the sample at approximately $43^{\circ}\text{C}/\text{min}$. The thermocouple was put in a close proximity to the pellet in order to read the temperature accurately. To make sure that the thermocouple was not degrading through all these temperature cycles, it was frequently removed and compared with other available temperature sensors in the laboratory. There was always agreement within 5°C for temperatures above 400°C .

A JEOL 6100 scanning electron microscope was used in order to observe the different phases that formed on the Ag/BSCCO interface. Fig. 3.2 shows the way that contrast is achieved when secondary electrons are detected. When the surface has rough topography secondary electrons have a better chance to escape the interaction volume and come out of the sample. This means that steep and rough portions of the sample appear much brighter than the corresponding flat ones. On the other hand, the number of backscattered electrons depend also on the average atomic number and a qualitative compositional analysis can be achieved. Most of the pictures presented in this work were taken in the secondary electrons mode. Because of the way that contrast is achieved in the secondary electron mode, it is hard to say whether small features that appear on the picture are due to small phases that sit on top or underneath the Ag surface as shown in Fig. 3.3.

It is known that when electrons of high enough energy collide with matter, x-rays are produced. This is a great advantage in an SEM because a chemical analysis

Figure 3.2: SEM contrast due to surface topography

can be obtained (Fig. 3.4). If the energy of the excited x-ray is detected by a Si-Li detector the method is called EDS (Energy Dispersive Spectroscopy), while if the wavelength is detected, it is called WDS (Wavelength Dispersive Spectroscopy). As it is known the two quantities are related through $E = hc/\lambda$. Although the resolution of the later method is definitely better (about 10 eV), the hardware is relatively large because it involves rotating crystals. EDS is compact, faster and cheaper because it uses a solid state Si-Li detector but the resolution is of the order of 150 eV. The technique in which the WDS spectrum is compared with standards and corrections are applied in order to figure out the concentration of the various elements in the sample, is known as EPMA (Electron Probe Micro Analysis). The software used in this case is known as ZAF, which accounts for corrections in atomic number (Z), absorption (A) and x-ray fluorescence (F).

Figure 3.3: SEM imaging of the Ag/BSCCO interface

Figure 3.4: X-ray production and detection

CHAPTER 4. EXPERIMENTAL RESULTS AND DISCUSSIONS

Growth of a new phase

As was mentioned above, earlier work on x-ray diffraction [47] in our group, revealed that the main 2212 peaks decreased as the temperatures were ramped from 500°C to 700°C. In an attempt to understand in more detail the cause of this decrease, samples were studied in the Scanning Electron Microscope after heat treatment at prescribed temperatures in this interval. Fig. 4.1 and 4.2 show SEM pictures of pellets heat-treated at $T=601^{\circ}\text{C}$ with and without Ag coating. Samples that were not heat treated are shown in Fig. 4.3 and 4.4 for comparison. While there is not much really happening on the uncoated samples, two clear features emerge on the coated ones (Fig. 4.2). First what appears to be the Ag coating, has a step structure with relatively smooth terraces. Second there is a growth of a new phase which has the form of an array of hillocks separated by a distance of about $1\text{ }\mu\text{m}$. Apparently this growth occurs at the Ag/BSCCO interface. These picture confirms that the hillocks seen in our earlier work [49] in a Enviromental Scanning Electron Microscope, can be reproduced.

In order to follow the growth of this new phase, six samples were prepared at temperatures 420, 518, 601, 654, 701 and 755°C . They are shown in Fig. 4.5, 4.7, 4.9, 4.13, 4.16 and 4.18 respectively. These pictures were taken with a magnification

Figure 4.1: Uncoated BSCCO grains at 601°C.

of around X9,000 and the straight white line on them corresponds to a distance of 1 μm .

These pictures demonstrate the kinetics of the growth. At 420°C the Ag coating has the form of grains of approximate size of 1 μm and a step-like form which consists of hexagonal terraces, most probably (111) planes Fig. 4.5 . The EDS analysis, Fig. 4.6 confirms that these grains are preliminary Ag. The fact that there is only Ag in the spectrum means that either (i) the interaction volume in Fig. 3.2 is less than 235 nm (the initial deposition thickness) deep or (ii) the Ag is thicker than our thickness monitor indicates. The situation is pretty much the same at 518°C, Fig. 4.7. As expected the EDS spectrum of Fig. 4.8 is identical to that for 420°C. However the terraces are sharper and it seems that there is a preferred orientation with their flat

Figure 4.2: Growth of nucleation sites on the Ag/BSCCO interface at 601°C.

Figure 4.3: Uncoated side of the starting BSCCO pellet

Figure 4.4: Silver coated side of the starting BSCCO pellet

edge parallel to the surface Fig. 4.7 . The question really is whether this orientation is due to the Ag structure or due to an orientation of the BSCCO grains underneath. Also it looks like that we have (001) planes now. Results for $T = 601^{\circ}\text{C}$, Fig. 4.9 show that this temperature is apparently the onset temperature of the growth of this new phase. There are three different features on Fig. 4.9: A dark region (probably a hole), the Ag steps and new bright spots. The corresponding EDS spectra are shown at Fig. 4.10-4.12. The high noise as well as the low scale in the spectrum indicates that the dark region A indeed is a hole and the Cu peak comes from the BSCCO underneath. Area C also is clear Ag as before and the only new information on B is the two small glitches of Bi and Sr next to the major peak of Ag. The density of these bright hillocks has increased at 654°C and the spectra at areas A and B, Fig. 4.14 and 4.15 are consistent with the ones above. The alignment of the Ag facets is also observed. It looks like the symmetry axis of this hexagonal structure is out of the page, perpendicular to the surface of the pellet. At 701°C both the density and the size of the hillocks have increased. This makes the chemical analysis easier and the spectrum of Fig. 4.17 at area A, reveals that Bi and Sr are the prevailing elements on the hillocks. It is not clear whether these hillocks grow on top of the Ag or on the Ag/BSCCO interface but in either case the electron beam of the SEM would excite a whole bunch of silver x-rays since it penetrates at least $1\text{ }\mu\text{m}$ inside the pellet. That would identify the Ag peak as a background peak, independent of the growth of the hillocks. The hillocks have various shapes and they preserve the orientation of the Ag, yet they do not exhibit a step-like structure which probably means that they are not single crystals. It should be noted that light elements such as oxygen can not be detected by EDS and we probably want to think of the new

Figure 4.5: Ag/BSCCO interface at 420°C.

phase as a possible Bi-Sr-O compound. Finally the hillocks form a continuous layer at 755°C and the spectrum (Fig. 4.19) is consistent with the ones at lower annealing temperatures. The ratio of the area of the Bi and Sr lines with respect to the silver one is shown in Fig. 4.20. This graph confirms that silver has nothing to do with the chemistry of the hillocks since the Bi and Sr are increasing proportionally with the size of the hillocks

Chemical analysis of the new phase

As it was discussed in the last section, the EDS analysis reveals that the hillocks are a possible Bi-Sr-O compound. To make sure that this is the case, we used the

Figure 4.6: EDS spectrum of Fig. 4.5

Figure 4.7: Ag/BSCCO interface at 518°C.

Figure 4.8: EDS spectrum of Fig. 4.7

Figure 4.9: Ag/BSCCO interface at 601°C.

Figure 4.10: EDS spectrum of area A of Fig. 4.9

Figure 4.11: EDS spectrum of area B of Fig. 4.9

Figure 4.12: EDS spectrum of area C of Fig. 4.9

Figure 4.13: Ag/BSCCO interface at 654°C.

Figure 4.14: EDS spectrum of area A of Fig. 4.13

Figure 4.15: EDS spectrum of point B of Fig. 4.13

Figure 4.16: Ag/BSCCO interface at 701°C.

Figure 4.17: EDS spectrum of area A of Fig. 4.16

Figure 4.18: Ag/BSCCO interface at 755°C.

Figure 4.19: EDS spectrum of area A of Fig. 4.18

Figure 4.20: Ratio of the net area of the Bi and Sr peaks with respect to the Ag peak for different annealing temperatures

EPMA technique to examine the 755°C sample. To our surprise, the analysis showed Ag, Ca, Sr and O instead of the Ag, Bi, Sr and O seen by EDS. This may indicate that the hillocks are rich of Ca instead of Bi. Fig. 4.21 and 4.22 which show the peak positions of a standard Bi and Ca spectrum correspondingly, reveal that there is a weak L-Ca line overlapping with the major $M\alpha$ -Bi one. But if indeed there is Ca present why do not we see the major Ca peak around 3.99 KeV? A possible explanation is that the hillocks indeed grow underneath the silver coating, on the Ag/BSCCO interface, and the electron beam of 20 KeV has lost much of its energy through the coating and is unable to excite the high energy peaks. That should also explain why all the spectra of the last section have a flat right side with the exception of Fig. 4.10 which was actually a hole. If Ca is indeed the right element, then we are really looking at a Ca-rich phase since the Ca peak at 1.99 KeV is really small.

We were also surprised with the x-ray diffraction results Fig. 4.23-4.26. Both the coated and the uncoated sides of the pellets show no structural change between the 420°C and 755°C samples. We observe some changes in various peaks due to different grain orientations, but we saw no new peak at all. A JC-PDF database search on diffraction data shows that the possible compounds of Bi-Sr-O do not fit with our results.

It should be mentioned that the Ag coating was quite porous. In order to see what is under this coating, the beam was condensed and passed through these holes. This way x-rays were emerging from the phases underneath. The spectrum of Fig. 4.10 was taken this way. Besides the major Ag peak which is due to excitations in the surrounding environment, there is a Cu line present in the spectrum. Actually Cu lines always emerge out of any hole for samples annealed at all higher temperatures.

Spectrum: Ca-lines Full Scale: 11000
Beam Current: 10 Count Time: 60 Accelerating Potential: 15.0 KeV

Figure 4.22: Standard Ca EDS lines

Figure 4.23: X-ray diffraction data for the sample annealed at 420°C, silver coated side

Figure 4.24: X-ray diffraction data for the sample annealed at 420°C, uncoated side

Figure 4.25: X-ray diffraction data for the sample annealed at 755°C, silver coated side

Figure 4.26: X-ray diffraction data for the sample annealed at 755°C, uncoated side

Figure 4.27: Pore on the Ag coating at 601°C

Fig. 4.27, 4.28, 4.29 and 4.30 show porous part of the 601, 654, 701 and 755° samples correspondingly, and Fig. 4.31, 4.32, 4.33 and 4.34 are the related EDS spectra. Note the scale change with respect to previous spectra. The height of these Cu-peaks progressively increases as the annealing temperature increases as Fig. 4.35 indicates. That probably means that some kind of Cu rich phase is growing underneath the hillocks layer or that the Cu x-rays are less absorbed on the way out.

From the above it becomes apparent that it is important to know whether or not the hillocks grow underneath the silver and if there is anything else on the interface. In order to have a clearer picture, a portion of the sample of 755°C was dipped inside a chemical etch to peel the silver off. The solution was consisted of 3 ml of H_2O_2 (hydrogen peroxide) plus 6 ml of NH_4OH (ammonia hydroxide) in 80 ml of

Figure 4.28: Pore on the Ag coating at 654°C

Figure 4.29: Pore on the Ag coating at 701°C

Figure 4.30: Pore on the Ag coating at 755°C

Figure 4.31: EDS spectrum of the pore of Fig. 4.27

Figure 4.32: EDS spectrum of the pore of Fig. 4.28

Figure 4.33: EDS spectrum of the pore of Fig. 4.29

Figure 4.34: EDS spectrum of the pore of Fig. 4.30

Figure 4.35: Temperature dependence of the Cu lines at the pores

de-ionized water. This Ag etching is a relative slow process, peeling off most of the 235 nm of Ag in about 1 hour. Fig. 4.36 shows the results of a 30 min etching. There are three distinguishable features on this picture: The coated grains (area A) that now are smaller and less dense, the background (area B), and the bright small grains on top of it (area C). The spectrum of B (Fig. 4.37) is what is expected: A typical BSCCO surface. But the spectrum of A (Fig. 4.38) has small peaks of Ca and Cu together with the strong Bi-Sr ones. The Ag is suppressed due to the etching. This may suggest that the hillocks before etching had a BSCCO composition but they were thin enough that the silver background did not let the Cu and Ca lines to show up. The fact that there is a lots of silver in Fig. 4.39 reveals that these new grains are pure Ag that were etched away from the hillocks (the other peaks come from the BSCCO background).

Onset of growth

As it was mentioned above, $T=601^{\circ}$ appears to be the onset temperature of the nucleation of these hillocks. In order to have a clearer idea of what is going on, two low magnification SEM pictures were taken at different areas of the 601°C sample. Fig. 4.40 has a lot of nucleation sites similar to the one of Fig. 4.9. It appears as if the nucleation happens around the pores of the Ag coating (look also the pores at Fig. 4.2 and 4.9). Possible reasons for that are (i) it is easier for the elements underneath to go through the hole, (ii) the Ag coating is thin near the holes, assuming smooth topology, and this makes it easy for the elements to diffuse through. The second picture, Fig. 4.41, is different from the last one and the hillocks in the form of very small dots are all over. A higher magnification picture of this area is shown in Fig.

Figure 4.36: Etched area of the sample of Fig. 4.18, uncoated side

Spectrum: Untitled 2
Beam Current: 10 Count Time: 50 Accelerating Potential: 15.0 KeV Full Scale: 2115

Figure 4.37: EDS spectrum of point A of Fig. 4.36

Figure 4.38: EDS spectrum of point B of Fig. 4.36

/ Spectrum: Untitled 1 Full Scale: 3946
Beam Current: 10 Count Time: 50 Accelerating Potential: 15.0 KeV

Figure 4.39: EDS spectrum of point C of Fig. 4.36

Figure 4.40: Hillocks growth around the pores on the 601° sample

4.42. The majority of the sample has areas that look like either of the Fig. 4.40 or 4.41 while all the other samples are pretty much uniform. That clearly indicates that the situation at 660°C is unstable and this is the onset temperature indeed.

Figure 4.41: Hillocks growth anywhere on the 601° sample

Figure 4.42: High magnification picture of Fig. 4.41

CHAPTER 5. CONCLUSIONS

A series of measurements of hillock growth on the Bi(2212) grains has been carried out in a furnace with carefully controlled temperature and oxygen partial pressure and the initial discovery of hillock growth in the E-SEM has been confirmed. The hillocks only grow when there is a Ag coating on the pellet and they first appear at $T = 600^\circ\text{C}$. The hillocks first grow as small grains about 100 nm in diameter in this low temperature regime. Above 700°C , the hillocks spread out to a width comparable to the Bi(2212) grain size. At 760°C , the hillocks cover most of the surface. It is not yet clear what is the chemical composition of these hillocks but definitely there is a great deal of Bi and Sr (EDS analysis) or Ca and Sr (EPMA analysis) and they may even be thin BSCCO grains developing on Ag by diffusion of the background elements.

BIBLIOGRAPHY

- [1] K. I. Sato, N. Shibuta, H. Mukai, T. Hikata, M. Ueyama, and T. Kato, *J. Appl. Phys.* **70**, 6484 (1991).
- [2] Y. Yamada, M. Satou, S. Murase, T. Kitamura, and Y. Kamisada, *Proc. 5th Int. Symp. on Superconductivity (ISS92)* ed Y Bando and H Yamauchi (1993).
- [3] R. Flukiger, B. Hensel, A. Pollini, J.-C. Grivel, A. Perin, and A. Jeremie, *Proc. 5th Int. Symp. on Superconductivity (ISS92)* ed Y Bando and H Yamauchi (1993).
- [4] U. Balachandran, A. N. Iyer, J. Y. Huang, R. Jammy, P. Haldar, J. G. Hoehn, G. Galinski, and L. R. Motowildo, *J. Metals* **46**, 23 (1994).
- [5] N. Merchant, J. S. Luo, V. A. Maroni, G. N. Riley, Jr., and W.J. Carter, *Appl. Phys. Lett.* **65**, 1039 (1994).
- [6] K. Sato, N. Shibuta, H. Hikata, M. Ueyama, T. Kato, and J. Fujikami, *Cryogenics* **33**, 243 (1993).
- [7] K. H. Sandhage, G. N. Riley, Jr., and W. L. Carter, *J. Metals* **3**, 21 (1991).
- [8] J. R. Clem, *Physica C* **162-164**, 1137 (1989).

- [9] J. R. Clem, Phys. Rev. B **43**, 7837 (1991).
- [10] P. H. Kes, Physica C **153-155**, 1121 (1988).
- [11] Y. Yeshurum, A. P. Malozemoff, T. K. Worthington, R. M. Yandroski, L. Krysinelbaum, F. H. Holtzberg, T. R. Digner, and G. V. Chandrashekhar, Cryogenics **29**, 258 (1989).
- [12] P. L. Gammel, L. F. Schneemeyer, J. V. Waszczak, and D. J. Bishop, Phys. Rev. Lett **61**, 1666 (1988).
- [13] K. Heine, J. Tenbrink, and M. Thoner, Appl. Phys. Lett. **55**, 2441 (1989).
- [14] N. Enomoto, H. Kikuchi, N. Uno, H. Kunakura, K. Togano, and K. Watanabe, Japan. J. Appl. Phys. **29**, L447 (1990).
- [15] T. Asano, Y. Tanaka, M. Fukutomi, and H. Maeda, Japan. J. Appl. Phys. **29**, L1066 (1990).
- [16] K. Sato, T. Hikata, and Y. Iwasa, Appl. Phys. Lett. **57**, 1928 (1990).
- [17] Y. Yamada, B. Oberst, and R. Flukiger, Supercond. Sci. Technol. **4**, 165 (1991).
- [18] J. Tenbrink, M. Wilhelm, K. Heine, and H. Krauth, Applied Superconductivity Conf. (Snowmass Village, CO, September 24-28, 1990).
- [19] K. Sato, T. Mikata, H. Mukai, M. Ueyama, T. Kato, T. Masuda, M. Nagata, K. Iwata, and T. Misui, IEEE Trans. Magn. **27**, 1231 (1991).
- [20] L. R. Motowidlo, E. Gregory, P. Haldar, J. A. Rice, and R. D. Blaugher, Appl. Phys. Lett. **59**, 736 (1991).

- [21] P. Haldar, J. G. Hoehn, Jr., J. A. Rice, and L. R. Motowidlo, *Appl. Phys. Lett.* **60**, 495 (1992).
- [22] K. Chen, L. Horng, H. S. Koo, C. Y. Shei, L. P. Wang, C. Chiang, T. J. Yang, W. H. Lee, and P. T. Wu, *Appl. Phys. Lett.* **59**, 1635 (1991).
- [23] T. Hikata, T. Nichikawa, H. Mukai, K. Sato, and M. Hiotsuyanayi, *Japan. J. Appl. Phys.* **28**, 288 (1989).
- [24] S. X. Dou, H. K. Liu, J. Wang, M. H. Apperley, C. C. Sorrell, S. J. Guo, B. Loberg, and K. E. Easterling, *Physica C* **172**, 63 (1990).
- [25] R. W. McCallum, J. D. Verhoeven, M. A. Noack, E. D. Gibson, F. C. Laabs, D. K. Finnemore, and A. R. Moodenbaugh, *Adv. Ceramic. Mater.* **2**, 388 (1987).
- [26] U. Balachandran et al., *JOM* **45**, 54 (1993).
- [27] S. X. Dou et al., *Supercond. Sci. Technol.* **6**, 297 (1993).
- [28] H. Maeda et al., *Jpn. J. Appl. Phys.* **27**, L209 (1988).
- [29] P. Majewsky et al., *Adv. Mater.* **3**, 488 (1991).
- [30] K. Schulze et al., *Z. Metal.* **81**, 836 (1990).
- [31] B. Hong et al., *J. Mater. Res.* **73**, 1965 (1990).
- [32] M. Takano et al., *Jpn. J. Appl. Phys.* **27**, 1041 (1988).
- [33] L. Pierre et al., *J. Appl. Phys.* **68**, 2296 (1990).
- [34] S. X. Dou et al., *Phys. Rev. B.* **40**, 5266 (1989).

- [35] P. Krishnaraj et al., *Physica C* **215**, 305 (1993).
- [36] B. Sarkar et al., *Mater. Res. Bull.* **28**, 263 (1993).
- [37] S. E. Dorris et al., *Physica C* **212**, 66 (1993).
- [38] R. Flukiger, A. Teremie, B. Hensel, E. Seibt, J. Q. Xu, and Y. Yamada, Presented at the ICMC (Huntsville, AL 1991).
- [39] Y. Ikeda et al., *Physica C* **190**, 18 (1991).
- [40] K. Osamura, S. S. Oh, and S. Ochiai, *Supercond. Sci. Technol.* **3**, 143 (1990).
- [41] S. X. Dou, H. K. Liu, and Y. C. Guo, *Proc. BHTSC-92* (Benijing, China, 25-29 May, 1992).
- [42] S. Jin and J. Graebner, *Mater. Sci. Eng. B* **7**, 243 (1991).
- [43] M. Wilhelm, H. W. Heuwuller, and G. Ries, *Physica C* **185-189** (1991).
- [44] N. Savvides, A. Katsaros, and S. X. Dou, *Physica C* **179**, 361 (1991).
- [45] K. H. Song, H. K. Liu, S. X. Dou, C. C. Sorrell, N. Savvides, and G. J. Bowden, *Mater. Sci, Mater.in Electron* **1**, 30 (1990).
- [46] J. Polonka, M. Xu, Q. Li, A. I. Goldman, and D. K. Finnemore, *Appl. Phys. Lett.* **59**, 27 (1991).
- [47] M. Xu, D. K. Finnemore, U. Balachandran, and P. Haldar, *Appl. Phys. Lett.* **66**, 24 (1995).

- [48] M. Xu, D. K. Finnemore, U. Balachandran, and P. Haldar, Appl. Phys. Lett. **78**, 1 (1995).
- [49] D. K. Finnemore, M. Xu, D. Kouzoudis, T. Bloomer, M. J. Kramer, S. McKernan, U. Balachandran, and P. Haldar, Appl. Phys. Lett. **68**, 22 (1996).