Conf-9108140--3

Presented at the Los Alamos Symposium "Phenomenology and Applications of High Temperature Superconductors", August 22-24 1991. To appear Addison Wesley, Ed. Kevin Bedell (1992).

SMRG 132

DEVELOPMENT OF HIGH TEMPERATURE SUPERCONDUCTORS FOR MAGNETIC FIELD APPLICATIONS

CONF-9108140--3

DE92 015930

David C Larbalestier
Applied Superconductivity Center
and
Department of Materials Science and Engineering
University of Wisconsin
Madison, Wisconsin 53706

Abstract

The key requirement for magnetic field applications of high temperature superconductor (HTS) materials is to have conductors with high transport critical current density available for magnet builders. After 3 or 4 years of being without any such object, conductor makers have had recent success in producing simple conductor prototypes. These have permitted the construction of simple HTS magnets having self fields exceeding 1 tesla at 4K. Thus the scientific feasibility of making powerful HTS magnets has been demonstrated. Attention to the technological aspects of making HTS conductors for magnets with strong flux pinning and reduced superconducting granularity is now sensible and attractive. However, *extrinsic* defects such as filament sausaging, cracking, misaligned grains and other perturbations to long range current flow must be controlled at a low level if the benefit of *intrinsic* improvements to the critical current density is to be maintained in the conductor form. Due to the great complexity of HTS materials, there is sometimes confusion as to whether a given sample has an intrinsically or extrinsically limited critical current density. Systematic microstructure variation experiments and resistive transition analysis are shown to be particularly helpful in this phase of conductor development.

DISCLAIMER

INTRODUCTION

The much-discussed technological applications of high temperature superconductors (HTS) to magnetic field technologies such as motors, generators, transmission lines, magnetic energy storage devices and train and ship propulsion systems all require high critical current densities (J_c). In fact the key requirement is for a high *transport* critical current density (J_{ct}) in a conductor form. A high J_c means of order 10^5 A/cm^2 and the qualifier transport means that the current be measured over macroscopic dimensions, thus crossing grain boundaries or other interfaces which produce the superconducting granularity which so strongly limits the J_{ct} of polycrystalline 123 compounds. The requirement of a conductor form establishes that the superconductor be paralled with a good normal metal conductor, that it be fabricable in long lengths at reasonable cost and that it be capable of being wound into a magnet while retaining these qualities[1-3]. Nothing like this existed during the first 3 or 4 years after Bednorz and Müller's discovery. However, the development of 2212-phase Bi-Sr-Ca-Cu-O (BSSCO) [4] and 2223-phase BSCCO phase [5] oxide-powder-in-tube (OPIT) conductor prototypes showed that Jct values of 10^4-10^5- A/cm^2 were possible when *genuinely polycrystalline* conductors were encased in a silver sheath. It was the development of these prototype conductors that today makes it realistic to invest important resources directed at making the technologies mentioned above practically feasible.

In this article I want to discuss some of the issues that arise in developing a technological understanding of the transport current of HTS materials. I do not discuss mechanical or fabrication properties because much of the knowledge on these topics is incomplete and empirical. A technological understanding of the J_c benefits enormously from a good scientific basis, even though scientific understanding is not absolutely necessary for technological progress. Indeed, the scientific and technical approaches to the problem may be quite different, as may the two communities who study the problem. Some interesting examples of this were found in the development of high current density in Nb-Ti, the material from which virtually all superconducting magnets are presently built, and this paper will accordingly recall some of the lessons learned in developing high J_c in conductors of this material.

One important difference of emphasis can be easily illustrated by contrasting the scientific and technological approach to the J_c. As argued elsewhere [1], there is a tendency to treat J_c as if it were as well-defined a parameter as the superconducting transition temperature, (T_c), is. In this simple view, current flow is dissipation-free below a well-defined J_c and dissipative above J_c. Flux creep and thermal activation phenomena make this approach conceptually wrong, as companion papers in this volume discuss[6-9]. However, discussion is undoubtedly simplified if a single value of J_c is chosen as the basis for a comparison of theory and experiment. Starting from a fundamental view of the J_c, the tendency is to identify the possible fluxon-microstructure interactions, calculate the energy of such interactions, estimate the length scale of the interactions in order to derive the elementary pinning force, sum all such forces over the different types of defects existing in the microstructure according to the most appropriate fluxon summation scheme and then, having determined the correct field dependence of the pinning functions from a knowledge of the pinning interaction and the appropriate thermodynamic parameters of the superconductor (eg H_c, λ, κ, ξ), finally predict $J_c(H)$. Such calculations, if truly *ab initio* are seldom accurate to better than a factor of 5 or 10, as might be expected from the many steps involved in the calculation. Conductor users and producers generally take a different approach. By virtue of the fact that the wire is being produced, they assume that the flux pinning is high enough and superconducting granularity restricted enough that the transport current density is usefully high. Their problem is to maintain J_{ct} near the level permitted by the microstructure, without interruptions of long-range current flow by irregularities of cross-section, cracks, misaligned grains or other defects which produce local variations of J_c. Their focus of attention is necessarily quite different from the flux pinner and tends to focus on fabrication and utilization issues.

Particular focus to the difference in the two viewpoints is given by the fact that their tolerable uncertainty scales are vastly different. As already stated, a first principles scientific calculation of J_c (J_{ct} is seldom explicitly distinguished from J_c in this approach) may well be considered good, if accurate to within a factor of 5 or 10 (particularly if the field or temperature dependence is accurately predicted), while a technological uncertainty in J_{ct} of even 50% for an established product would be a commercial disaster. Thus most present development of Nb-Ti conductor neglects flux pinning in favor of controlled material or fabrication parameter variation studies. For HTS conductors the best approach is still unclear, since the parameter space inhabited by the materials themselves, as well

as present prototype conductors, is so large that it is frequently debatable what controls the properties of any given sample. The present uncertainties in J_{ct} for apparently well-made prototype silver-sheathed BSCCO conductors are still quite large, of order at least 2 and perhaps as high as 5 or more.

This paper will explore some of the reasons for discrepancies such as the above, developing a viewpoint complementary to the more physics-based ones of Kes[6], Fisher[7], Nelson[8] and Kapitulnik[9]. The paper will explore some microstructural issues from the viewpoint of the need to design experiments which bring the *macro*structure, as well as the *micro*structure under explicit control. We take the view that the development of HTS magnetic field applications is underway and that such conductor development issues, as well as the fundamental ones of flux pinning, flux creep, phase transitions of the vortex lattice, granularity and other basic issues of fluxon dynamics all need to be understood if the technological applications that so many have dreamed of since the first discoveries of high temperature superconductors are actually to come to fruition.

INTRINSIC AND EXTRINSIC CONTROL OF THE CRITICAL CURRENT DENSITY

In the development of optimized Nb-Ti conductors, a key step was the explicit recognition that, although the upper limit to the J_c is determined by *intrinsic* elementary fluxon-microstructure pinning interactions (f_p) and by the summation of these elementary interactions into the bulk pinning force (F_p), in practice the transport J_{ct}, defined as the critical current (I_c) divided by the cross-sectional area (A), is subject to a second limit introduced by *extrinsic* factors which produce larger-scale, frequently macroscopic variations of the critical current [10]. Figures 1-4 illustrate this point, both for a Nb-Ti and for a Bi-Sr-Ca-Cu-O (BSCCO) conductor. Fig. 1 shows the nanometer scale α-Ti precipitates within an optimized Nb48wt%Ti filament that provide the strong elementary flux pinning interaction which makes a high J_c possible. These precipitates have a ribbon-like morphology and are highly anisotropic in shape. By measuring the precipitate volume fraction, size (in particular, the thickness) and separation and by correlating these quantitative microstructural parameters to the electromagnetic properties, it was possible to prove[11,12] that it is these α-Ti particles which determine the flux pinning and that the particles exert their maximum effect when thinner than and separated by less than a coherence length (ξ). Given that ξ(4K) is 5nm for

Nb47wt%Ti, this sets the natural length scale needed for flux pinning studies of Nb-Ti. This is of order 1nm or 0.2ξ, a scale which is fortunately accessible to existing transmission electron microscopes.

The extrinsic, more macrostructural-scale limits are provided by many factors[10]. One of the simplest to understand is shown by Fig 2. A filament which has a periodically varying filament cross-section is said to be sausaged. Such a filament has an I_{ct} which is extrinsically limited by the smallest local cross-section. If the current in such a necked region exceeds the local critical current, dissipation occurs due to flux flow within the superconductor or by resistive current transport across the matrix as the excess current transfers to a neighboring filament. Sausaging has many causes and for this reason can be difficult to understand and control. It is the most common limit on performance of all practical conductors[10,13,14].

Similar phenomena certainly exist in HTS materials too, but much less is explicitly understood about both intrinsic and extrinsic factors. Fig. 3 provides a high magnification view of a misaligned pair of grains in a silver-sheathed 2223-BSCCO conductor prototype. The magnification is larger than that used in Fig 1 to reveal the flux pinning microstructure of Nb-Ti and the anisotropic, atomic-scale planar nature of the microstructure is clear. In principle, the microstructural defects responsible for flux pinning and/or superconducting granularity ought to be visible. However, transmission microscopes are not very sensitive to individual atoms, particularly if they are the important, but low atomic number, oxygen atoms. By analogy to the 123 compounds[15], there is a tendency to assign the flux pinning of BSCCO to oxygen vacancies[6,16]. However, microscopy cannot yet give the sort of quantitative picture of the defect structure exemplified by Fig.1, either for oxygen or for cation defects or vacancies. Figs. 1 and 3 are strikingly different, in that the Nb-Ti microstructure is clearly heterogeneous and two phase, while that of BSCCO appears single phase and almost featureless, except on the periodic scale of the crystal structure itself. Nor is it yet possible to deduce from TEM grain boundary images whether the grain boundaries have depressed superconducting properties and exhibit superconducting granularity or whether they are fully coupled and exhibit no granularity. Thus we already see a major difference between Nb-Ti and HTS materials: microstructural examination can define the magnitude and origin of the defect microstructure in Nb-Ti but, so far, there are very few cases where this has been possible for HTS materials. A crucial consequence of the difference between

the two materials is that much experimentation with HTS materials occurs "blind", because the consequences of changing the processing cannot be explicitly defined by microstructural examination.

By contrast, at the present early stage of HTS conductor development, the imaging of extrinsic defects is rather easy. As Fig 4 shows, there are many possibilities that must be taken into account when considering possible extrinsic limits on J_{ct}. Fig 4 is a macroscopic view on a scale of about 50 x 100μm of a silver-sheathed 2223-BSCCO tape. In this case the grain structure has been made visible by etching[17]. The macrostructure is seen to be anything but uniform: the sheath thickness is not uniform, the grain alignment varies both through the thickness of the tape and along the tape axis. Insulating second phase particles also disrupt the overall cross-section and the local grain alignment. In contrast to the almost perfect microstructure of Fig.3, the macrostructure is clearly highly defective.

In conductors, rather than scientific single crystal samples, it is almost invariably the extrinsic aspects of the microstructure illustrated in Figs. 2 and 4 that control J_{ct}. Apparently well-planned experiments frequently do not have a logical explanation unless this is appreciated. These technological issues do not make it any less important to understand the basic flux pinning or granularity issues that are central to so many scientific studies of HTS. What is important is to recognize that both aspects be treated, generally simultaneously.

When do the extrinsic factors become important and how large are their magnitude? In Nb-Ti conductors the extrinsic factors can be easily assessed by measuring the resistive transition. It has long been common to fit the resistive transition to a power law, where the voltage V is related to the current I by the resistive transition index n ($V \propto I^n$). Fig 5 shows that the index n has a characteristic dependence on magnetic field. In the intrinsic limit, n(H) increases steeply from a value of order 10 to one of more than 100, as H decreases from about 0.1 H_{c2} to 0.9 H_{c2}. This progressively changes to a flattened plateau-like characteristic as the J_{ct} becomes extrinsically limited. The intrinsic to extrinsic transition for Nb-Ti conductors occurs as the wire is drawn to progressively finer sizes. Deformation instabilities, provoked by a variety of microstructural causes, produce the sausaging visible in Fig. 2 and this can be clearly correlated to the flattened n-H characteristic seen at small sizes, where filament sausaging is extensive[13,14]. The characteristic can be correlated to the Coefficient of Variation (COV) in the filament cross-sectional area, where the COV is defined by

the standard deviation of the measured filament cross-section (σ) divided by the mean cross-sectional filament area (A) and thus to the J_{ct} defined by I_{ct}/A[13,14].

The magnitude of the effects can be obtained by treating the resistive transition more quantitatively. As originally suggested by Baixeras and Fournet[18] and then experimentally studied by Warnes and Larbalestier[13], the curvature of the resistive transition contains information about the distribution of local critical currents $f(I')$ within the conductor:

$$V(I) = A \int_0^I (I - I')\, f(I')\, dI' \qquad (1)$$

where V(I) is the voltage produced at a given current I and A is a factor appropriate to the particular dissipative processes occurring within the conductor when I is greater than I'. By differentiating Equation 1 twice with respect to the current, one obtains:

$$d^2V/dI^2 = A\, f(I) \qquad (2)$$

Two typical distribution plots are shown in Fig. 6. In the case of smooth filaments the I_c distribution is sharp and the full width of the distribution at half maximum (FWHM) divided by the average critical current of the distribution $\langle I_c \rangle$ is of order 15%. When the COV of the filament cross-section is large, FWHM/$\langle I_c \rangle$ can easily reach 50%. Nb-Ti conductors having such properties are practically unusable.

Few similar measurements have yet been made on BSCCO conductors. One indication that the resistive transition characteristics may be more complex than for Nb-Ti is shown in an investigation by Heine et al[19]. They compared the n values of Ag-sheathed YBCO and BSCCO conductors (Fig.7). Their n(H) characteristics are rather different from those seen for Nb-Ti in Fig.5. The two HTS conductors have n values which fall sharply in only weak millitesla fields,

then tending to a plateau value of less than 10. The initial fall is presumably associated with the field-induced destruction of some Josephson-coupled current paths, particularly in the YBCO conductor. The low plateau values may be associated with the locally variable cross-section which is active in passing transport current. One component is the real longitudinal variation of cross-section which is still very common in prototype conductors (Fig. 3); a second contributor may be a variation in the active cross-section because of variability in the local grain-to-grain connectivity associated with local grain misalignments. This variable can operate in both radial and length-wise directions. Flux creep, particularly in the BSCCO tape, should also contribute to the shape of the transition, indeed making a power law fit of the resistive transition inappropriate. The essential point is that multiple factors can operate and that all need to be identified and brought under control. Certainly the resistive transitions of present BSCCO conductors tend to be very broad, as compared to Nb-Ti conductors of even moderate quality.

The best J_{ct}(0T,77K) values for the 2223 conductors are developed by multiple pressing and reaction cycles which tend to produce an aligned grain structure which is largely 2223 phase[5,20,21,22]. However, nominally identical thermal treatments applied to rolled samples produce J_{ct} values which factors of 2 to 5 less than the present maximum of 50,000A/cm^2[5]. Is it an *intrinsic* flux pinning or an *extrinsic* macrostructural variation which produces such a big difference? Given the evidence of cross-sections like Fig. 3, it appears likely that the controlling factors often lie in differences of crack density, grain alignment and second phase distribution. Thus controlled flux pinning enhancement experiments will only achieve full success when the extrinsic factors limiting the J_{ct} are identified and controlled.

FLUX PINNING

A high level of flux pinning is very desirable, since this is the only way to develop a high bulk current density. Granularity and extrinsic factors can only reduce the intrinsic flux pinning current density. Broadly speaking, it appears that the 123 compounds have high flux pinning even at 77K, while the development of greater flux pinning in the more anisotropic 2212 and 2223 BSCCO compounds is still needed. Thus flux creep and low flux pinning are more of a problem for the BSCCO compounds than for the 123 compounds. Unfortunately, granularity of polycrystalline samples is severe in the 123 compounds and J_{ct}(H) is typically 2 to

4 orders of magnitude below the flux pinning values[23]. For BSCCO, the flux pinning and transport J_c can be rather similar, thus showing that granularity need not be a problem in HTS materials[19]. One of the key goals of present research is to understand the specific factors that produce such contrasting behavior, with a view towards engineering the best features of each into one or both of these material classes.

Flux pinning and flux creep are covered in detail in the companion paper by Kes[6], where calculations of pinning by various microstructural defects observed in YBCO and BSCCO are presented. These calculations are useful for establishing the general magnitude of the pinning that is feasible for HTS materials. However, such calculations are subject to at least three important uncertainties. One is that few experiments exist where the density of a given proposed pinning site has been varied in a controlled way. Such experiments are vital if the choice of pinning site is to be verified and if the magnitude of the pinning interaction (and its temperature and field dependence) is to be checked. A second issue is the choice of appropriate thermodynamic parameters. Almost all elementary pinning interactions have the thermodynamic critical field $H_c(T)$ as the parameter which scales the strength of the elementary pinning interaction:

$$\delta E = -\mu_o \delta H_c^2(T) \cdot V_i / 2 \qquad (3)$$

where δE is the change in fluxon energy as an interaction volume (V_i) of fluxon occupies a pin having a difference in critical field $\delta H_c(T)$ from the matrix. In general, of course, the most favorable pinning sites are not superconducting and $\delta H_c(T)$ then equals the full $H_c(T)$ of the superconducting matrix.

Respectable investigations of the properties of single crystals yield values of H_c which are not yet all consistent with each other [6,24-26]. Thus the zero temperature extrapolations for $H_c(0)$ range from 0.7 to 1.55T for YBCO. For 2212-BSCCO a value of 0.35T is frequently chosen, although no explicit variation of $H_c(0)$ as T_c varies from about 80 to 95 K is yet available [6,24]. Since $f_p(=\delta E/\xi)$ is proportional to $H_c^2(T)$, any uncertainty in H_c leads to significant imprecision in the calculated pin strength f_p. A third difficulty lies in identifying the correct elementary pinning force summation scheme. In a strong pinning LTS system such as Nb-Ti, full summation can be explicitly verified[12]. The J_c values of HTS materials, at least the 123 compounds, are sufficiently high that full summation of

f_p also seems intuitively reasonable. However, collective pinning summations have found more favor than full summation schemes[6]. This may be because there is as yet no general agreement on how to treat the experimental difficulties of taking J_c data over wide ranges of temperature and field space without introducing significant uncertainty factors associated with granularity and flux creep[27-28]. The net result of these uncertainties is that *a priori* calculations of the flux pinning in HTS systems are remarkably hard to verify. For example, early flux pinning assessments tended to emphasize pinning by twins[29]. When experiments varying the twin density failed to show any systematic dependence of the J_c on the twin density[30], it became clear that other defects or mechanisms must control the J_c. A similar situation appears probable in so far as the pinning effect of growth dislocations in thin films is concerned[31-32]. As Jin et al.[33] have reported, there is in fact no positive correlation between J_c and dislocation density that can yet be made. The true reason for much of this uncertainty is probably that the coherence lengths of HTS materials are so short that almost any defect can pin flux[34]. Whether any one particular defect in fact controls the pinning can only be addressed by experiments that systematically vary that particular defect density. Unfortunately, HTS microstructures cannot, in general, yet be controlled to the extent required.

The lesson of conventional low temperature superconductors (LTS) is that J_c is maximized by providing both a strong elementary pinning interaction and a high density of interactions[11,12]. Optimized Nb-Ti represents a very interesting case, because the bulk pinning force F_p is optimized at a precipitate thickness t considerably smaller than that which optimizes the elementary pinning force f_p. In fact F_p is optimized when t is 0.2ξ (Fig. 8) and when the separation of pinning centers is about ξ. This clearly corresponds to a very dense pinning situation, in which the density of pinning sites (assuming that each α-Ti precipitate acts as an independent pinning site) exceeds the density of fluxons over almost all temperature and field space.

Can such a situation be developed for HTS materials? An interesting analysis is provided by Hylton and Beasley[35]. They asked what pin site density would be required to explain the very high J_c(4K,0T) values ($\sim 10^7 A/cm^2$) measured on the best thin films. Their conclusion was that strong pins need to be spaced ~5 nm apart. This spacing is very comparable to Nb 47wt%Ti: the important difference is that the pins are visible in Nb-Ti but have not been identified in thin films. The lack of microstructural evidence for dense pinning centers in YBCO thin films led

us to consider alternative explanations for the high J_c values of thin films. One characteristic of the best films is that their thickness (d) is comparable to or less than the penetration depth λ. In this case a substantial fraction of the current can be due to shielding currents, whose magnitude is limited by depairing rather than flux pinning. The conclusions of Stejic et al.[36] are that J_c tends to the depairing current density $J_d = H_c/\sqrt{3}\lambda$ for $d< \lambda$ and to a limit of $2J_d(\lambda/d)$ for $d>\lambda$. In the thick film limit, however, J_c becomes dominated by flux pinning rather than depairing.

This prediction has been experimentally checked on thin films of Nb47wt%Ti having a *low* density of pinning centers. For a $\lambda/2$ thick film, it was possible to develop J_{ct} which reached $J_d/3$, while a microstructurally similar 4λ thick film reached a limit almost an order of magnitude lower. Comparison can be made to the very best values attained in bulk-scale Nb-Ti conductors[12] where the high J_c values are certainly developed by flux pinning. In this case (Fig.9) the maximum values are about a factor of 3 less than those seen in the λ /2 thick film. Thus we conclude that calculations which attribute all of the J_c of thin films to flux pinning are unlikely to be correct. This conclusion can also provide a plausible explanation of the contrasting normal and superconducting state behavior of high quality single crystals and thin films. Good single crystals have J_c values which are typically 1 or 2 orders of magnitude below thin films[30]. The natural hypothesis is to invoke the atomic scale defect density as the difference. Good thin films have lattice parameter anomalies that suggest some disorder[30]. However, such disorder is hard to reconcile with the low normal state resistivities of high J_c thin films, which are almost identical to those of good quality (but low J_c) single crystals[37]. Indeed, thin films and single crystals show quite different responses to small oxygen deficiencies: small deficiencies significantly raise the J_c of crystals[15] but depress the J_c of films[38,39]. Cation site disorder might produce strong pinning in films and could be compatible with the lattice parameter anomalies but this explanation appears incompatible with the similar normal state resistivity of films and crystals already quoted. Again, therefore, this emphasizes the need for experiments in which the microstructure is varied in a controlled manner. However, in the absence of agreement on what are the controlling microstructural parameters of thin films, we turn to bulk samples, where all dimensions are large compared to the penetration depth and concerns about the contribution of shielding currents to the measured transport or magnetization currents do not apply.

One set of interesting experiments on bulk materials are those on melt-processed quasi-single crystals of YBCO in which the diameter of insulating Y_2BaCuO_5 (211 phase) particles can be varied in a size range of order 0.1-10 μm and with a volume fraction of order 10-30%. The accompanying paper by Murakami[40] describes the properties of such samples. Excluding irradiation methods, such dispersions of fine 211 particles, when small in size, have produced the highest J_{ct} values yet seen in bulk materials, of order 10^5 A/cm^2 and $5x10^4$A/cm^2 in fields of 0 and 1T at 77K. The dependence of J_c on added volume fraction of 211 particles has been demonstrated, as has the dependence on size of the particles. For example, no explicit addition of 211 particles (it should be noted, however, that even nominally stoichiometric 123 samples have about 20% of 211 phase) produces J_c values almost 10 times lower than those quoted above[15,40]. A dependence of J_c on inverse particle diameter in the range 1-10μm for samples containing 10% of added 211 phase has been demonstrated. Such dependencies demonstrate that the significant pinning centers have been identified and that the system is useful for modelling flux pinning. By comparison to the Nb-Ti benchmark quoted earlier, we see that the volume fraction of pinning center is high (about 20% in Nb47wt%Ti, as compared to 20-40% in YBCO), that the properties of the precipitate phase are appropriately different from the matrix (α-Ti is normal, while 211 is insulating), but that the size of the 211 particles is still far from optimum (the smallest particles are 0.1μm in diameter and are still 2 orders of magnitude larger than the coherence length.)

A complementary view of the flux pinning possibilities of a much smaller-sized and higher density defect population in 123 compounds is provided by oxygen vacancies. The systematic effects of changing δ (in the composition $YBa_2Cu_3O_{7-\delta}$) over the approximate range 0.05 to zero were first explored by Daeumling et al.[15]. Fig. 10 shows that the magnetization hysteresis of good single crystals continuously declines as δ declines. A characteristic signature of the deficiency is the intermediate field minimum in the hysteresis, which is the result of the more weakly superconducting O-deficient regions being driven normal by the increasing field. In good crystals containing little or no mosaic sub-structure, diffusion is very slow at the temperatures below 400°C needed to produce δ of 0.02 or less[41]. Thus this behavior is common and we were able to show that these vacancies are the dominant pinning centers in good single crystals, as well as in melt-textured crystals containing large (>5nm) 211 particles[15]. The behavior is reversible when oxygen is taken in and then discharged[42].

An interesting question is how the oxygen vacancies are distributed, whether as individual lattice defects or as ordered regions. For large values of δ (e.g. δ>0.2), there is abundant evidence of ordering into superstructures, particularly the $O_{6.5}$ or OII phase[43-48], but this has not been possible to observe for δ<0.1. However, ordering at small δ seems very likely on many grounds. For example, the trends of the a and b lattice parameters do not show any smooth extrapolation to the tetragonal (i.e. a=b) value for any value of δ<0.4[43]. These various considerations stimulated Vargas and Larbalestier[49] to consider the consequences of flux pinning if the oxygen vacancies order themselves by a spinodal decomposition of $YBa_2Cu_3O_{7-\delta}$ into O_7 and $O_{6.5}$ regions.

One characteristic of a spinodal decomposition is that there is a characteristic wavelength of the precipitation. From observations at larger values of δ this can be measured to be of order 25nm[45,50]. Knowing the equilibrium δ(T) relationship, one can then calculate the concentration and size of OII domains as a function of temperature. A typical oxygenation temperature is 425°C, yielding a δ of 0.037, an OII volume fraction of 0.074 and diameter (on a spherical approximation) of 2.8nm. An interesting consequence of such an oxygenation treatment is that it produces a very high density of pinning centers (the flux line lattice(FLL) spacing, ϕ_0/B, is 22nm at 5T) with a size comparable to a fluxon diameter (~3nm). Thus the oxygen defect microstructure is much more comparable in size and spacing to that seen in Nb-Ti (Fig. 1) than to that produced by the 211 particle dispersions discussed above. Unfortunately the OII phase is itself superconducting (its bulk T_c value is 60K) and its elementary pinning force is thus reduced.

The flux pinning due to the core interaction with the OII domains can be calculated using standard models[49]:

$$\delta E = -\frac{1}{2}\mu_o \left[(H_{COI})^2 - (H_{COII})^2\right] V_i \ [J] \qquad (4)$$

The elementary pinning force is then given by:

$$f_p = \delta E / \xi_{ab} \ [J/m] \qquad (5)$$

An upper limit to the bulk pinning force F_p is given by the full summation of the

elementary pinning interactions, i.e. $F_p = nf_p$ [N/m^3], where n is the number density of interactions. The predicted area density of OII domains exceeds the fluxon density $n_{fl} = B/2\phi_0$ [m^{-2}] over the whole field range B < 10 tesla ($n_{fl} \leq 2 \times 10^{15}$ m^{-2}) so that full summation then occurs over all fluxons, n_{fl}. Thus F_p can be calculated from:

$$F_p = \frac{\pi B \mu_o \left[(H_{COI})^2 - (H_{COII})^2\right] r^2 v_{OII}}{4\phi_0 \xi_{ab}} \; [N.m^{-3}] \qquad (6)$$

and the critical current density is calculated using $J_c = F_p / B$. Values of $H_{cOI}(0)$= 1.55T, $H_{COII}(0)$=0.38T(0) 0.38 T and $\xi_{ab}(0)$=1.6 nm from single crystal measurements are used. We assume that $H_c(T)$ follows $H_c(0)(1 - t^2)$ where t = T/T_c, and $\xi_{ab}(T)$ is is calculated from $(2 \pi \phi_0 / H_{c2}(T))^{1/2}$.

Such calculations appear to fit the data well in the low temperature limit at 4K (Fig. 11). Indeed, the predicted dependence of F_p on the radius r and volume fraction of the O_{II} phase ($F_p \propto r^2 v_{OII}$) is observed experimentally [51]. Thus when the annealing temperature is reduced from 425°C to 375°C, J_c (4.2K, 3T) falls from 3.5 x 10^6 A/cm^2 to 2.4 x 10^5 A/cm^2, as compared to the predicted decline from 2.6 x 10^6 A/cm^2 to 2.4 x 10^5 A/cm^2. The temperature dependence is not well-fitted by the simple model, however. Flux creep and single crystal granularity [15] cannot be ignored in deducing J_c values from magnetization measurements. The whole problem of how to treat the temperature dependence is complex. For example, Kes [6] has calculated the pinning due to uncorrelated single oxygen vacancies using the quasi-particle scattering model. Such a model has a strong temperature dependence almost identical to that of Figure 11, *without* needing to take account of flux creep or granularity. This all points to the fact that multiple models can be applied to HTS pinning. With no decisive reason to choose one or the other, systematic microstructural variation experiments are crucial.

Few systematic experiments have yet been performed on BSCCO. Oxygen vacancies in the CuO_2 planes have been suggested as the principal pinning centers [6,16], although there is no evidence for such vacancies either in BSCCO or YBCO. One set of systematic experiments have been performed in 2212-phase BSCCO by Nomura and Chiang [52]. They found that cation (i.e. Bi, Cu, Sr or Ca) vacancies in the 2212-phase of order 10^{23} cm^{-3} could be achieved. J_c and the flux creep rate were both strongly dependent on the cation vacancy concentration, the

improvements reaching almost an order of magnitude in both J_c (60K,1T) and creep rate for the high defect concentrations.

Controlled microstructural variation experiments of the sort described above are not easy to perform or to interpret because of the rather imperfectly known phase relationships of HTS materials and because of the limitations of electron microscopy for determining the true density of atomic-scale defects. Thus, developing, a verifiable scientific understanding of naturally occurring flux pinning centers in HTS materials may be slow. Artificial pinning centers, such as those introduced by heavy ion irradiation, are particularly interesting in this context, since they allow the formation of line pins, whose size and density should be susceptible to quantitative measurement[53].

SUPERCONDUCTING GRANULARITY

It is well-established that high angle grain boundaries (HAGB) impede the transport of current. The reason for this is that many grains are only weakly coupled across the grain boundaries, this leading to a lowered and strongly field-dependent depression of the supercurrent across the boundary. The most explicit demonstration of this was provided by the artificial thin film bicrystal experiments of Dimos et al.[54]. By investigating a variety of tilt and twist misorientations, they concluded that Josephson junction behavior was seen when the misorientation across the boundary exceeded about 5°.

These thin film bicrystal results have been central to setting the framework within which to understand the role of grain boundaries in limiting current flow in HTS materials. The Josephson junction character of HAGB can explain the low and strongly field-dependent J_c of polycrystalline 123 compounds very well. On the other hand, there are important situations which were not addressed by the experiments. For example, few measurements were made in magnetic field (and then only in weak fields). Even the weakly coupled bicrystals had J_{ct} values exceeding 10^5 A/cm^2 (0T,4.2K), values 1 to 2 orders of magnitude higher than seen in bulk-scale bicrystals. Given the previous discussion concerning the role of depairing and flux pinning currents in determining the J_{ct} of thin films, it is not surprising that to rely only on the magnitude of the J_{ct} is not an infallible guide to the character of the coupling across the boundary.

In work at Wisconsin, we have tried to develop a deeper understanding of the

character of the behavior of grain boundaries by measuring the electromagnetic properties of bulk-scale bicrystals and then determining the grain boundary microstructure and composition of the *same* grain boundary[55-57]. Thus we hope to develop the first direct microstructural description of the grain boundary electromagnetic properties for HTS materials. Our analysis of the properties of HAGB is somewhat more complex than that used for the thin film bicrystals, because it assesses the character of the superconducting coupling across the boundary by analyzing the $J_c(H)$ characteristic of the boundary. In such a description, the boundaries are described as being fully coupled (i.e. flux pinning controls the J_{ct} across the boundary), weakly coupled (i.e. the boundary acts as a Josephson junction) or resistive. The goal is to understand why the boundaries have such different properties. So far some 20 naturally grown bicrystals have been studied. An overview of their properties is shown in Table 1.

Naturally grown bicrystals may have different properties from the artificially prepared bicrystals of Dimos et al.[54]. They grow while slowly cooling from the melt, thus allowing opportunities for abutting crystals to rotate and to seek low energy orientations[58]. This was not the case for the thin film bicrystals, because the misorientation was imposed by the misorientation of the underlying $SrTiO_3$ bicrystal which serves as the substrate. There is a definite tendency for certain crystal misorientations to be favored in the bulk-scale bicrystals. The favored misorientations tend to be those having low Σ, that is misorientations for which the Coincidence Site Lattice (CSL) formed by the interpenetration of the two lattices has a relatively small volume. The ratio of the CSL cell volume to the crystal unit cell is denoted Σ and this ratio is generally held to be significant up to values of at least 50. Σ5, Σ17 and Σ41 misorientations were all found to be favored for YBCO bicrystals[59]. The structural units which form the boundary are also important: grain boundaries are not amorphous and their particular structure clearly can be expected to determine the local superconducting coupling.

To support this statement, several pieces of evidence can be presented. For example, two bicrystals of nominally identical misorientation (C10 - ie parallel [001] c axes with a 10° rotation about the [001] axis and P15 - ie crystal II rotated 90° about the common b axes of both crystals, crystal II then again being rotated 15° about the c_{II} axis) had contrasting character. In each case, one was flux pinning and one a Josephson Junction (Table 1). The P type misorientations are interesting because they were not studied in the thin film bicrystal studies and because they cause the basal (001) planes of the two crystals to be normal to each

other. In principle, therefore, the coupling across such a boundary might be expected to be weak because one direction is the short coherence length (ξ_c ~ 0.3nm). Figure 12 shows the J_c(H, 77K) characteristics of 2 high angle grain boundaries (P3, C14), as compared to one low angle grain boundary (C3) and a single crystal. The essential point is that, even though the magnitude of the J_c varies from one sample to another, all have a J_c(H) characteristic which smoothly diminishes towards zero at 7-8T, field values which are quite similar to the irreversibility fields H^* observed in epitaxial thin films and single crystals.

What microstructural feature is it that permits strong coupling across the highly misoriented P type boundaries? Unfortunately, we were not able to perform TEM on this particular bicrystal but the P0 misorientation has been studied in MOCVD films by Gao et al [60]. This misorientation occurs in predominantly c-axis films; a small proportion of grains grow with an a/b axis normal to the substrate. Chan et al [61]. have shown that high zero field J_c values can be obtained across such boundaries. High resolution transmission electron microscopy (HREM) on such films [60] showed that the macroscopically planar (001), boundary actually facets into steps which lie alternately along (001) and (013). Across the (001) facet the CuO_2 planes in the two abutting crystals do not contact, since they have a T orientation. Gao et al. made the reasonable suggestion that it is the (013) facets which provide the strongly-coupled flux pinning connection shown in Figure 12.

Reasonable though this suggestion is, it cannot be accepted without question. A significant problem is that the (013) orientation is found in step-edge Josephson Junctions, where clearly the boundary is weakly coupled. Of course, one can postulate that Josephson behavior occurs by contamination of the step-edge junction boundary which is much easier than for a bulk-scale bicrystal, since the film is in close proximity to the substrate. Such arguments, while plausible, merely reinforce how many variables there are in these systems and how vital it is to build a parallel microstructural and electromagnetic understanding of grain boundaries.

A natural question is to ask what it is that goes wrong at Josephson Junction grain boundaries? Figure 13 shows an HREM image of a C26 (~ 2° away from the Σ17 CSL which occurs at 28°) grain boundary. What is most striking about this image is the perfection of the atomic structure right up to the boundary. Observable displacements of the atoms (in fact it is the cations which are imaged) occur only within a thin layer right at the boundary, the thickness of which

appears comparable to or less than ξ_{ab} (~ 1.5nm at 4K). Whatever produces the weak coupling of this boundary occurs on a very fine scale.

Transmission microscopy is, unfortunately, not very sensitive to light elements. Oxygen is of course a key element for HTS compounds and its electromagnetic effects can be large, as Figure 14 shows. In this case a C27.5° bicrystal was studied (this lies within 0.5° of the Σ17 CSL). When leads were attached, the crystal lost a little oxygen because it was heated in air to ~ 250°C. Its $J_c(H)$ behavior showed a steep fall in only weak fields, behavior characteristic of a Josephson junction. After re-oxygenating for 50 hrs at 420°C, the characteristic had markedly changed, now exhibiting a double step characteristic of parallel weak and strong coupling paths [56]. A further oxygenation of 72 hrs at 420°C raised J_c(77K,7T) by two orders of magnitude. These results directly show the important role that oxygen can play in changing both the magnitude and character of current transport across a high angle grain boundary. Recent analysis of the structure of grain boundaries within a CSL framework suggests that the local oxygen content could be a direct function of misorientation[61].

Little direct information about the properties of BSCCO grain boundaries is yet available. However, the very striking property of polycrystalline BSCCO is that it is possible to achieve J_{ct} exceeding 10^5 A/cm^2 to fields exceeding 20T at 4.2K and J_{ct} exceeding 10^4 A/cm^2 at fields of ~0.5T at 77K[5]. Polycrystalline 123 compounds seldom achieve more than 10^2 A/cm^2 under these conditions[62]. Is the grain boundary structure of 2212 - or 2223 - BSCCO inherently more strongly coupled than that of the 123 compounds? We do not know the answer to this question, since bicrystal experiments have not yet been performed on BSCCO. A new view of the high J_{ct} values in BSCCO has recently been provided by Bulaevskii et al [63] and Malozemoff [64]. The microstructural basis of this model is that BSCCO grains tend to grow as plates which align themselves with mutually parallel c axes (see Figure 4), such that neighboring plates overlap each other, as in a brick wall. This grain morphology is not developed in 123 compounds. The basis of the model is that the current transfers around the "bad" (001) tilt boundaries by traversing the large area planar (001) twist boundaries. This current is a Josephson current. The key points that make c axis current transport possible across the boundary are (i) that the CuO_2-CuO_2 plane spacing does not increase across such a grain boundary because the boundary forms at the double Bi-O layers without increasing the plane separation; (ii) that the length (L) to thickness (D) aspect ratio of the grains is very large; (iii) that the c axis [001]

current is a Josephson current and (iv) that the characteristic size of the Josephson junctions is very small, the characteristic dimensions being set both by the insulator thickness (d ~ 1nm) between the CuO_2 planes and by the spatial variation of coupling (r_0) within the grain boundary. This latter dimension is not very well-defined: it may originate in grain boundary dislocations, incommensurate distortions of the Bi-O layers or other yet to be defined parameters. The predictions of the model are in general accord with the behavior of BSCCO tapes. The model predicts that the J_c will first drop at a field $H_1 = \phi_0/Ld$, stabilize at a plateau and then exhibit a second fall off to zero at a field H_2, where $H_2 = \phi_0/r_0d$. BSCCO tapes indeed exhibit a plateau in J_c which starts at about 1 T, a value compatible with grain lengths of order 2μm and an insulator thickness of 1 nm. The second fall-off beyond the plateau has not yet been seen in BSCCO; however, it is intriguing to note that it has been seen for a c-axis aligned $DyBa_2Cu_3O_7$ sample which has the plate-like grain morphology of BSCCO. In this case the fall off occurred at ~ 25T at 4.2K[65], thus yielding a value of 80nm for r_0, a not unreasonable value nor one which should be impossible to verify.

The contrasting behavior of 123 and BSCCO polycrystalline materials is of enormous technological significance. Whether HAGB in BSCCO and YBCO are fundamentally different in their properties is not yet known, nor is it known whether the brick wall model provides the correct explanation of the excellent high field J_{ct} of BSCCO. If so, this is hypothesized as being is a direct consequence of the grain boundary being a sub-divided Josephson junction. Just as in the flux pinning boundaries, the local atomic structure of the boundary should control the properties and thus the grain boundary structure needs to be identified. In this regard, the recent demonstration by Lelay et al. [66] that grain boundaries of the short coherence length lead and tin molybdenum sulfides are <u>not</u> weak-linked is a provoking result. This adds further complexity to the issue of whether short coherence length superconductors are inherently granular, as suggested by Deutscher and Mueller [67].

SUMMARY

Factors important to the development of high transport critical current density of polycrystalline HTS materials have been described and reviewed. High flux pinning within the grains can be produced in 123 compounds by observable defects. Neglecting irradiation methods, the highest J_c values have been obtained

with 0.1-1μm dia insulating 211 particles. Oxygen defects having a diameter of order 3nm can produce a finer and denser dispersion of pinning centers, but such defects have a small elementary pinning force and tend to produce intra-grain granularity and are thus not desirable pinning centers. Optimum flux pinning would in principle combine the best features of these two defect classes. Flux pinning in epitaxial 123 films is still not well understood, but the high J_{ct} values of films having thicknesses of order a penetration depth or less have a significant contribution from shielding currents and therefore J_c should not all be attributed to pinning. Whatever level of flux pinning is possible within grains, the transport current of HTS materials is controlled by the currents which can cross grain boundaries. Transport across high angle grain boundaries of the 123 compounds remains difficult but some high angle grain boundaries do have a flux pinning character which responds strongly to oxygenation condition. Much less is understood about the significant microstructural defects of BSCCO: flux pinning and granularity appear less strong and less marked, respectively, than in 123 compounds. The more 2 dimensional nature of BSCCO produces a plate-like grain morphology which aligns more easily than does 123. This may permit high critical current densities to cross grain boundaries even if they are weak linked.

ACKNOWLEDGEMENTS

I am grateful to many colleagues for discussions, in particular S.E. Babcock, X.Y. Cai, L.D. Cooley, H. Edelman, Y. Feng, E.E. Hellstrom, P.J. Lee, A.P. Malozemoff, G. Stejic, A. Umezawa and J.L. Vargas. The support of our work by DARPA, Electric Power Research Institute, the Department of Energy and the National Science Foundation is gratefully acknowledged.

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