OXYGEN SELF-DIFFUSION IN $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$: GRAIN-BOUNDARY EFFECTS

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Abstract

Polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ samples with different grain size have been elaborated by sintering. Magnetic properties exhibit a strong dependence on grain size. Oxygen self-diffusion experiments in some of the samples show that this process is highly anisotropic. The diffusion profiles measured by SIMS are influenced by short-circuit effects, they are well-fitted by a grain-boundary diffusion solution. Nevertheless microstructure studies show that beside grain-boundaries few other extended defects (microcracks, thick and heterogeneous intergranular phases...) are present in the samples. Slowest volume diffusion coefficients and grain-boundary diffusion coefficients have been determined.

1 - INTRODUCTION

Grain-boundaries, and more generally extended defects, have a great influence on the electronic transport properties of the ceramic superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ /1/. Magnetic properties have also been seen to exhibit strong effects due to grain-boundaries (GBs), that will be shown. The aim of this work is to study the influence of the extended defects on the oxygen self-diffusion in polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and to correlate the observations to the microstructure of the same samples.

2 - SAMPLE PREPARATION AND CHARACTERIZATION

2.a - Preparation

Two ways of preparation have been used/2/. In the first one, the ceramic powder $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, as prepared by Rhône-Poulenc, was pressed into pellets (isostatic or uniaxial charge) at room temperature and then sintered under oxygen gas flow. In the second one, the ceramic was sintered under quasi isostatic pressure with oxygen gas flow. Six samples have been synthesized (called A to F in table I). The three first samples have been annealed at 926°C (13 to 96 hours), with a following second step at 480°C (24 to 72 hours); the three last ones have been annealed at 940°C (240 hours) and at 480°C (72 hours). Optical microscopy observations show an increase of the grain sizes (from 2 μm up to 130 μm) and of the density (78 % to 95.5 %) from A to F. X-ray diffraction characterization of the samples show mainly the orthorhombic phase formation which presents different values of the parameters (Table I). Chemical analysis by EPMA indicate a systematic copper deficiency compared to the "123" phase. These effects could be associated with local oxygen composition changes.

2.b - Microstructure by TEM

Thin foils were prepared from the samples by ion milling before observation by Transmission Electron Microscopy (TEM). Bearing in mind the atomic transport properties, the met extended defects can be classified in two types:

- Type I : Clean grain-boundaries
- Type II : Thick and heterogeneous intergranular phases

Any phases have been observed in the GBs or in the triple grain-boundary junctions. Particularly we did not see amorphous precipitates to GBs /3/ in our samples, the Si and Ca content being low.

Figure 1 shows a type I defect and, beside and parallel to the first one, a type II defect which contains some CuO microprecipitates as it has also been observed by Romano et al /4/ or Sirikaya et al /5/. Microcracks can also be present in these intergranular zones /2/. Similar observations were previously done by other authors, see for exemple Laval et al /3/ or Murr et al /6/. We have nevertheless observed that the proportion of type II defects is quite low

Samples	Grain size	Compacity	Cu	Cell parameters (nanometer)		
				a	b	c
A	2 μm	78 %	2.89	0.383	0.389	1.164
B	10 μm	84 %	2.91	0.383	0.389	1.162
C	15 to 25 μm	90 %	2.91	0.382	0.388	1.167
D	5 to 10 μm	91 %	2.88	0.383	0.389	1.170
E	25 to 100 μm	92.5 %	2.86	0.381	0.388	1.165
F	7 to 30 μm	95.5 %	2.83	0.384	0.388	1.165
	70 to 130 μm		2.87			

Table I.

Fig. 1 - TEM micrograph of type I defect (grain-boundary) (arrow) and of type II micrograph of an intragranular zone (double arrow) with microprecipitates of CuO and a void.

2.c - Magnetic properties /7/

In the high T_c superconducting materials, magnetic properties are known to be strongly linked with their structural properties. For example, low field magnetic susceptibility measurements can be used to detect the presence of various phases inside a granular superconducting sample. On the other hand, high field ($H > H_{c1}$) magnetization measurements are correlated to the defects which pin the vortex lines inside the grains of a granular superconductor.

We have carried out hysteresis measurements in an intermediate magnetic field range ($0 < H < 300$ Oe) in order to show that the irreversible phenomena in this field range are mainly localized at the grain boundaries and that the corresponding hysteresis loops depends on the size of the grains. Samples A, B and D have been studied (grain size respectively 2,5-10,10 μm). The measurements of magnetization M were performed at 4.2 K in alternate magnetic field H using various amplitudes ($H_{\text{max}} = 300$ Oe) looking for hysteresis cycles at low frequency (20 Hz).

As seen on figure 2, there is a strong dependence of the hysteresis cycles on the grain size.

The total magnetization can be considered as the addition of the two contributions: intergranular magnetization $M_1(H)$ and intragranular one $M_2(H)$. $M_1(H)$ corresponds to the whole junction between grains, the porosity between grains and a zone close to the grain surface whose thickness corresponds to the penetration length. The influence of the intergranular zones increases when the grain size decreases, the magnetization loop at the applied low magnetic field becoming more and more important. On the contrary, $M_2(H)$, which is the intragranular part of the magnetization, corresponds to the shielding of the applied field by supercurrents circulating at the surface of the grains. The volume corresponding to this diamagnetism decreases when decreasing the size of the grains. Thus the slope of the $M(H)$ curve in the region where M is almost linear with H (i.e. when most of the weak links between the grains have been broken), decreases when the size of the grains is reduced as it clearly appears on Fig. 2. The obtained results suggest that samples with very small grain sizes (< 1 μm) exhibit a typical intergranular behaviour, the hysteresis cycle observed corresponding to the vortex penetration in the material through the boundaries and junctions.

Fig.2 - Hysteresis cycle $M(H)$ of the samples A, B and D showing the effect of grain size.

3 - OXYGEN SELF-DIFFUSION

3.a - Experimental Techniques.

We have measured the oxygen self-diffusion coefficient, D , using the gas/solid isotope

exchange method ($^{18}\text{O}_2$ in our case). The samples D and E were used for those experiments were mechanically polished with diamond sprayed past to $2\text{ }\mu\text{m}$ before annealing. Temperature T ranged between 300°C and 600°C , the annealing time t and the oxygen pressure $p\text{O}_2$ were the same for all diffusion experiments i.e. : respectively one hour and 22 kPa . Before the diffusion annealing, the samples were equilibrated at the same T and planed for the diffusion experiments to avoid chemical gradients in the sample. The samples were quenched in air immediately after the annealing diffusion.

The diffusion profiles were analysed by Secondary Ion Mass Spectrometry (CAMECA IM 60). A Cesium source was used to sputter the samples. Figure 3 shows a typical diffusion profile on short penetrations obtained using the "crater method" /8/ (the analysed area is a circle of $62\text{ }\mu\text{m}$ in diameter) but for large penetrations, a bevelled section of the samples at a small angle was necessary and the analysis was carried out by the step scanning method (the analysed area is a band of about $62\text{ }\mu\text{m}$ large and several hundred microns long). Figure 4 illustrates this method in the case of a particular profile.

Fig. 3 - Diffusion depth profiling using the crater method ($T=300^\circ\text{C}$, $t=1\text{ hour}$, $p\text{O}_2=22\text{ kPa}$).

Fig.4 - Diffusion depth profiling using the step scanning method on a sample polished with a small angle ($\alpha = 1.56^\circ$, $T=550^\circ\text{C}$, $t=1\text{ hour}$, $p\text{O}_2=22\text{ kPa}$).

Fig.5 a - Oxygen self-diffusion coefficient strongly depends on the grain orientation. GB's effects may be masked by the strong contrast of the grains.

Fig.5 b - In few samples, annealed long time at high temperatures (480°C) before the diffusion treatment, microcracks appear to locally mask the oxygen diffusion.

3.b - Results

Figures 5a and 5b are ionic images obtained on mass 18 showing the heterogeneous distribution of the tracer in the material and the influence of microcracks in few samples. The profiles shown on figures 3 and 4 were obtained on samples corresponding to the ionic images seen respectively on figures 5a and 5b.

The strong diffusion anisotropy observed by J. Routbort et al /9/ on single crystals is responsible for the images of figure 5. Microcracks, when they are present on a part of the sample, fully perturb the profiles as seen on figure 4 (local short circuits). Such profiles were discarded in the following. Volume diffusion coefficients, D , can be deduced from profiles such as the one seen on figure 3 using the Ficks law corresponding to a constant surface concentration, C_s , of the tracer. We have taken into account for a limited exchange rate, H , through the surface using the solution /10/ :

$$\left(\frac{C(x,t) - C_s}{C_\infty - C_s} \right) = \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right) - e^{H^2 Dt} + Hx \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} + H\sqrt{Dt} \right) \quad (1)$$

C_∞ is the natural concentration of ^{18}O (0.2%)

Figure 6 shows that the experimental curve (+) is well fitted by the calculated one (□) only in the first part. A discrepancy appears at large penetrations that we have attributed, in a first attempt, to GB diffusion.

Fig.6 - Concentration versus penetration of experimental(+) and theoretical(□) curves taking into account for an exchange term at the surface.

Assuming that the grain-boundaries play the main role and that the boundary conditions are similar to those leading to the Whipple's solution, the GB diffusion coefficient D' is related to D by the relation :

$$D'\delta = 0.661 \left(- \frac{d \log (C - C_\infty)}{d x^{6/5}} \right)^{-5/3} \frac{2\sqrt{Dt}}{t} \quad (2)$$

Where δ represents the GB effective thickness ($\delta = 1\text{nm}$). When $\log (C - C_\infty)$ is plotted as a function of $x^{6/5}$, the behaviour is linear (see figure 7). This result is in good agreement with this idea that a large part of the oxygen self-diffusion happens through grain-boundaries.

Another way to analyse the profiles such as the one shown on figure 6 is to consider that they result from the superposition of two (or more) contributions obeying the equation (1) but characterized by different diffusion coefficients. Figure 8 shows such an analysis.

Fig. 7 - $\log (C - C_{\infty})$ versus penetration x to the power $6/5$ showing a grain-boundary diffusion behaviour.

Fig. 8 - Concentration versus penetration curves showing the experimental diffusion profile (+), two theoretical volume contributions ($\diamond$ and $\blacksquare$) and their sum ($\square$) which gives a good fit to the experimental curve.

The deduced values of the coefficients D and D' (represented by $\square$ and $\ast$) are given in figure 9. We can notice that the first series of points well agree with the work of Roulet et al (represented by $\diamond$) [11]. Another interesting point is the small difference (of the order of the departure from stoichiometry) with the study of Tu et al [12] on the chemical diffusion coefficient $\tilde{D}$ (represented by $\times$). The activation energy for each mechanism of diffusion were estimated respectively to be $Q = 118$ kJ/mole and $Q' = 174$ kJ/mole; the preexponential terms to be $D_0 = 1.12 \times 10^{-3} \text{ cm}^2/\text{s}$ and $D'_0 = 7.41 \times 10^{-4} \text{ cm}^2/\text{s}$.

Fig.9 - Arrhenius plot of volume and GB diffusion : ∇ and $\triangle$ represent respectively volume diffusion coefficients in (a,b) plan and in c direction /9/ , $\diamond$ volume diffusion coefficients in polycrystals /11/ , $\times$ chemical diffusion coefficient /12/ , $\square$ and $*$ represent respectively volume diffusion coefficients and GB diffusion coefficients (Q' and D' are calculated from the lower volume diffusion coefficients($\ominus$) corresponding to the first part of the diffusion profiles).

3.c - Discussion

Despite of the problems existing in applying classical solutions of volume and GB diffusion to a system exhibiting an anisotropic behaviour and several kinds of extended defects, it seems possible to attribute to GB diffusion a large part of the diffusion process. Type II defects are in smaller number than type I (clean GBs) and can be neglected. The behaviour of the analytical Whipple solution is well obeyed.

The D coefficients which have been measured are probably not exactly those corresponding to the slowest directions in all cases but represent a biased average of all directions by the fact we have chosen the apparently larger grains on the surface to analyse the profiles (that is equivalent to analyse a textured material). The spread of D values is explained by the anisotropy.

The choice of D to deduce D' s from diffusion tails leads only to an order of magnitude of D' (δ has been taken equal to 1 nm).

D. R. Clarke et al /13/ and G. Collin et al /14/ have suggested that the presence of other phases (such as BaO or CuO) at grain-boundaries would be barriers for diffusion. Our GBs are generally clean and it seems that they can act as short circuits.

The ratio of activation energies $\frac{Q'}{Q} = 1.5$ is rather surprising. A similar result has been observed by Prot et al /15/ looking for diffusion in sub-boundaries of Alumina. The general ideas to interpretate this result are : a diffusion mechanism different in GBs as it is in bulk or a segregation effect of impurities which are in large amounts in such

materials. The effect on Q' explains also the large preexponential factors D'_0 obtained.

We have seen that an alternative analysis of the results consists in considering the diffusion profiles come from the superposition of several volume contributions. Both preceding analysis lead to volume diffusion coefficients in good agreement with measurements performed on polycrystals /11/ and are higher than those measured in direction c on single crystals /9/. New experiments carried out on highly textured material would help to distinguish between the two interpretations.

4 - CONCLUSION

We have seen the effects of the grain size (i.e. of the grain-boundaries) on magnetic properties. The grain-boundaries seem also to act as short-circuits on self-diffusion.

A systematic study of the samples after annealing diffusion (microstructure, crystallographic microchemistry) is necessary to emphasize the role of grain-boundaries, and the influence of diffusion anisotropy in this system.

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