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Anomalies of the Fickian Diffusion During 2D-Decomposition of Superconducting $YBa_2Cu_3O_{6+X}/Y_2BaCuO_5$ Composites

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Abstract

Based on a thermodynamic analysis of the relevant experimental data, some anomalies of the diffusion mass-transport during two-dimensional (2D) decompositioning high-temperature superconducting (HTSC) cuprates are considered. Possible mechanism for the manifestation of phase fluctuation-like effects in the HTSC cuprates, especially with respect to the physical properties of melt-textured composites, thin films, coatings, nanomaterials and heterostructures are discussed.

Keywords

Superconducting Y123, diffusion-controlled topo-chemical decomposition, standard oxygenation treatment, diffusion anomalies, a phase fluctuation

1. Introduction

As has been shown in numerous studies[1-5], the formation and growth of large (up to a few microns) stacking faults (SFs) occurs in $YBa_2Cu_3O_{6+X}$ / Y_2BaCuO_5 (123/211) melt-textured composites, from low-angle boundaries and especially around 211 precipitates, as well as degradation layers within gaps of microcracks around 211 precipitates, which themselves are filled with Cu-rich phases, upon increasing the oxygenation time (at $Po_2 = 1$ bar, $T = 723$ K, as used in study[1]). Both SFs and 123 matrix degradation layers are observed[1,5] along the (001) planes, giving rise to a pronounced two-dimensionality (2D) of the aged microstructure. SFs in 123 orthorhombic phase have been assumed[1,5] to consist of an additional CuO chain layer adjacent to the BaO plane, giving rise to a double chain layer, that is a local $YBa_2Cu_4O_8$ (124) structure or a $Y_2Ba_4Cu_7O_{14+Z}$ (247) structure. Large splitting widths observed in TEM studies have been assumed[1,5] to be relevant to a negative SF energy which is associated with a local phase transformation to a 124 structure or to a 247 structure.The dissolving of large SFs in the melt textured composites has been studied[2,3] (at $Po_2=10^{-9}$-10^{-10} bar, 613-629 K, and at 0.2-1 bar, 1073-1203 K, correspondently). The chemical character of the decomposition processes has been experimentally shown in studies[3,4]. In the present study, the thermodynamic analysis[6,7] of such processes in the cuprates has been carried out with the aim of finding the rate-controlling steps, the nature of the SFs-like precipitates, the role of the lattice defects' regions in the internal topo-chemical reactions, and, finally, to show a possibility of a manifestation of a phase fluctuation-like effect.

2. Results and Discussion

According to studies[8-12], the 123 orthorhombic structure is thermodynamically unstable at all temperatures and compositions, and particularly, under experimental[1] conditions corresponding to a standard oxygenation treatment of the ceramics (Fig. 1, point [1]). Within extrapolation of the corresponding lines in Fig. 1 to 723 K, the decomposition processes can occur as follows:

$$6YBa_2Cu_3O_{6+X}=Y_2BaCuO_5+2Y_2Ba_4Cu_7O_{14+Z}+3BaCuO_2+0.5(6x-3-2z)O_2, \qquad (1)$$

$$6YBa_2Cu_3O_{6+X}=2Y_2BaCuO_5+Y_2Ba_4Cu_7O_{14+Z}+3Ba_2Cu_3O_{5+Y}+0.5(6x-3-z-3y)O_2, \qquad (2)$$

$$4YBa_2Cu_3O_{6+X}=2Y_2BaCuO_5+3Ba_2Cu_3O_{5+Y}+CuO+0.5(4x-2-3y)O_2; \qquad (3)$$

reactions (1) and (2) correspond to the solid lines 1 and 2 in Fig. 1, and the metastable reaction (3) - to the chained-dotted line 3 in Fig. 1.

Some other reactions can be also taken into account[8-12]:

$$2\ YBa_2Cu_3O_{6+X} + CuO + 0.5\ (1 + z - 2x)\ O_2 = Y_2Ba_4Cu_7O_{14+Z}, \qquad (4)$$

$$YBa_2Cu_3O_{6+X} + CuO + 0.5\ (1 - x)\ O_2 = YBa_2Cu_4O_8. \qquad (5)$$

Then, the decomposition reaction can be considered as (1) or (2), where (2) can be combined as the sum of (3) and (4). Another decomposition reaction (6) can be combined as the sum of (3) and (5), resulting in:

$$5YBa_2Cu_3O_{6+X}=YBa_2Cu_4O_8+2Y_2BaCuO_5+3Ba_2Cu_3O_{5+Y}+0.5(5x-3-3y)O_2. \qquad (6)$$

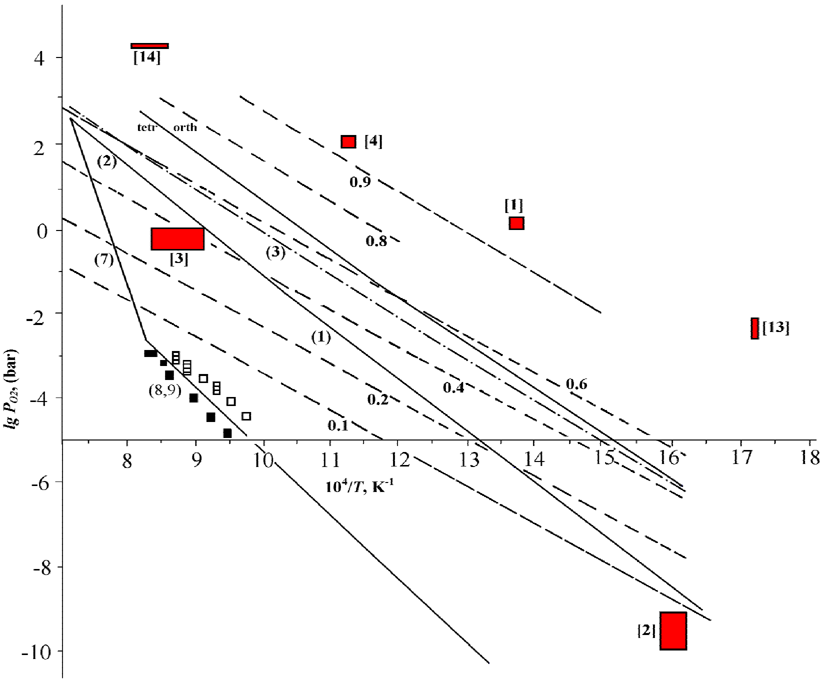

Figure 1. Evaluated, extrapolated and experimental stability range of Y123 phase, in the light of studies[8-12]. The dashed lines represent the intercalated oxygen content (x). The "tetr/orth" line corresponds to the tetragonal-orthorhombic phase transition. Solid lines 7 - 9 represent: $YBa_2Cu_3O_{6+X} \rightarrow Y_2BaCuO_5$ + (Liquid

phase) + O_2; $9YBa_2Cu_3O_{6+X} = 4Y_2BaCuO_5 + YBa_4Cu_3O_{8.5+Q} + 10BaCu_2O_2 + 0.5(5.5+9x-q)O_2$; $2YBa_2Cu_3O_{6+X}=Y_2BaCuO_5 + BaCuO_2+2BaCu_2O_2 + 0.5(2x+1)O_2$. The points ▲, □, ■, [1], [2], [3], [4], [13], [14] are the known experimental data.

All these reactions can be used for the interpretation of processes[1-5,13,14], if SFs are equivalent to two-dimensional 247 or 124 phases, as it has been mentioned above. The thickness of SFs is assumed[1,2,5] to be $h_{SF} \approx 2$ Å, that is the same as the double layer. The thickness of the SFs' phase of 247 may be assumed [6,7] to be $h_{SFP} \approx 10$ Å, comparable with the c-axis size of the cell of the 247 structure, that is the phase layer of a nanometer thickness.

There are reasons[1-12] to assume that the first (obviously, fast) step (3) of the decomposition reaction ((2) or (6)) is mainly localized in the vicinity of pre-existing 211 precipitates, which can grow due to the formation of new layers of 211 phase. Then it can provide the flowing of the second (obviously, sluggish) step [(4) or (5)] of the decomposition reaction [(2) or (6)]. It can be controlled[6,7] by the diffusion supply of oxygen and/or copper atoms (from the 211 vicinity) through the 123 matrix to the tops of the growing (from there) SFs of 124 or 247.

The apparent chemical diffusion coefficient can be evaluated as[6,7]:

$$D_{(app)} \approx L^2 / t, \qquad (7)$$

where L is the characteristic diffusion length (about the SFs′ linear size), and t is the oxygenation time. According to TEM data[1], the SFs elongated in one of two mutually perpendicular ‹100› directions about 2 μm away from the 211/123 interface, from which they originated ($t = 156$ h, T=723 K); hence, $D_{(app)} \approx 1 \cdot 10^{-13}$ cm^2/s.

The obtained value is smaller than the experimental values[15,16] of the chemical diffusion coefficient for oxygen in the ab-plane of the 123 matrix ($D_{O(123)ab}$), and higher from the experimental value[15] of the tracer diffusion coefficient for copper in the ab-plane of the 123 matrix ($D^*_{Cu(123)ab}$), Table 1; the latter can be of the same order or by one order lower than the chemical diffusion coefficient[15,16].

Table 1. Experimental values[15,16] of the tracer diffusion coefficients (D^*, cm^2/s) and the chemical diffusion coefficients (D, cm^2/s) of the relevant elements in the Y(123) and Y(124) ceramics (for P_{O2}-T conditions[1]).

$D^*_{O(123)c}$	$D^*_{O(124)ab}$	$D_{O(123)ab}$	$D^*_{O(124)c}$	$D^*_{Cu(123)ab}$	$D^*_{Cu(123)c}$	$D^*_{Ba(123)ab}$
$1 \cdot 10^{-16}$	$3 \cdot 10^{-16}$	$7 \cdot 10^{-10}$	$3 \cdot 10^{-20}$	$1 \cdot 10^{-18}$	$3 \cdot 10^{-20}$	$2 \cdot 10^{-38}$

By taking into account a high anisotropy of the diffusion in the 123 matrix (Table 1), and the above mentioned orientation of the SFs with respect to 211 precipitates in single-domain samples[1], one can predict the diffusion supply of copper and oxygen in the ab plane of the matrix. This is consistent with TEM data[1] that the SFs propagate easier along the ‹100› direction, and the shear component of their associated displacement vectors is exchanged between the a and b axis directions of the 123 matrix at every twin boundary.

According to the data of ref.[15] revealing a strong anisotropy of the oxygen diffusion in the ab plane of the 123 matrix, the quantity for the b axis direction ($D_{O(123)b}$) is much larger than for the a axis direction ($D_{O(123)a}$). Hence, for randomly twinned samples, there is $D_{O(123)ab} \approx 0.1\, D_{O(123)b}$, because oxygen atoms diffuse preferably along the b axis direction (Fig. 13, in reference[15]).

From these two facts, one can conclude that the rate-controlling stage of the process[1] is the oxygen diffusion supply, which is characterized by a decrease of several orders of magnitude of the diffusion coefficient. On the other hand, the copper diffusion supply is obviously characterized by an enhancement of the diffusion coefficient over several orders of magnitude.

In this respect, it can be noted that the oxygen diffusion supply through SFs areas of 124 or 247 can be neglected (due to the relatively small diffusion coefficient ($D^*_{O(124)ab}$, Table 1). It is also relevant to emphasize that (as it is seen from Table 1) the diffusion redistribution of barium and yttrium atoms in the 123-matrix (which is necessary for flowing of step (3)) is possible only in the close vicinity of the 211 precipitates.

Results[1] indicate that the 123 matrix undergoes a local severe plastic deformation, mainly, in the 211 vicinity, when the composite is submitted to the oxygenation treatment. The most apparent feature of the treated microstructure is a drastic increase of the dislocation density within the 123 matrix up to 10^{10} cm^{-2}, as well as the dislocation-twin interaction modes. Samples[1] are also characterized by both a high density of low-angle grain boundaries, and a high concentration of homogeneously distributed fine 211 precipitates (31-36 vol. %), which provide a high effective 211/123 interface area, as well as a high density of microcracks in the matrix at the interfaces.

There is a basis[17] to assume that in the studied samples[1] both the oxygen diffusion decrease, and the copper diffusion enhancement are caused by the influence of the co-segregation at dislocations. This is also consistent with the fact pointed out in study[15] that twin boundaries in the 123 matrix do not contribute apparently to the effective bulk oxygen diffusion.

The local deformation, cracking and the dislocation formation in the composites[1] under the oxygenation treatment, obviously, occur at the expense of the energies of the internal reactions[17].

By using Fig. 1, the free energy change per mole of the ceramics, for instance for step (3), can be evaluated as:

$$\Delta G_{(3)} = RT \ln \left[(P_{O2(3)}/P_{O2}^{eq})^{(2x-1-1.5y)/4} (a_{Oy}/a_{Ox}^{eq})^{3/4} /(a_{Ox}/a_{Oy}^{eq})\right], \qquad (8)$$

where P^{eq}_{O2} can be found from the extrapolated line 3 in Fig. 1; R is the gas constant; thermodynamic activities of oxygen (a_O) can be found by using the data of ref.[16]; the internal stresses can be estimated (10^2-10^3 bar, as it is obtained in study[17]).

If the SFs (phase) concentration (ρ_{SFP}, cm^{-1}) is obtained from TEM observation[3], the volume percentage of SFs (phase) can be evaluated as:

$$Vol.\ \%\ (SFs) \approx \rho_{SFP}\, h_{SFP}\, 100, \qquad (9)$$

where $h_{SFP} \approx 1 \cdot 10^{-7}$ cm. By using stoichiometric coefficients of the reactions ((2) or (6)), and taking into account 31-36 vol. % of the pre-existing 211 phase, the phase composition of the treated samples[1-5] can be evaluated.

The plausibility of the concepts developed above can be confirmed by results of such data analysis[2-4,13,14], see Fig. 1.

The results of the data analysis show the possibility of a manifestation of a phase fluctuation-like effect with respect to physical properties of HTSC cuprates, which can be evaluated for different oxygenation regimes.

3. Conclusion

The growth of the SFLP under the conditions of the standard oxygenation treatment of the ceramics can be described by two successive reactions. The first fast one provides the CuO precipitate formation, and it is localized in the lattice defects' regions (cracks, interfaces and grain boundaries near the Y_2BaCuO_5 inclusions). The second "sluggish" step (with participation of the CuO phase) provides the SFLP formation in the near lattice defects' regions.

Depending on the conditions, the processes can be controlled by anomalous diffusion of oxygen or the other elements (Cu, Ba) to the active regions with lattice defects, the 'reactors'. The anomalies of diffusion transport are mainly related to the influence of impurity segregation at lattice defects of the dislocation type.

Thermodynamic analysis of the relevant experimental data is used to develop options for the manifestation of a phase fluctuation-like effect in high-temperature superconducting (HTSC) cuprates, especially with respect to the physical properties of melt-textured composites, thin films, coatings, nanomaterials and heterostructures.

4. References

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