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Creep and diffusion in high T_c superconductors

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Abstract. — Data from steady-state creep and tracer diffusion tests are presented for the high-T_c superconductors $YBa_2Cu_3O_x$ and $Bi_2Sr_{1.7}CaCu_2O_y$. Both compounds exhibit oxygen nonstoichiometry and possess orthorhombic, layered perovskite crystal structures in which Cu occupies the B sites and the other cations occupy the A sites. For each, the A-site cations diffuse most slowly. For every species that has been measured, diffusion is much faster in the *ab*-plane than in the *c*-direction. At low stresses, both superconductors deform by diffusional creep with the rate-controlling species being a A-site cation in $YBa_2Cu_3O_x$.

Introduction.

Creep is among the few experiments able to yield information about the diffusion processes of the minority point defects. When a material is compressed at high temperature, the pure transport of matter, i.e. grain boundary sliding accommodated by transport of matter (GBS) and the nonconservative motion of dislocations are among the different mechanisms controlling its plastic deformation. Isolated or clustered point defects can act as elementary steps for diffusion. These diffusion processes are responsible for dislocation climb (recovery creep) or for transport of matter (Nabarro, Coble, or GBS creep).

The different models describing high-temperature plastic behaviour lead to a generalized creep relation between the strain rate ($\dot{\varepsilon}$) and an effective diffusion coefficient (D^{eff}) :

$$\dot{\varepsilon} = A \left(\frac{b}{d} \right)^h \frac{\mu b}{kT} \left(\frac{\sigma}{\mu} \right)^n D^{\text{eff}} \tag{1}$$

where A is a dimensionless constant, b the Burgers vector, d the grain size, μ the shear modulus and σ the applied stress. The other parameters have their usual meaning. In this creep equation A, h, and n are model-dependent parameters.

The effective diffusion coefficient requires some explanation. If the material is a pure element, only one species participates in the diffusion. On the other hand, if the material is a compound all species must participate in diffusion. At the same time, each species can have different diffusion paths. An equation for the effective diffusion coefficient of each species, x, in the compound, can be written :

$$D_{\mathrm{x}}^{\mathrm{eff}} = D_{\mathrm{x}}^{\mathrm{l}} + 10\left(\frac{\sigma}{\mu}\right)^2 D_{\mathrm{x}}^{\mathrm{P}} + \frac{\pi\delta}{d} D_{\mathrm{x}}^{\mathrm{GB}} \tag{2}$$

where the superscripts indicate the path for the diffusion (l = bulk, p = dislocation cores and GB = grain boundaries) and δ is the grain boundary width.

In a compound, the point defects are often associated with a deviation from stoichiometry. The thermodynamic equilibrium is fixed by the vapour pressure of the different components of the compound. In oxides, where the oxygen pressure (P_{O_2}) is large, the two thermodynamic conditions T and P_{O_2} can be easily controlled, so at high temperature where kinetics are fast, thermodynamic equilibrium is easy to achieve.

Plastic deformation under these conditions occurs without decomposition of the material. Therefore, the fluxes of the components must be in the same ratio as in the compound. For $\mathrm{A}_\alpha\,\mathrm{B}_\beta\,\mathrm{O}_\gamma$,

$$\frac{I_{\mathrm{A}}}{I_{\mathrm{B}}} = \frac{\alpha}{\beta}, \quad \frac{I_{\mathrm{A}}}{I_0} = \frac{\alpha}{\gamma} \quad \text{and} \quad \frac{I_{\mathrm{B}}}{I_0} = \frac{\beta}{\gamma} \tag{3}$$

These equations can be rewritten in two different forms, depending on whether we assume that the overall composition is constant or is constant along each path. Details may be found in [1].

If it is assumed that the overall composition is constant, the effective, combined diffusion coefficient can be written

$$D_{\mathrm{com}}^{\mathrm{eff}} = \left[\frac{\alpha}{D_{\mathrm{A}}^{\mathrm{eff}}} + \frac{\beta}{D_{\mathrm{B}}^{\mathrm{eff}}} + \frac{\gamma}{D_0^{\mathrm{eff}}}\right]^{-1} \tag{4.a}$$

or if it is assumed that the composition along each path is constant,

$$D_{\mathrm{com}}^{\mathrm{eff}} = \left[\frac{\alpha}{D_{\mathrm{A}}^{\mathrm{l}}} + \frac{\beta}{D_{\mathrm{B}}^{\mathrm{l}}} + \frac{\gamma}{D_0^{\mathrm{l}}}\right]^{-1} + 10\left(\frac{\sigma}{\mu}\right)^2 \left[\frac{\alpha}{D_{\mathrm{A}}^{\mathrm{P}}} + \frac{\beta}{D_{\mathrm{B}}^{\mathrm{P}}} + \frac{\gamma}{D_0^{\mathrm{P}}}\right]^{-1} + \\ + \frac{\pi\delta}{d}\left[\frac{\alpha}{D_{\mathrm{A}}^{\mathrm{GB}}} + \frac{\beta}{D_{\mathrm{B}}^{\mathrm{GB}}} + \frac{\gamma}{D_0^{\mathrm{GB}}}\right]^{-1} \tag{4.b}$$

It is easy to see that the forms of $D_{\mathrm{com}}^{\mathrm{eff}}$ are quite different and are only equal if the diffusion coefficient of one species is much smaller than the others, for any path.

If we assume that A and B have diffusion coefficients smaller than the coefficient 0, $D_{\mathrm{com}}^{\mathrm{eff}}$ becomes (Eq. (4a)) :

$$D_{\mathrm{com}}^{\mathrm{eff}} = \frac{\left[D_{\mathrm{A}}^{\mathrm{l}} + 10\left(\frac{\sigma}{\mu}\right)^2 D_{\mathrm{A}}^{\mathrm{P}} + \frac{\pi\delta}{d} D_{\mathrm{A}}^{\mathrm{GB}}\right]\left[D_{\mathrm{B}}^{\mathrm{l}} + 10\left(\frac{\sigma}{\mu}\right)^2 D_{\mathrm{B}}^{\mathrm{P}} + \frac{\pi\delta}{d} D_{\mathrm{B}}^{\mathrm{GB}}\right]}{\beta\left[D_{\mathrm{A}}^{\mathrm{l}} + 10\left(\frac{\sigma}{\mu}\right)^2 D_{\mathrm{A}}^{\mathrm{P}} + \frac{\pi\delta}{d} D_{\mathrm{A}}^{\mathrm{GB}}\right] + \alpha\left[D_{\mathrm{B}}^{\mathrm{l}} + 10\left(\frac{\sigma}{\mu}\right)^2 D_{\mathrm{B}}^{\mathrm{P}} + \frac{\pi\delta}{d} D_{\mathrm{B}}^{\mathrm{GB}}\right]} \tag{5.a}$$

or (Eq. (4.b)) :

$$D_{\mathrm{com}}^{\mathrm{eft}} = \left[\frac{\alpha D_{\mathrm{B}}^{\mathrm{l}} + \beta D_{\mathrm{A}}^{\mathrm{l}}}{D_{\mathrm{A}}^{\mathrm{l}} \times D_{\mathrm{B}}^{\mathrm{l}}}\right]^{-1} + 10\left(\frac{\sigma}{\mu}\right)^2 \left[\frac{\alpha D_{\mathrm{B}}^{\mathrm{P}} + \beta D_{\mathrm{A}}^{\mathrm{P}}}{D_{\mathrm{A}}^{\mathrm{P}} \times D_{\mathrm{B}}^{\mathrm{P}}}\right]^{-1} + \\ + \frac{\pi\delta}{d}\left[\frac{\alpha D_{\mathrm{B}}^{\mathrm{GB}} + \beta D_{\mathrm{A}}^{\mathrm{GB}}}{D_{\mathrm{A}}^{\mathrm{GB}} \times D_{\mathrm{B}}^{\mathrm{GB}}}\right]^{-1} \tag{5.b}$$

If the diffusion through one path is much faster than through the other two, the two effective combined diffusion coefficients become equal. If, for example, grain boundary is the fastest

$$D_{\text{com}}^{\text{eff}} = \frac{\pi \delta D_{\text{A}}^{\text{GB}} \times D_{\text{B}}^{\text{GB}}}{d\ \alpha D_{\text{B}}^{\text{GB}} + \beta D_{\text{A}}^{\text{GB}}} . \tag{6}$$

It is always possible to write the effective diffusion coefficient as :

$$D^{\text{eff}} = D^0 \left(\frac{P_{\text{O}_2}}{P_{\text{O}_2}^*} \right)^m \exp\left[-\frac{\Delta H}{kT} \right] \tag{7}$$

where, D^0 is the preexponential term, P_{O_2} is the partial pressure of oxygen, $P_{\text{O}_2}^*$ is the reference partial pressure of oxygen and ΔH is the activation energy for the diffusion process. See [2] for more details. If one species has the smaller diffusion coefficient, m and ΔH are characteristic of the point defects responsible for self-diffusion. However, in the more general case that $D_{\text{A}} \simeq D_{\text{B}}$, and assuming that diffusion proceeds *via* the same atomic defect, m is still characteristic of the point defects, but ΔH represents an average activation energy of the A and B species.

When the concentration of point defects is small, the equations for defect creation or annihilation and the law of mass action are applicable for each species, and the values of m and ΔH obtained for creep correlate with the one obtained for diffusion. However, if the concentration of point defects is large (normally > 1 %), the correlation between m and ΔH and the point defects is more complicated because of defect-defect interactions.

High-T_c superconductors present several problems. One is that at least two species have very similar diffusion coefficients. Another is that the concentration of anion point defects is large. In addition, oxygen ions have multiple sites, each with a different cation environment. The results of creep and diffusion studies in the $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (BSCCO) high-T_c superconductors will now be discussed.

Diffusion.

$\text{YBa}_2\text{Cu}_3\text{O}_x$. — Oxygen ion vacancies are the majority species in YBCO. Tracer diffusion of oxygen has been measured in both polycrystalline and single-crystal YBCO using ^{18}O as the tracer [3-5]. Concentration profiles were determined by secondary ion mass spectrometry. The diffusion coefficient in the c-direction is 10^6 lower than the diffusion in the a-direction at 300 °C. Diffusion in polycrystals is given by $D = 1.4 \times 10^{-4} \exp(-93.5 \text{ kJ mole}^{-1}/RT)$ cm^2/s and is, within a factor of two uncertainty, independent of P_{O_2}. Diffusion in the c-direction is governed by an activation energy of about 174 kJ/mole. The results suggested that diffusion in the ab-plane may take place *via* a modified interstitial mechanism which results when an oxygen ion at the end of a row of O(1) sites jumps into an O(5) site, moves along O(5) sites until it comes to another row end, and attaches itself there. The activation energy for diffusion is then made up mostly of the energy to move from an O(1) site at the end of a row to a neighboring O(5) site.

Cation vacancies are minority species in YBCO. Tracer diffusion of Cu [6], and Ba and Y [7, 8] has been investigated in YBCO. The results are presented in Arrhenius equation form and compared to ^{18}O diffusion in figure 1. Diffusion of some rare earth elements, Dy, Ho, and Gd are also shown. Cu diffuses more slowly than oxygen, but faster than Ba, Y or the rare earths. The activation energies and the dependencies of diffusion on P_{O_2} are given in table I. The slowest moving species is Y. These results are in accord with recent atomistic simulations

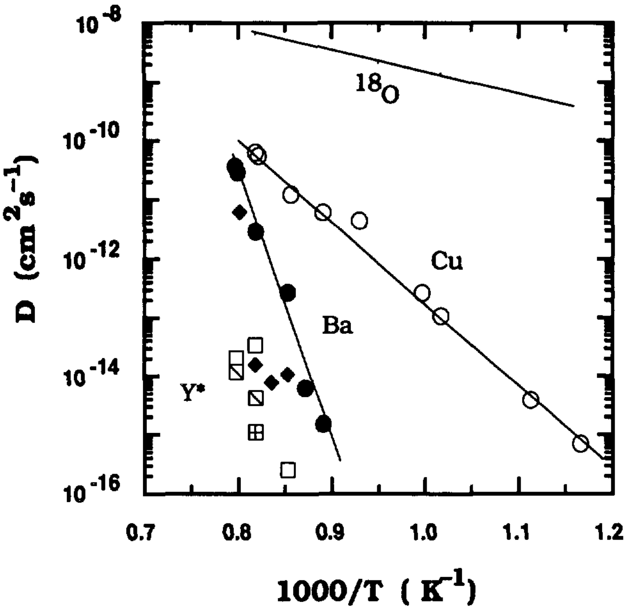

Fig. 1. — Arrhenius plots for diffusion of O, Cu, Ba, Y, and rare earths in YBCO at $P_{O_2} = 1 \times 10^5$ Pa (filled diamonds represent Y, squares with central dots represent Dy, squares with single diagonal lines represent Ho, and the square with the cross represents Gd); from reference [7].

Table I. — *Activation energies and oxygen partial pressure dependencies for diffusion of components in bulk polycrystalline* YBCO.

Tracer	Q (kJ/mole)	P_{O_2} Dependence	Reference
O	93.5 ± 2.9	no effect	3-5
Cu	256 ± 4	negative	6
Ba	890 ± 125	no effect	7,8
Y	10^3 ± 200	unknown	7,8

of point defects in YBCO, which indicate that the formation energies of Ba and Y defects are extremely high [9]. Calculations using the same potential yield values of 820 and 1 350 kJ/mole for the activation energy for the diffusion of Ba and Y, respectively [10]. It should be mentioned that the diffusion of Ba is anisotropic, with diffusion along the c-axis being more than three orders of magnitude slower than diffusion in randomly oriented polycrystals [8].

Bi-Sr-Ca-Cu-O. — Oxygen (whose vacancies are the majority species in BSCCO) tracer diffusion has been measured in single- and poly-crystalline $Bi_2Sr_2CaCu_2O_y$ (2212) and in single crystals of $Bi_2Sr_2CuO_z$ (2201) [11, 12]. The diffusion coefficients in polycrystalline 2212 are given by $D = 1.7 \times 10^{-5} \exp(-89.7 \text{ kJ mole}^{-1}/RT)$ cm^2/s, while the diffusion coefficients parallel to the c-axis are $D = 0.6 \exp(212.3 \text{ kJ mole}^{-1}/RT)$ cm^2/s. Coefficients for diffusion in the ab-plane of 2201 single crystals are identical to those measured for polycrystalline 2212, while those measured for diffusion in the *c*-direction of 2201 are close to. but slightly smaller than, those obtained for the 2212. The results suggest that diffusion in the *ab*-plane occurs *via* an interstitial mechanism and that diffusion in the *c*-direction occurs *via* a vacancy mechanism. The dependence of the oxygen diffusivity on P_{O_2} has not been investigated.

Little is known about the diffusion of cations in 2212. To date, the only cation investigated has been Ag [13]. The diffusion coefficient of Ag in polycrystalline BSCCO is given by $D = 8.9 \exp(181.4 \text{ kJ mole}^{-1}/RT) \text{ cm}^2/\text{s}$ and is not a sensitive function of P_{O_2} [13]. The Ag results are compared to those of oxygen in figure 2.

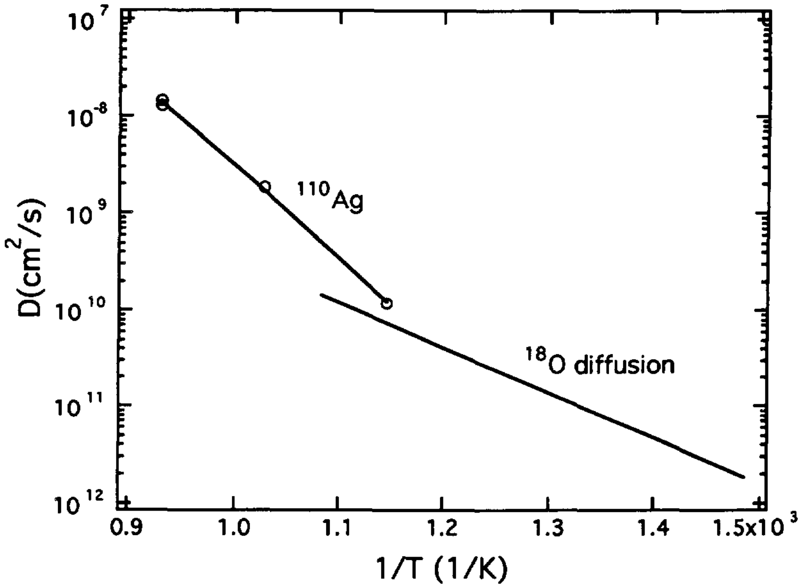

Fig. 2. — Arrhenius plot of the diffusion of Ag and oxygen in polycrystalline 2212 at $P_{O_2} = 1 \times 10^5$ Pa (after Ref. [13]).

Creep.

$YBa_2Cu_3O_x$. — The samples used in the deformation experiments are the same as those used in diffusion. The sample preparation is described in [14]. The samples, with average grain sizes ranges from 7 to 76 μm, were deformed in compression under controlled atmosphere at a constant crosshead velocity or at constant load under controlled atmosphere [15]. Temperatures ranged between 850 and 980 °C and the P_{O_2} between 10^3 and 10^5 Pa. In all cases a steady state was reached after about 2 % deformation and the parameters of the creep equation were determined by strain rate, load, or temperature changes. Strains of 20 % were routinely achieved without cracking. For more details, see [14, 15].

The stress exponent ($n = 1$) and grain size exponent ($h = 2.8$), together with a microstructural observations indicating a constant grain shape, are consistent with deformation by grain boundary sliding accommodated by diffusion.

The identification of the rate-controlling species is complex due to the change of the activation energy with P_{O_2} (964 kJ/mole P_{O_2} from 10^4-10^5 Pa and 646 kJ/mole at 10^3 Pa).

These results are shown in figure 3. The P_{O_2} exponent (m), the other parameter related to the rate-controlling diffusing species cannot be determined due to the change of ΔH with P_{O_2}. However, from figure 3 it is possible to determine m, assuming that the mechanism controlling the plastic deformation does not change with the P_{O_2}.

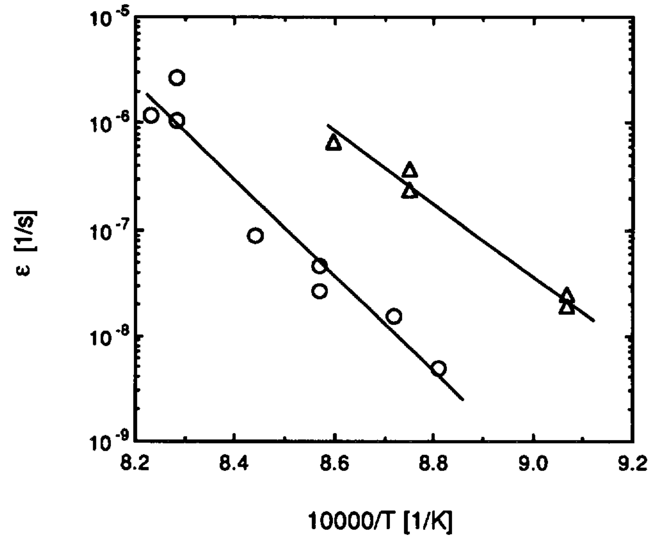

Fig. 3. — Dependence of strain rate in YBCO on $1/T$ for P_{O_2} of 10^3 (triangles) and 10^4 Pa (circles) at $\simeq$ 1 MPa.

In this case, we can write :

$$\frac{\dot{\varepsilon}_1}{\dot{\varepsilon}_2}=\frac{\sigma_1}{\sigma_2}\left(\frac{(P_{O_2})_1}{(P_{O_2})_2}\right)^m \exp\left[\frac{\Delta H_2-\Delta H_1}{kT}\right]$$

and m will be equal to -15.3 for $10^4/T = 8.5$. Although m changes with T (Fig. 3), the main value of m is due to the difference in activation energy with P_{O_2}. This value probably does not have a physical meaning so the assumption made to obtain m may not be valid and the mechanisms or species controlling the plastic deformation may change with P_{O_2}. This behaviour has been found in CoO [16, 17] where the activation energy changes with P_{O_2}. In the CoO case, the explanation was that the nature of the minority point defects controlling the mechanical behaviour changed from oxygen interstitials to oxygen vacancies [16, 17]. If the same change from interstitials to vacancies happens in the cationic sublattice in YBCO, from figure 3, a single m value cannot be obtained, however insufficient information concerning the minority species on the cationic sublattice exists to carry this speculation further.

Recent tracer diffusion results indicate that Ba diffuses independently of P_{O_2} so we may assume that the deformation of polycrystalline YBCO is controlled by the diffusion of Y. However, more work needs to be done on self-diffusion of Y as function of T and P_{O_2} in order to verify the results obtain by creep. The hypothesis of a change of the nature of the point defects can explain the change of ΔH and the unrealistic value of m.

$Bi_2Sr_{1.7}CaCu_2O_x$. — The sample preparation has been described in [18]. The samples were deformed in compression as described for YBCO. Most of the tests were performed in air, but in a few tests, a mixture of flowing 1 % O_2/99 % N_2 or 10 % 10 % O_2/90 % N_2 was used. Temperatures ranged from 785 to 835 °C. In all cases, apparent steady states were generally achieved within 2 % of strain. The parameters of the creep equation were determined as for YBCO. For $\sigma < 3$ MPa, $\dot{\varepsilon} \alpha \sigma$. The activation energy was 10.3 ± 2.0 eV/kT and the oxygen partial pressure dependence was equal to 0. The dependence with grain size was not examined.

These results suggest that the plasticity occurred by diffusional flow, however the effect of grain size combined with a microstructure study will be necessary to determine the actual mechanism controlling the plastic deformation.

There is a lack of cation diffusion data for the 2212 compound so it is impossible to know which specie controls plasticity. As in the YBCO compound, much more work needs to be pursued in deformation as well as diffusion to have a true picture of the mechanism controlling the plasticity.

Conclusions.

Steady-state creep for $YBa_2Cu_3O_x$ and $Bi_2Sr_{1.7}CaCu_2O_y$ occurred by diffusional flow in the ranges of temperature and stress that were studied. The activation energy for each material was 9-10 eV. For $YB_2Cu_3O_x$, this value agress with the activation energy measured for Y diffusion. Diffusion of the A-site cations has not been measured for $Bi_2Sr_{1.7}CaCu_2O_y$. $YBa_2Cu_3O_x$ exhibits a wide range of oxygen nonstoichiometry and it was found that creep rates increased as oxygen partial pressure decreased. $Bi_2Sr_{1.7}CaCu_2O_y$ exhibits a much smaller range of nonstoichiometry and no dependence of creep on oxygen partial pressure was observed.

Acknowledgments.

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