INTERACTIONS OF HIGH-TEMPERATURE SUPERCONDUCTORS
WITH THE ATMOSPHERE

P.K. Gallagher
AT&T Bell Laboratories, Inc.
Murray Hill, N.J. 07974 USA

ABSTRACT

Various reactions of several high-temperature superconductors with the gaseous environment are utilized both to characterize the material and to establish its electrical properties. The following examples are described, the exchange of oxygen to control the oxygen content (x) of the ceramic, the reduction by hydrogen to determine the actual value of x, and the reactions with moisture and carbon dioxide which degrade the electrical performance.

INTRODUCTION

In recent years the appearance of a number of oxide systems containing copper and exhibiting superconductivity at temperatures >77 K has stimulated enormous interest; evidenced by this workshop and its counterparts at many other scientific meetings. As pointed out by Kamimoto and Ozawa[1] in this proceedings, thermal analysis has played a key role in many areas associated with the preparation and characterization of these materials. One of the most vital aspects of such work has been concerned with the interactions between these oxides and the surrounding atmosphere.

Several of these oxide systems exhibit exceptionally wide ranges of oxygen stoichiometry, particularly the $Ba_2YCu_3O_x$[2] and $Pb_2Sr_xY_{1-x}Ca_xCu_3O_x$[3,4] systems. The actual oxygen contents, x, in these systems has been one of the major factors in determining the superconducting properties of these materials. Consequently, the evaluation and control of x becomes a critical factor in the technology of these materials and related devices.

Thermogravimetry (TG) has played a prominent role in both the measurement of the oxygen content and in following the equilibria and kinetics for variations of x with temperature, partial pressure of oxygen, and time. TG has also been of great value in assessing the stability of these oxides. Because of the great stability of alkaline and rare earth carbonates and hydroxides, the materials are subject to reactions with carbon dioxide and moisture. This paper is, therefore, divided into three sections to cover the following aspects of the topic; 1) determination of the specific value of x in these oxides by reduction with hydrogen, 2) following the value of x as a function of subsequent conditions, and 3) evaluation of the stability in the presence of various atmospheric contaminants.

REDUCTION BY HYDROGEN

     In order to equate any subsequent changes of weight with the
precise oxygen stoichiometry as process variables are changed, it
is necessary to establish the exact value of x at some point.
Several methods have been used successfully to accomplish this
determination, e.g., titration[5], neutron diffraction[6], and
reduction by hydrogen[7]. The latter method is based upon the
reduction of the more easily reduced cations such as Cu, Pb, and
Bi to the metal while the alkaline and rare earth metals remain
as well defined oxides. Equation 1 represents the reduction
process for $Ba_2YCu_3O_x$. Provided the metals or reduced oxides are
   $Ba_2YCu_3O_x + (x-3.5)H_2 = 2BaO + 0.5Y_2O_3 + 3Cu + (x-3.5)H_2O$ (1)
not volatile at the temperatures required for reduction, the
weight loss will establish the oxygen content of the original
sample. For the highest accuracy it is advisable to subtract a
blank run under the identical conditions.

     Figure 1 shows the TG curves for several examples of
$Ba_2YCu_3O_x$, having different values of x, run at 10 C min^{-1} in 15%
$H_2/85\%N_2$.[7] The presence of inflection points at consistent
values of x in these curves suggests the presence of intermediate
species during the reduction. Attempts to identify these
intermediates, however, have not been particularly successful.[7]
The analogous curve for the reduction of $Pb_2Sr_2YCu_3O_x$ under the
same conditions is presented in Fig. 2.[4] There does not appear
to be any structure in this curve but the loss beyond 600 C
reflects the volatility of lead. This gravimetric reduction
analysis is not applicable to the bismuth and thallium containing
compositions because of their greater tendency to vaporize prior
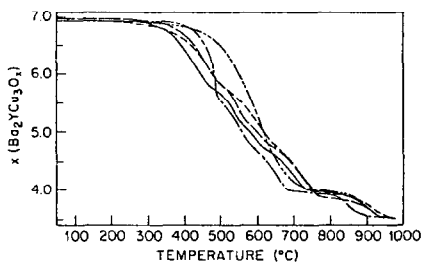to complete reduction.

Fig. 1. TG curves for the reduction   Fig. 2. TG curve for the
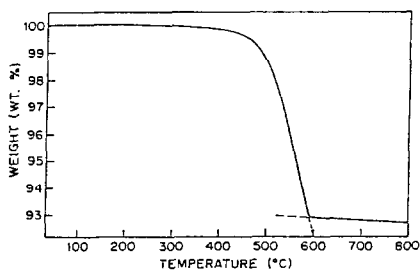of $Ba_2YCu_3O_{7-x}$ in 15%H_2/85%N_2, 10 C   reduction of $Pb_2Sr_2YCu_3O_e$
min^{-1} in 15%H_2/85%N_2, 10 C min^{-1}

VARIATION OF OXYGEN CONTENT WITH TEMPERATURE, OXYGEN PARTIAL
PRESSURE, AND TIME

     Having established the value of x for a particular material
it is now possible to follow changes of weight as the sample is
exposed to different conditions of temperature and pressure and
thereby track the changes in oxygen content with each new set of
conditions. The kinetics for powdered $Ba_2YCu_3O_x$ are favorable
enough so that TG curves taken at 1 C min^{-1} represent equilibrium

conditions at partial pressures of oxygen greater than a few tenths of a percent and temperatures above about 500 C.[8] A series of such TG curves in various atmospheres is shown in Fig. 3. The individual points displayed on the curve taken in oxygen represent constant values obtained isothermally. The open points are during heating and the filled points during cooling. Their correspondence with the curve clearly indicates the attainment of equilibrium during the dynamic experiment.
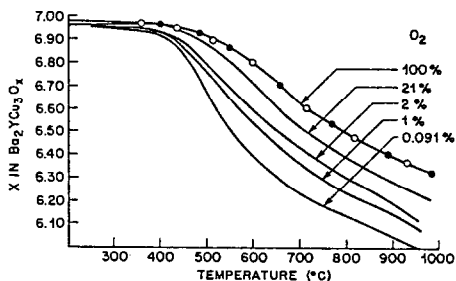

Fig. 3. TG curves for $Ba_2YCu_3O_{6.96}$ heated at 1 C min^{-1} in flowing atmospheres. Points shown in O_2 are for an isothermal experiment, open= heating and closed=cooling.
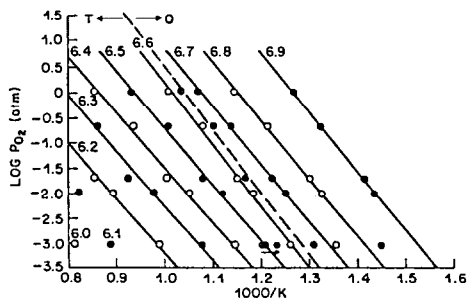
Fig. 4. Isocompositional plots of $Ba_2YCu_3O_{7-x}$, log P_{O_2} versus reciprocal temperature.

This data can be displayed in a much more useful and meaningful manner in the form of van't Hoff plots as shown in Fig. 4.[8] Such a format provides an easier framework for predicting, via interpolation or extrapolation, the conditions necessary to attain a particular composition or to determine the equilibrium composition for a particular set of conditions. The enthalpy for the oxidation process evaluated from the slopes of the isocompositional lines in Fig. 4 is in the range of -24 to -27 kcal mol^{-1} depending upon composition.   A recent review[9] of the several sets of TG data in the literature presents a critical appraisal of the thermodynamics for this process. The exothermic nature of the oxidation can be readily observed by DTA and DSC as well.[6]

In addition to the superconductivity it is also fascinating that these systems can accommodate such an enormous range of oxygen stoichiometry and preserve the same structure. There is, however a structural transformation from orthorhombic to tetragonal which accompanies this exchange of oxygen.[2]   The dashed line in Fig. 4 represents the approximate position of that transformation. A better description is presented in Fig. 5.[10] It is interesting to note that the transformation point is more sensitive to the atmosphere than to the temperature. This means that the material will readily transform under isothermal conditions as the partial pressure of oxygen changes.

There is a large volume change associated with this exchange of oxygen which can be easily followed by thermodilatometry.[11]

Consequently, the isothermal transformation referred to above can be demonstrated by the change in length that occurs as the atmosphere is changed at constant temperature, see Fig. 6.[11] Although the kinetics are reasonably fast for the exchange of oxygen from the powder, they are quite slow for sintered dense pieces and this volume change can have a pronounced effect upon the rate of this process.[12] The volume change associated with the oxidation and transformation from the reduced tetragonal form to the oxidized orthorhombic form frequently leads to microcracking of a dense polycrystalline sample. The microcracks provide increased surface and an opportunity for the atmosphere to penetrate into the piece, leading to a significant enhancement of the rate of oxidation. The cracks, however totally destroy the effective superconductivity of the sample.
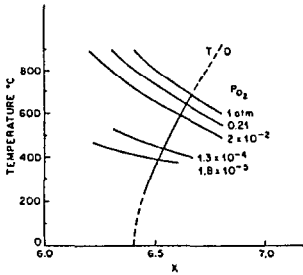

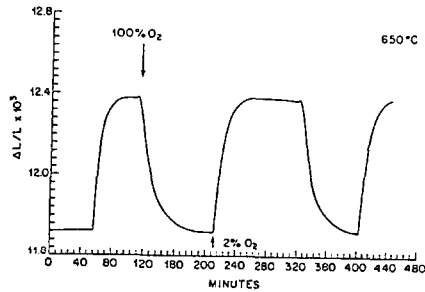Fig. 5. Phase diagram for $Ba_2YCu_3O_x$ with oxygen isobars.

Fig. 6. Expansion versus time as the atmosphere is switched.

Added fascination in these materials is introduced through the contrasting behavior exhibited by the $Pb_2Sr_2YCu_3O_8$ based systems.[4] There is an uptake of oxygen when superconducting specimens of the calcium substituted superconductor are heated in oxygen containing atmospheres which destroys the superconducting properties. In addition, the volume expands for these materials as the oxygen content is increased. Both of these properties are in direct opposition to those exhibited by the $Ba_2YCu_3O_7$. The weight changes which occur during heating in oxygen are shown for several levels of calcium substitution in Fig. 7.[4] An orthorhombic to tetragonal transformation also accompanies the reversible uptake of oxygen below 600 C. Uptake of oxygen at temperatures >630 C represents oxidation of the lead and decomposition to mixed phases. Isothermal changes in volume which occur during the switching of atmospheres are the opposite to those shown earlier in Fig. 6. Yet a different behavior is exhibited by bismuth containing superconductors where the exchange of oxygen with the atmosphere has a less important role.[13]

REACTIONS WITH ATMOSPHERIC MOISTURE AND CARBON DIOXIDE

The stability of materials in the $Ba_2YCu_3O_7$ related systems have been of considerable concern. It was noted[14,15] that the materials will react with water liberating oxygen and inducing concomitant reduction and decomposition of the superconductor. Similarly, the great stability of $BaCO_3$ has not only been a factor to overcome during synthesis but also has been postulated

to be the source of "weak links" that are responsible for the
inability of these materials to conduct large currents and still
remain superconducting.[16] Reaction with carbon dioxide or
monoxide can lead to the formation of insulating grain boundaries
in the polycrystalline ceramic. Improper storage of the powders
can also result in their contamination by moisture and carbon
dioxide in the ambient, but this is frequently alleviated by the
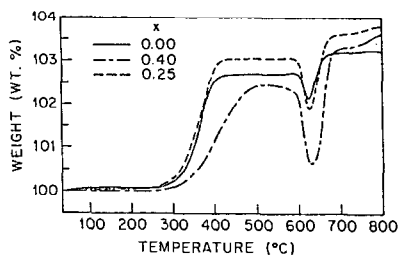subsequent high temperature firing used to sinter the powder.

Fig. 7. TG of $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+x}$
at 1 C min^{-1} in oxygen.
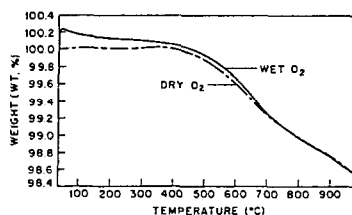
Fig. 8. TG of $Ba_2YCu_3O_{6.98}$
in wet and dry oxygen at
1 C min^{-1}.

Figures 8 and 9 show TG curves for samples heated in
moisture or various amounts of carbon dioxide respectively.[16] It
must be remembered that the loss of oxygen occurs simultaneously
with the other reactions. The moisture results in an almost
immediate weight gain which is lost at intermediate temperatures
when the hydroxides become unstable. Although the weight gain in
carbon dioxide does not become apparent in Fig. 9 until above
about 500 C, it destroys the superconducting properties of the
material at a much lower temperature. The reduction in the
critical current becomes apparent almost immediately as it does
for the reaction with moisture, see Fig. 10. The weight gains in
Fig. 9 clearly indicate that total decomposition to form $BaCO_3$
occurs by 800 C in pure carbon dioxide. As in the case of
reaction with atmospheric water, the weight change as a function
of temperature returns to the normal trend once the decomposition
temperature of the product is reached. This is also reflected in
the ability to regenerate the superconducting properties for the
reheated specimens in Fig. 10.

CONCLUSIONS

This brief review has indicated how important the
interactions between the superconducting material and the ambient
are. Reduction with hydrogen has been extensively used to
analyze for the oxygen content which is so critical to its
superconducting properties. This method does not apply, however
to those compounds which contain bismuth or thallium because of
the increased volatility of these oxides and metals. Once the
oxygen content of the source material has been established, then
TG has been used very sucessfully to follow its change as the
time, temperature and partial pressure of oxygen are varied.
Similarly, TG can be used to detect the reaction of the material
with ambient gases. The electrical properties, however, are
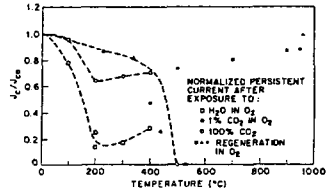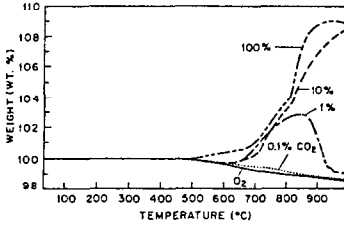generally more sensitive to these reactions than TG.

Fig. 9. TG of $Ba_2YCu_3O_{6.98}$ in oxygen carbon dioxide mixtures at 2 C min^{-1}.

Fig. 10. Normalized values of critical current for different treatments.

Thermoanalytical techniques other than TG and dilatometry are also useful. The phase equilibria have been studied by DTA and the electrical conductivity as a function of temperature and time has revealed a metallic to semiconductor transition[17] and shown some potential as an oxygen sensor for the higher partial pressures.[18]

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