Journal of Alloys and Compounds, 195 (1993) 671–674
JALCOM 7555

Investigation of oxygen exchange of Y-Ba-Cu-O powders and AgPd sheathed tapes

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Abstract

Oxygen exchange between YBaCuO mixed oxides and the gas phase was investigated in all stages of preparation of HTSC material (powder, compact samples, metal sheathed tapes) especially under reduced oxygen pressure by a solid electrolyte based coulometric technique in a carrier gas mode. Influences of the conditions of heat treatment on structure of HTSC cores in AgPd sheathed tapes were obtained.

1. Introduction

The physical properties of perovskite-type rare earths (RE)- alkali earths (AE)-transition metal (TM) mixed oxides of the general formula $(RE)_{1-z}(AE)_z(TM)O_{3-x}$ strongly depend on variation of x. Common to all these substances is the enormous influence of oxygen vacancies on their electrical properties, especially on the HTSC characteristics of $YBa_2Cu_3O_{7-x}$. Systematical investigation of the oxygen stoichiometry and its relation to other properties has become an actual demand of the solid state research. The general reactions

$$(RE)_{1-z}(AE)_z(TM)O_{3-x} = (RE)_{1-z}(AE)_z(TM)O_{3-x-\delta} + \delta/2O_2,$$

$$(RE)_{1-z}(AE)_z(TM)O_{3-x} + \delta H_2 = (RE)_{1-z}(AE)_z(TM)O_{3-x-\delta} + \delta H_2O$$

and especially

$$YBa_2Cu_3O_{7-x} = YBa_2Cu_3O_{7-x-\delta} + \delta/2O_2$$

were investigated by a solid electrolyte based coulometric technique in a carrier gas mode.

2. Experimental

The changes in concentrations of hydrogen and oxygen as well as the oxygen potential during the solid-gas interaction were registered continuously by coulometric titrations and potentiometric measurements, respectively.

The experimental arrangement has been described earlier /1,2/. This method was used for the investigation of stoichiometry and the exchange of oxygen in all stages of thermal treatment of Y-Ba-Cu-O phases in defined oxygen containing atmospheres ranging from 4 Pa to 100 kPa for optimization of HTSC properties (T_c,J_c). Investigations were carried out with powder and compact materials as well aswith silver- or silver-palladium sheathed wires and ribbons fabricated by the powder-in-tube method.

0925-8388/93/$06.00

3. Results

Examples of coulometric measurements are shown in figures 1 to 3. Reduction of $YBa_2Cu_3O_y$ powder in argon-hydrogen (140 Pa) for precise analysis of oxygen stoichiometry starts at about 380 °C.
"Active part" of oxygen (y>6.0) is indicated by the first peak of the reaction curve (see Fig. 1).

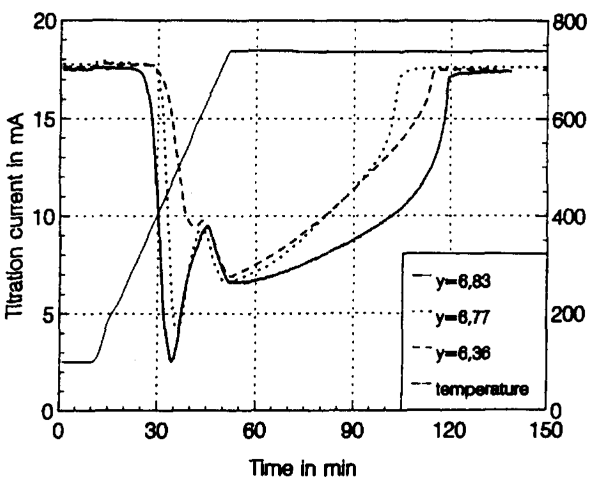


Figure 1. SEC measurement of reduction of $YBa_2Cu_3O_y$ in Ar-H_2.

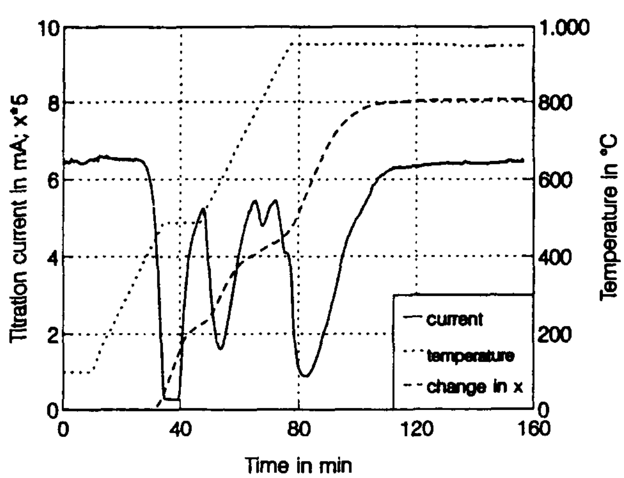


Figure 2. SEC measurement of reaction of $YBa_2Cu_3O_{6.7}$ powder in Ar-O_2(24 Pa).

The temperature depending behaviour of HTSC phase (phase transition, decomposition, melting) is reflected in the oxygen desorption spectrum, especially at reduced oxygen pressure. An example is given in fig. 2. The character of oxygen desorption of an YBaCuO core in a metal sheathed tape during linear heating is shown for two different partial pressures of oxygen in figure 3.

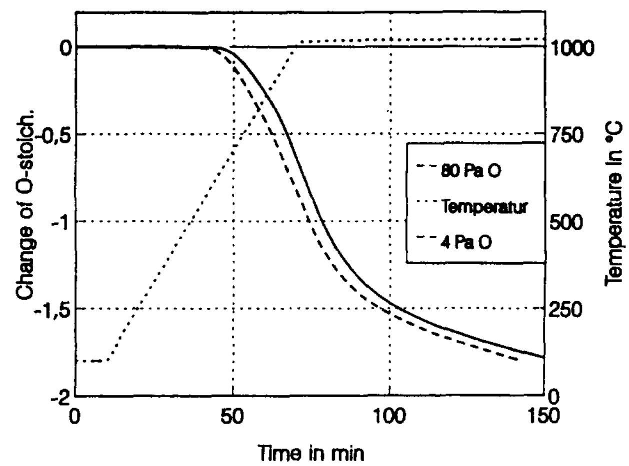


Figure 3. SEC measurement of change of O-stoichiometry of YBaCuO core in an AgPd tape.

The relatively high O_2-permeability of the AgPd sheath (15 % Pd) at a temperature > 700 °C (see Fig. 3) suggests that the oxygen pressure of the firing atmosphere influences the sintering behaviour of the core of AgPd sheathed YBaCuO wires and tapes.

In this study the tapes were subjected to a stepwise heat treatment schematically shown in fig. 4. The heating up and tempering at T_{max} were performed in nitrogen containing about 14 Pa oxygen followed by slow cooling in oxygen. Results of XRD investigations have shown, that the $YBa_2Cu_3O_x$ core of the tapes has been decomposed during tempering in N_2 atmosphere and due to the following treatment in oxygen the products of decomposition have reacted inversely to the 123 phase again /6/.

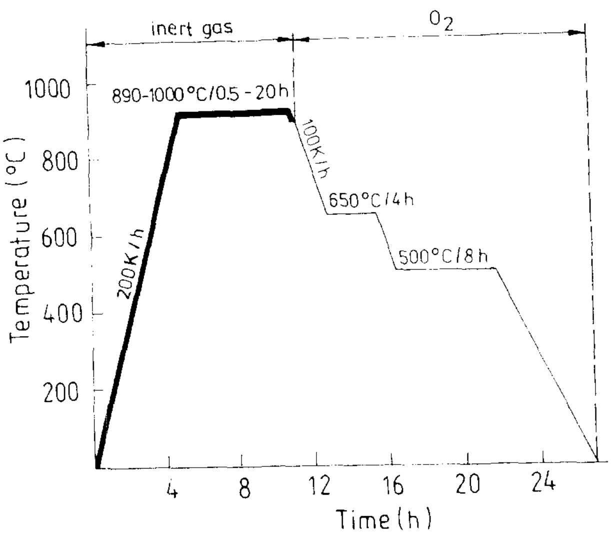


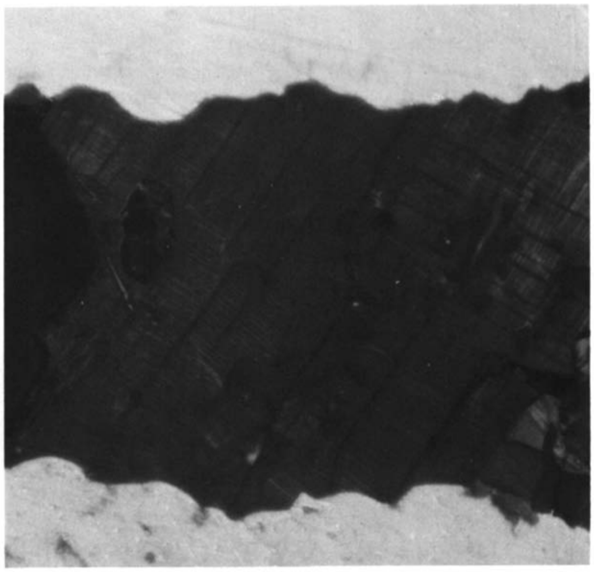
Fig. 4. Heating profile for annealing of AgPd sheathed tapes. Before cooling the nitrogen is exchanged for oxygen.

Figure 5 shows the microstructures of $YBa_2Cu_3O_x$ cores of Ag-sheathed tapes annealed in N_2 at 980 °C and 900 °C, respectively, and subsequently cooled down in O_2 as shown in figure 4. The coarse grained structure (Fig. 5a) is very similar to those observed for bulk samples after partial melting and subsequent slow cooling in air [7]. This suggests, that the YBCO core at 980 °C in N_2 atmosphere has decomposed forming a liquid phase, from which the 123 phase has crystallized after switching the atmosphere from N_2 to O_2.

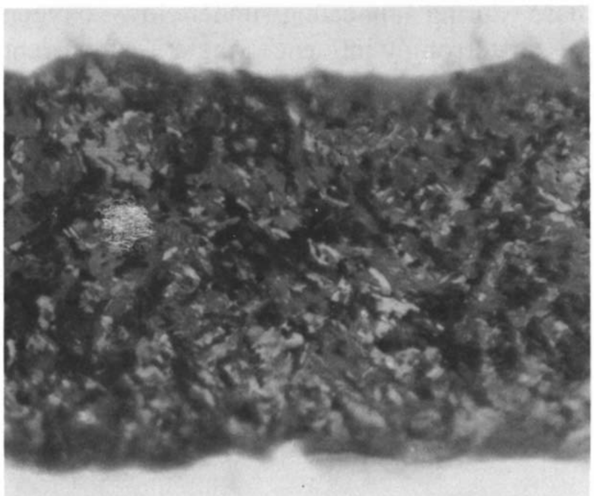
From the fine grained microstrucure of fig. 5b it is concluded, that the mechanism of decomposition in N_2 at 900 °C and the subsequent reversal reaction in O_2 is quite another as described above.

These results are consistent with those of Lindemer, which clearly show, that the mechanism of the decomposition of bulk $YBa_2Cu_3O_x$ samples depends on oxygen pressure and temperature (Fig. 6) [5].

At higher temperatures and oxygen pressures the $YBa_2Cu_3O_x$ decomposes by a peritectic reaction arising both a liquid and solid phase while at lower temperatures and oxygen pressures only solid phases originate from the decomposition.



a) $J_c = 1100$ A/cm^2



b) $J_c = 6000$ A/cm^2

Fig. 5. Microstructure of the YBaCuO cores of AgPd sheathed tapes annealed in nitrogen at 980 °C (a) and 900 °C (b) respectively and subsequently cooling down in oxygen.

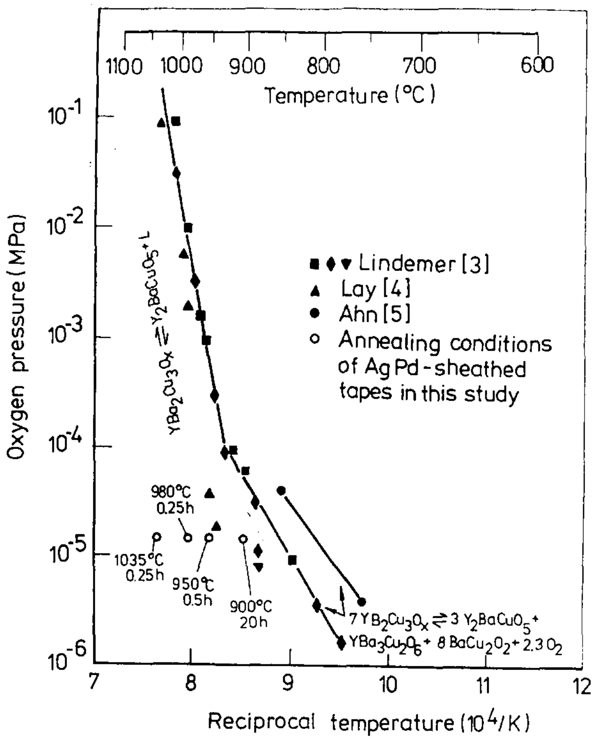


Fig. 6. Dependence of $YBa_2Cu_3O_x$ stability on oxygen pressure and temperature.

The mechanism of decomposition of the 123 phase during annealing under low oxygen pressure strongly influences the critical current density of the recomposed superconducting phases as shown in fig. 7. The data in fig. 7 also demonstrate, that the critical current densities of samples annealed in N_2 and cooled down in O_2 drastically exceed those of tapes which were heat treated only in oxygen.

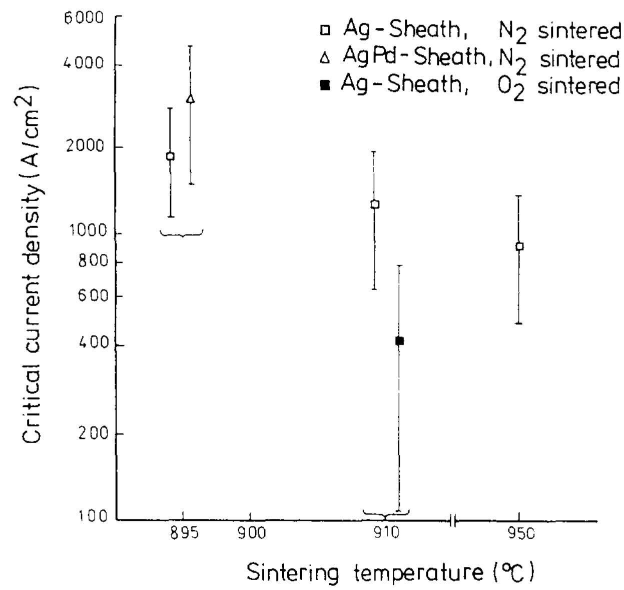


Fig. 7. Critical current densities of Ag- and AgPd sheathed tapes at 77 K in zero field in dependence on annealing temperature and atmosphere. The symbols indicate the mean values and the bars the standard deviation, respectively.

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