A possible using of superconducting measurements to better understanding of catalytic properties of $YBa_2Cu_3O_x$

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Abstract

The high temperature $YBa_2Cu_3O_x$ (Y-123) superconductor represents a new class of oxidation catalysts. It allows to achieve desired activity, selectivity and stability of the catalyst due to presence of active copper cites in the - Cu-O-chains along the [010] direction. They are closely related to the *x* - value adjustable by quenching the sintered Y-123 sample from the properly selected temperature level at suitable pO_2 parameter. The *x*-value can be estimated from the critical temperature T_c or crystallographic measurements. Stability and intergrain bonding can be inferred from magnetization measurements in superconductive state at low magnetizing field. Some measure of openness or closeness of pores can be estimated from magnetic susceptibility measurements. Conditions for the regeneration of the catalyst can be easily carried out due to high mobility of oxygen along the copper chains at proper temperature and pO_2. The stability of structural skeleton and formation of open pores in the sample can be easily regulated by the sintering temperature. It was realized in the range 910 °C up to 950 °C in this work.

1. Introduction

Among the wide range of applications, a new class of oxidation catalysts were coming up, based on Y-123, with a possibility to catalyse selectively the chemical reactions. As useful properties appeared: the phase stability of the sintered bulk, open pores increasing the active surface, mobile oxygen species (from atmosphere) in sandwich – like sheets of Cu –layers surrounded by parallel Ba- and Y – layers. The Cu – layer easily absorb oxygen giving Cu^{3+} and nucleophilic oxygen species which can be reversibly involved in selective oxidation.

The oxidation of toluene using $YBa_2Cu_3O_{7-x}$ as catalyst was occurring at *x* close to 6, [1]. The activity of oxidation depended not only on *x*, but also on pO_2 in the gas stream. At low pO_2 (2.5 - 5.0 kPa at 400 °C), the system was selective for formation of benzonitrile. In comparison with the vanadium oxide catalyst the Y-123 catalyst is more effective. The relative portion of CO_2 increased with increasing pO_2, but the rate of total oxidation decreased probably due to decreasing concentration of active sites at increasing *x*. The composition close to $YBa_2Cu_3O_6$ enabled adsorption of toluene and production of electrophilic oxygen species.

The reaction [2]:

$$2\,CO + O_2 = 2\,CO_2 \qquad (1)$$

is typical for automobile exhaust. The Y-123 fresh sintered catalyst had a surface area of 0.48 m^2/g. At $x > 6.5$, the Y-123 phase has a metallic conductivity. Some stable non-superconducting phases may accompany the Y-123 compound: Y_2BaCuO_5, $BaCuO_2$, CuO. The green phase, Y_2BaCuO_5, contributes to activation process of reaction (1). $BaCuO_2$ is inactive. The activation process (1) was measured at 170 °C with 55% conversion. The catalyst could be regenerated at 350 °C. The reaction (1) was found as zero-order one. The activation energy was evaluated by Arhenius plot as 104 +/- 13 kJ/mol. The presence of multiple oxidation state of copper in Y-123, representing electron pair donors (Cu^{1+}) and acceptors (Cu^{3+}) are important for catalytic activity. Possibly, they might have higher activity for oxidation than those of Y_2BaCuO_5 in which the oxidation state is Cu^{2+}.

Dehydrogenation of isopropyl alcohol on the Y-123 system to acetone was tested in the temperature range 430-495 °C [3]. The kato- and enol-forms of acetone were then condensing to mesityl oxide which could be further hydrogenated to isobutyl methyl keton. The specific absorption of isopropyl alcohol was occurring only on $YBa_2Cu_3O_{6.5}$. The optimal condition of the necessary amount of active sites in the Cu-O chains was $x = 6.5$. The Y-123 catalyst could be regenerated by air flow at 575 °C/4h. At present, superconducting state of Y-123 was identified for *x*-values from 7.0 to 6.4.

The common features of processes involving catalytic oxidation of gaseous components (e.g. CO, toluene, acetone, etc.) over the Y-123 catalyst comprised temperature of catalytic process, pO_2, order of reaction, activation energy, conversion degree and other thermic and thermodynamic quantities. The aim of this work is explanation of the effect of preparation route of the catalyst on the formation of open pores and porosity, oxygen stoichiometry, different valence states of copper, the phase composition, the stability of the catalyst's frame work and the possible role of weak links in Y-123.

2. Experimental

The tested $YBa_2Cu_3O_x$ materials were bulk sintered polycrystalline samples prepared by solid state reaction of stoichiometric mixture of CuO, Y_2O_3 and $BaCO_3$ powders. The powders were homogenized, calcined at 930°C for 40 hours and repeatedly homogenized and pressed at 200 MPa into final cylindrical form. The pressed pellets (of diameter of 12 mm and height about 3 mm) were sintered at different temperatures ranging from 910 °C to 950 °C for 72 hours in flowing oxygen (20 ml/min). The final oxygenation was performed at 590 °C for 24 hours. The phase composition of sintered materials was controlled by the X-ray powder diffraction (XRPD) method using a Philips PW 1710 goniometer and CuKα radiation. Microstructural features of the samples were determined by the optical polarization microscope.

The AC and DC volume magnetization characteristics were measured in the zero-field cooled condition by 2-nd order SQUID gradiometer compensating method [4]. All magnetization characteristics of the samples were measured at 77 K in the range of weak magnetic fields 10^{-1} to 2×10^4 A m^{-1}. For AC magnetization measurements the frequency of 0.1 Hz has been used. For both AC and DC magnetization the applied magnetic field was parallel to sample's axis.

The characteristic penetration magnetic field H_1^{wl} was determined as a field of the first deviation from the initial linear behavior of the virgin magnetization. Taking some aspects (e.g. Bean-Livingston barrier [5], edge-shape or other geometric surface barriers [6, 7]) into account, this parameter characterizes the onset of the flux penetration into the intergrain weak link network. The values of H_1^{wl} in Table 1 are corrected for demagnetizing effects. The demagnetizing factor was determined from the sample dimensions using the ellipsoid approximation.

3. Results

Inspection of Table 1 gives evidence, that crystallographic properties (like the unit cell parameters *a*, *b*, *c* and the unit cell volume *V*) show only statistical, but no systematic deviations from the average values of parameters, when they correspond to different sintering temperatures. Similar properties show the *x* values representing the oxygen content in $YBa_2Cu_3O_x$ superconductor. The *x* values vary within the interval 6.90 to 6.97. They were derived from the known relation between *x* and the unit cell parameter *c* or *V*.

The prepared bulks show high T_c values of 88.1 to 89.9 K and only traces of impurities: $BaCO_3$, $BaCuO_2$,Y_2BaCuO_5. Quite evident is the decrease of porosity *P* and the increase of density D_m, average grain dimensions and bulk contraction with increasing sintering temperature (Table 1). The surfaces of some of the samples taken by polarization microscope are shown in Figures 1a)-c). The values of H_1^{wl} do not change significantly, except for the sample No. 1. It means, that the onset value of flux penetration into the intergrain weak link network is presumably determined by other factors than sintering temperature in given range. They could be, for example, Bean -Livingston or other surface barriers.

With increase of sintering temperature the total number of grains decreases and consequently, the total number of intergrain weak links decreases, too. This could explain the decrease of magnetization curve hysteresis in Figure 2.

Table 1. The crystallographic data on $YBa_2Cu_3O_x$: the unit cell parameters a, b, c and V, the oxygen content x. The physical parameters and microstructural characteristics are: the measured density D_m (the theoretical value D_{cal} is 6374 kg m^{-3}), the porosity P, the average dimensions of the rod-like grains, the sintering temperature T_s , the critical temperature T_c and the first magnetic flux penetration field H_1^{wl} (characterizing the penetration into the intergrain weak link medium).

Sample No.	1	2	3	4	5	6	7
a (Å)	3.823(1)	3.820(1)	3.823(3)	3.824(2)	3.817(2)	3.823(2)	3.822(4)
b (Å)	3.893(6)	3.890(3)	3.892(5)	3.890(4)	3.891(6)	3.890(4)	3.889(6)
c (Å)	11.675(13)	11.674(12)	11.674(1)	11.691(5)	11.676(8)	11.684(1)	11.687(6)
V (Å^3)	173.76	173.47	173.70	173.91	173.41	173.76	173.71
x	6.93	6.96	6.94	6.90	6.97	6.92	6.92
D_m (kg m^{-3})	4920	5160	5350	5560	5660	5850	5940
P (%)	21.2	18.5	16.3	12.7	10.7	8.4	6.2
Average grain size (μm)	10 × 3	15 × 5	25 × 8	50 × 10	50 × 15	100 × 20	100 × 40
T_c (K)	88.6	88.8	88.1	89.1	88.7	89.9	89.6
T_s (°C)	910	916	921	924	931	942	947
H_1^{wl} (A m^{-1})	810	1140	1050	990	1050	1010	1170

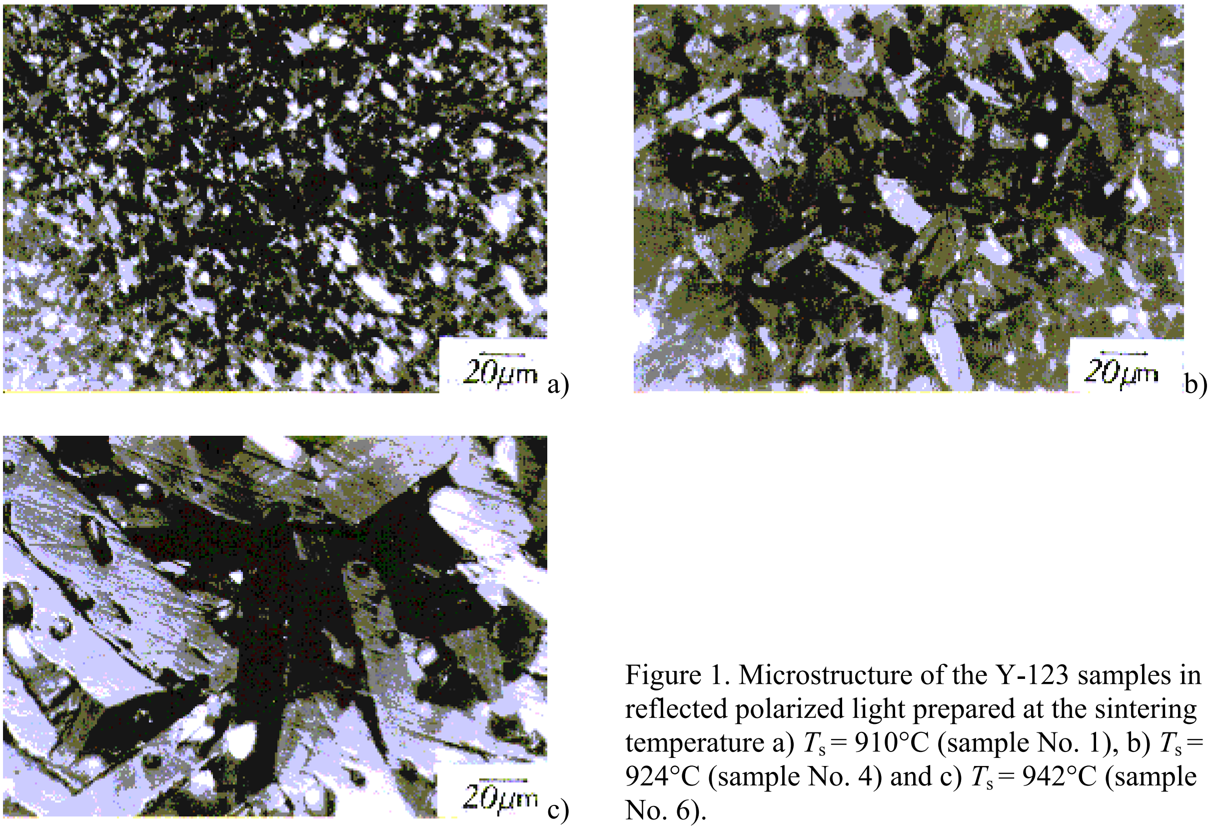

Figure 1. Microstructure of the Y-123 samples in reflected polarized light prepared at the sintering temperature a) T_s = 910°C (sample No. 1), b) T_s = 924°C (sample No. 4) and c) T_s = 942°C (sample No. 6).

The values of effective magnetic susceptibility χ (determined from the slope of the linear part of DC magnetization curves), characterizing the superconducting bonding of grains, for all samples are close to −1.0. The values of χ much greater than –1 could indicate the presence of open pores. This would require even lower sintering temperatures as T_s < 910°C.

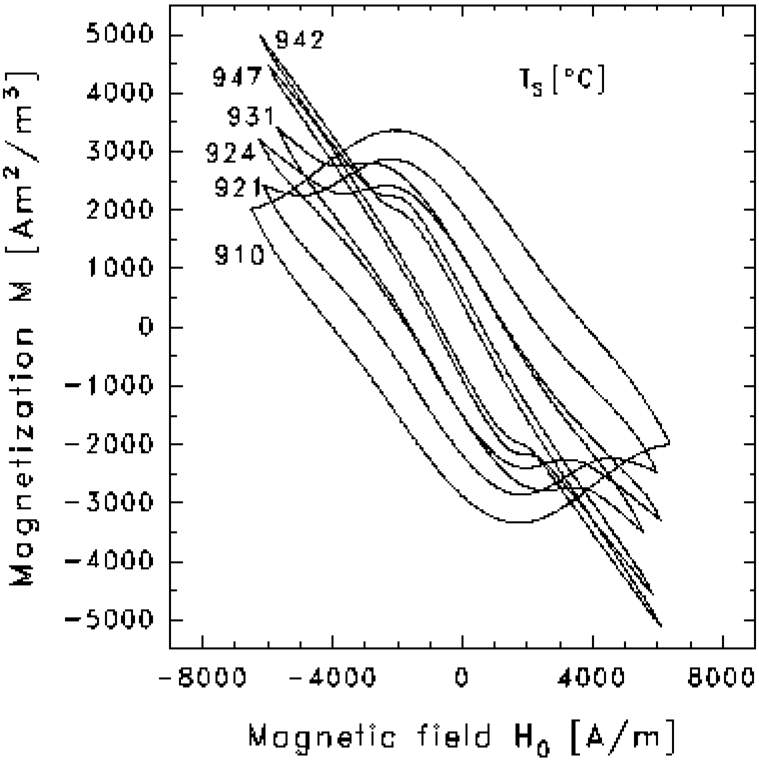

Figure 2. Magnetization M vs. applied magnetic field H_0 for sintered YBCO-123 bulk samples prepared at different sintering temperatures T_s. The values of H_0 are corrected for demagnetizing field.

4. Conclusions

The value of x (oxygen concentration) can be regulated by rate of cooling. At fast cooling, the lower value of x can be obtained by quenched from high temperature level. The porosity of Y-123 samples depends on the sintering temperature. The highest porosity was obtained in our experiments at T_s = 910 °C for 72 h. This temperature is still positively influencing the stability of Y-123 skeleton. The impurity content is in limits of traces. Due to high mobility of oxygen in Y-123, regeneration of the catalyst is a rather easy process.

Acknowledgments

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References

1. Octamiri T. C., Andersson A., Hansen S., Bovin T.O. In New Developments in Selective Oxidation (editors G. Centi and F. Trifiro, Elsevier Science Publ., 1990. Amsterdam; Hansen S., Otamiri J., Anderson: Catalysis Lett. **6** (1990) 33.
2. Halacz I., Brenner A., Shelef M., Simon K.Y.: J. Catal. **126** (1990) 109.
3. Viswanathan B., Roman N.S., Varadarajan T.K.: Indian J. Chem. **29** A (1990) 1135.
4. Zrubec V., Cigáň A., Maňka J.: Physica C **223** (1994) 90.
5. Bean C. P., Livingston J. D. Phys. Rev. Lett. **12** (1964) 14.
6. Zeldov E. et al.: Phys. Rev. Lett. **73** (1994) 1428.
7. Provost J. et al.: J. Phys. F **4** (1974) 439.