

## Moist Corrosion and Surface Protection of YBCO Superconductors

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### Abstract

The critical currents of sintered  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$  were measured as the variables with the corrosive time in the humid air. The corrosive process was studied by means of the current changes. Ag coating on the textured YBCO and polytetrafluoroethylene (PTFE) coating on the sintered YBCO were prepared. The critical current densities of different YBCO samples with and without coatings were compared. Both Ag coating and PTFE coating can well protect YBCO from moisture and  $\text{CO}_2$ .

### Introduction

Since the high  $T_c$  oxide superconductors were discovered [1,2], a great progress has been attained in the area. There are two standard methods being used for preparation powders of copper ceramic superconductors: Solid-state reaction method and SHS method. First method involves mixing of carbonate or oxide powders followed by ball milling. The length of this process depends on homogeneity required but usually varies from 2 to 10 hours. This is repeated until the desired composition is obtained. In the second method, Self-propagating high temperature synthesis (SHS) is a process that enables the rapid formation of the materials by utilizing the energy given out in a very exothermic solid-state reaction [3,4]. The powders produced by either of the two methods are tested for the uniformity, stoichiometry,  $\text{CO}_2$  for the carbonate powders. The validity of these studies is based primarily on the assumption that the phases observed in quenched samples are representative of the equilibrium conditions at high temperature.

In YBCO system, we performed high-energy ball milling for a mixture of metal oxide powders under various conditions. Benefits that offered by mechanical activation in preparing fine dispersed materials are well recognized. Whenever mechanical activation is employed at an early synthesis stage, of great

importance is the proper choice of the original components. Barium carbonate  $\text{BaCO}_3$  is an example of improper choice in the synthesis of YBCO. Particles of these compounds diminish in size in the course of mechanical grinding (with ordinary activation doses) rather than become amorphous, as do many other materials. This is apparently attributable to the strong bond between atoms in the lattice, which is supported by the high melting point of this compound. It was found, that the mechanism of compound formation either remains identical to the ordinary one, i.e. synthesis involves the green  $\text{Y}_2\text{BaCuO}_5$  phase, or proceeds concurrently through the blue  $\text{Y}_2\text{Cu}_2\text{O}_5$  and green  $\text{Y}_2\text{BaCuO}_5$  phase. The mechanism changes drastically when barium oxide  $\text{BaO}$  is chosen as the starting material [5]. This reaction pathway not only provides the highest phase homogeneity, but also significantly reduces the time (up to 12-40 h) and lowers the temperature of synthesis of the desired compound [6]. There are some practical problems that need to be solved. One of them is the protection of YBCO material from the environmental corrosion.

In the test, the critical current ( $I_c$ ) of YBCO samples welded with 4 metal lines were measured with corrosive time in the water vapor to study the reactive process. In order to protect YBCO from the corrosion of humid air and  $\text{CO}_2$ , silver coating on the textured YBCO and polytetra-fluoroethylene (PTFE) coatings on the sinter-ed YBCO were prepared and the protective examinations of the coat-

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ings were taken place in the case of the hot humid air.

## Experimental

The standard process for synthesizing high -  $T_c$  ceramic superconductors involves mixing oxides of the constituent elements, followed by subsequent heat treatments at temperatures of 900-1100°C, when the material is synthesized through the solid state reaction known as sintering. However, the volume fraction of the resulting superconducting phase in the oxides thus prepared generally amounts to only about 20-30%, indicating the difficulty in achieving a homogeneous single phase material [7], especially using  $BaCO_3$ . In this case the mixed powder is pre-calcined in an electric furnace at 880-940°C for about 12 h in an oxygen or air atmosphere.

Oxide superconductors with general formula  $YBa_2C_3O_{7-x}$  have been made with using barium oxide initial powder instead of traditional barium carbonate.

Appropriate amounts of  $Y_2O_3$ ,  $CuO$ ,  $BaO$  are mixed and ground thoroughly. The calcined powder is ground and then pelletized into a disk form. The pellets are sintered at 890 - 920°C for 12 h under oxidizing atmosphere and then cooled slowly to room temperature. It is very important to cool slowly in an oxygen or air atmosphere, especially passing the 400-600°C region, for at least 2 h. These conventional processes are energy intensive and time-long process. Alternative processing route SHS has been attempted to decide the problem. All preparations were conducted in a nitrogen-filled glove box. Reactions were typically conducted in air on a supporting ceramic tile with additional coating from ( $BaO + CuO$ ) mixture and initiated by the application of chemical termite ( $Al + Fe_2O_3$ ) at 800°C. Reagents  $Cu$  (10-15  $\mu m$ ),  $Y_2O_3$  and  $BaO_2$  were purchased from Aldrich Chemical Co. and used as supplied. Powders were mixed in a Spex mill for 1 h. The mixed powder was compacted in a steel die into a disk-shaped pellet under 50 MPa pressure. The green pellet was 10 and 20 mm in diameter and 28 and 46 mm in height. The pellet was then placed in a reaction chamber (Fig. 1) under atmosphere pressure. Initiated at 800°C reaction of termite produced a self-propagating reaction of 0.5-1.5 mm/s velocity [8]. The combustion temperature was measured using a C-type thermocouple inserted into the pellet and was recorded by a computer data acquisition system. The maximum

temperature reached in the reactions was ranged between 1100 and 1300°C.

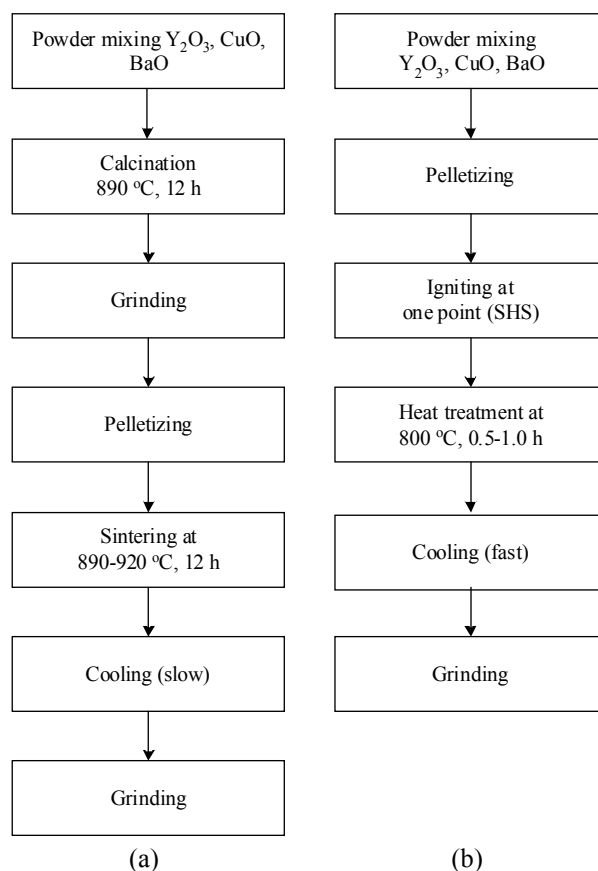


Fig. 1. Block diagram of YBCO (123) powder preparation by solid state reaction (a), by SHS method (b).

## Corrosive tests in moist air

The critical current changes with corrosive time measured by 4 probe method were shown in Table 1, Table 2, and Table 3. Both the reducing rate of critical current for a partial vapor pressure,  $\alpha = (I_0 - I_t)/I_0$ , and a selected equation for kinetic calculation,  $[-\ln(1 - \alpha)]^{1/3}$ , were shown in these tables too.

The relationship curves between the critical currents and the corrosive time was drawn in Fig. 2, using the current values in Tables 1, 2 and 3.  $y = [-\ln(1 - \alpha)]^{1/3}$ , was assumed as a function in the regressive calculation. For the three different partial vapor pressures the regressive results are straight lines, that can be expressed as  $y = b + kt$ , where  $b$  is the intercept of a regressive line on the vertical coordinate,  $k$  is the reaction rate constants,  $r$  is the regressive coefficient. as shown in Fig. 3, and their regressive parameters  $k$ ,  $b$  and  $r$  are listed in Table 4.

The values of natural logarithm of partial vapor

**Table 1**  
I<sub>c</sub> changes of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> with corrosive time under P<sub>H<sub>2</sub>O</sub> = 55.32 mmHg

T (min)	0	35	65	95	125	185	210	280	340	390	420
I <sub>c</sub> (A)	1.02	1.00	0.98	0.94	0.92	0.84	0.80	0.68	0.46	0.40	0.22
α	0	0.02	0.04	0.08	0.10	0.18	0.22	0.33	0.55	0.61	0.78
$[-\ln(1-\alpha)]^{1/3}$	0	0.27	0.34	0.43	0.47	0.58	0.63	0.74	0.93	0.98	1.15

**Table 2**

I<sub>c</sub> changes of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> with corrosive time under P<sub>H<sub>2</sub>O</sub> = 92.51 mmHg

T (min)	0	30	50	90	210
I <sub>c</sub> (A)	1.26	1.00	0.84	0.80	0.18
α	0	0.21	0.33	0.37	0.86
$[-\ln(1-\alpha)]^{1/3}$	0	0.62	0.74	0.77	1.25

**Table 3**

I<sub>c</sub> changes of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> with corrosive time under P<sub>H<sub>2</sub>O</sub> = 233.70 mmHg

T (min)	0	30	50	70
I <sub>c</sub> (A)	1.76	0.64	0.36	0.14
α	0	0.64	0.80	0.92
$[-\ln(1-\alpha)]^{1/3}$	0	1.01	1.17	1.36

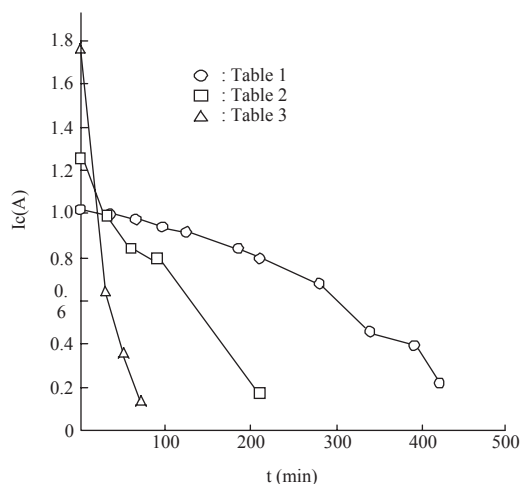


Fig. 2. The changes of critical current with the corrosive time

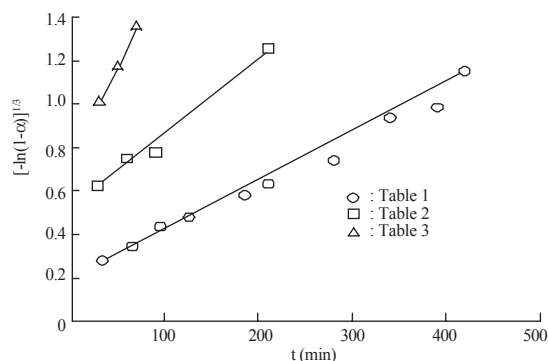


Fig. 3. Regressive curves of  $[-\ln(1-\alpha)]^{1/3}$  and corrosive time.

pressures p and reaction rates k listed in table 4 were shown in Table 5, and the data of which could be

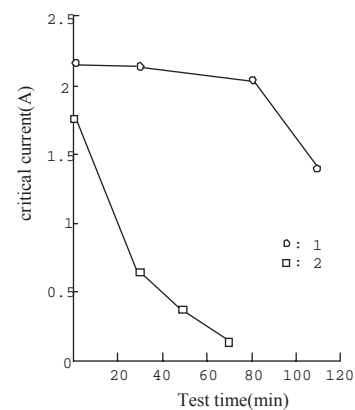


Fig. 4. I<sub>c</sub> changes of PTFE coated YBCO with the test time in hot moisture

**Table 4**

Regressive parameters for the different partial vapor pressures (p.v.p.)

p.v.p.mmHg	k	b	r
55.324	0.0021	0.199	0.990
92.510	0.00349	0.50	0.993
233.70	0.00875	0.74	0.999

regressed as the following equation:  $\ln k = 0.984 \ln p - 10.1$

From Fig. 2 and Fig. 3 it was known that at higher temperature the corrosive rate of YBCO by the vapor was much faster. Using the above regressive curves the corrosive time under the ambient condition can be predicted. For instance, if the partial va-

por pressure is 5 mm Hg, in 180 hours (7.5 days) the critical current ( $I_c$ ) will reduce to half of the original critical current ( $I_0$ ).

**Table 5**

The values of natural logarithm of partial vapor pressures and reaction rates

p(mmHg )	ln p	-ln k
55.32	4.0	6.17
92.51	4.5	5.66
233.70	5.45	4.74

For the Ag coated YBCO, the samples were placed in top part of a glass container, the water at the bottom of the container was heated at 60°C, its humidity was 98%, the hot moisture test was lasted for 24 hours. For the PTFE coated YBCO, the temperature of the moisture test was 70°C, the samples included the Ag electrodes were suspended on the top part of the glass container. The values of  $J_c$  were measured in each certain amount of minutes.

### **Preparation of protective coatings and corrosive tests**

The samples coated with polytetrafluoroethylene (PTFE) which were 15-20 mm in length and 5×5 mm in cross section were cut from the sintered YBCO bulks. The samples coated Ag which were 100 mm in length and 5×2 mm in cross section were cut from the YBCO bars made by the Melted-Textured-Growth (MTG) from the above described work [9]. The Ag<sub>2</sub>O paste was brushed on the surface of textured YBCO homogeneously, and it was dried at room temperature and then it was heated at 500°C for 2 hours in a furnace. After the treatment Ag<sub>2</sub>O was decomposed to metal Ag which was firmly contacted onto the surface of YBCO.

On each sample four Ag wires were welded for the measurement of critical current in advance because of insulation of the PTFE coating. Xylene solvent was put into the mixture of PTFE and resin and stirred by a glass stick homogeneously and let the bubbles escape completely. The solution was coated on the surface of YBCO, and then the samples were put in the baker heated at 100°C for 10 minutes. In order to form a continuous PTFE film, the brush process could repeat several times.

In order to examine the anticorrosion effect of

PTFE coating, two samples were cut from the same sintered YBCO bar. And then one of them was coated by PTFE and 4 Ag wires were welded on each of the YBCO samples to measure the critical current, which were used as the variable with the time changes of hot moisture test. The results tested in hot moisture were shown in Fig. 4, in which line 1 was the  $I_c$  changes of YBCO sample (without PTFE coating) with test time, and line 2 was the  $I_c$  changes of YBCO sample (with PTFE coating) with test time. From the comparison of line 1 and line 2, it was seen that the anticorrosive ability of PTFE coated YBCO was improved obviously. But point 4 of line 2,  $J_c$  declined very fast and the  $I_c$  measurement could not be done at point 5 due to the damage of the electrode contact.

### **Conclusions**

The corrosive process of YBCO in water vapor obeys the kinetic equation  $[-\ln(1 - \alpha)]^{1/3}$  and the relation of the reaction rate constant k and vapor pressure p can be expressed as  $\ln k = 0.986 \times \ln p - 10.1$ . The reaction rate constant will increase and the critical current will decrease with the increasing partial vapor pressure. Ag coating can be prepared simply by Ag<sub>2</sub>O brush coating method on the textured YBCO. The Ag coating does not influence the oxygen absorption of YBCO and its superconductivity and has a very good protective effect for the YBCO from moisture and CO<sub>2</sub>. The PTFE coating also has a good protective effect for the YBCO, which can be used when the conductive coating do not hoped such as Ag coating.

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