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THE EFFECT OF CALCINATION CONDITIONS ON THE SUPERCONDUCTING PROPERTIES OF Y–Ba–Cu–O POWDERS

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Abstract

Calcination conditions of the precursor powders, i.e. temperature, type of atmosphere and duration, were determined with a view to obtain superconducting powders with the most advantageous physico-chemical properties. Investigated were powders in the Y–Ba–Cu–O system prepared by the sol–gel method. Thermogravimetric examinations of the powders have revealed that the decomposition kinetics of $BaCO_3$ determines the formation rate of the superconducting $YBa_2Cu_3O_{7-x}$ ('*123*') phase. It follows from the decomposition kinetics of $BaCO_3$ that the process is the most intensive in argon, whereas in static air and oxygen it is the slowest. The phase composition analysis (XRD) and low-temperature magnetic susceptibility measurements of the calcinated powders, confirm the above mentioned changes in the decomposition kinetics. The reaction of barium carbonate can be completed if the calcination process is conducted at the temperature of 850°C for 25 h, yielding easily sinterable powders for obtaining single-phase superconducting bulk samples with advantageous functional parameters.

Keywords: HTS (High Temperature Superconductors), $YBa_2Cu_3O_{7-x}$, $BaCO_3$, thermal decomposition

Introduction

The main problem in the fabrication of ceramic superconducting materials in the Y–Ba–Cu–O system is the preparation of powders with appropriate physico-chemical properties, which determine the microstructure and the phase composition of HTS (High Temperature Superconductors) bulk samples. It has been found [1, 2] that one of the factors impairing the physico-chemical properties of the superconducting powders is the slow formation of $YBa_2Cu_3O_{7-x}$ compound ('*123*'). The reason for this phenomenon according to the authors of these studies should be looked for in limitation of the '*123*' phase synthesis from the oxides and carbonates used as a precursor. Moreover, considerable shrinking of the precursor grains during sintering at temperatures below the

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synthesis temperature does not allow a material with good superconducting properties to be prepared. It is worth to consider that the evolution of carbon on the grain boundaries of the superconducting phase as a result of the simultaneous processes of the barium carbonate decomposition and sintering is possible. As it follows from [3] this phenomenon has a disadvantageous effect on the superconducting properties of the bulk samples.

The described phenomena, accompanying the crystallization of the '*123*' phase from oxides-carbonates mixture, indicate that the decomposition of $BaCO_3$ determines the formation of $YBa_2Cu_3O_{7-x}$. Thus, the problem is to create such conditions of powder calcination that would guarantee sufficient degree of the appriopriate phase synthesis. According to this concept, in the present work an attempt has been made to determine the effect of the calcination conditions, i.e. temperature, duration and atmosphere in the Y–Ba–Cu–O system on their superconducting properties.

Experimental

The powders in the Y–Ba–Cu–O system were prepared by the sol–gel method. The method, described in detail in [4, 5], consisted in complexing the metal cations in a water solution with ethylene-diamine-tetra-acetic acid (EDTA), and then in the dehydration process in vacuum at the temperature 60–80°C with the formation of amorphous gel. The precursor powder obtained after further thermal treatment, i.e. pyrolysis, at 530°C for 1.5 h in oxygen was subjected to calcination. The calcination process was performed either in oxygen, or argon or in static air in the temperature range: 775–950°C for 2, 10 and 25 h. The partial pressure of oxygen in argon was determined with OPM-5 analyser. The calcinated powder were sintered in oxygen at 925°C for 24 h. After sintering the powders were cooled at a rate of 20 $\text{deg}\cdot\text{h}^{-1}$ to 500°C, at which they were kept for 12 h and next cooled again at the above rate to ambient temperature.

The powders obtained from the pyrolysis and calcination were examined using thermogravimetric (DTA, DTG and TG) methods. The phase composition of these powders was determined by X-ray diffraction (XRD) method. The content of the $YBa_2Cu_3O_{7-x}$ phase was estimated from the relative intensity of the (*hkl*) reflexion [1]. Low-temperature magnetic measurements of the powders were performed by the induction method of measuring the dispersive part χ' of magnetic susceptibility.

Results and discussion

Preliminary thermogravimetric and X-ray examinations of the organometallic precursor gels in the Y–Ba–Cu–O system [6] have shown that the micropowders prepared from them in pyrolysis are composed of multiphase grains. They contain oxides and carbonates, from which the superconducting phase was formed, by high-temperature solid state reaction. In order to estimate the temperature range in which the superconducting phase is formed, the powders after thermal decomposition of the gel at 530°C for 1.5 h in oxygen, were subjected to thermogravimetric measurements. Figure 1 shows the DTA curve, made in the temperature range 300–1080°C, indicates the presence of five endothermic peaks. The firs thermal effect occurring at 830°C can be attributed to the $BaCO_3$ polymorphic transition from the orthorhombic (γ) into the hexagonal form (β) [7]. Two smaller effects: the first at 870°C, and the second at 890°C correspond, respectively, to the formation of a $YBa_3Cu_6O_{18.5}$ liquid phase [8] and to the evolution of another liquid phase resulting from the $BaCuO_2$ and CuO eutectic [9]. The peak at 940°C is connected with the $YBa_2Cu_3O_{7-x}$ phase formation [10]. During further heating in the temperature range 1020–1040°C [10] the newly formed '*123*' phase undergoes peritectic decomposition into Y_2BaCuO_5 and a liquid. The DTA curve shown in Fig. 1 indicates that the polymorphic transformation of $BaCO_3$ from the stable and not reactive γ-phase

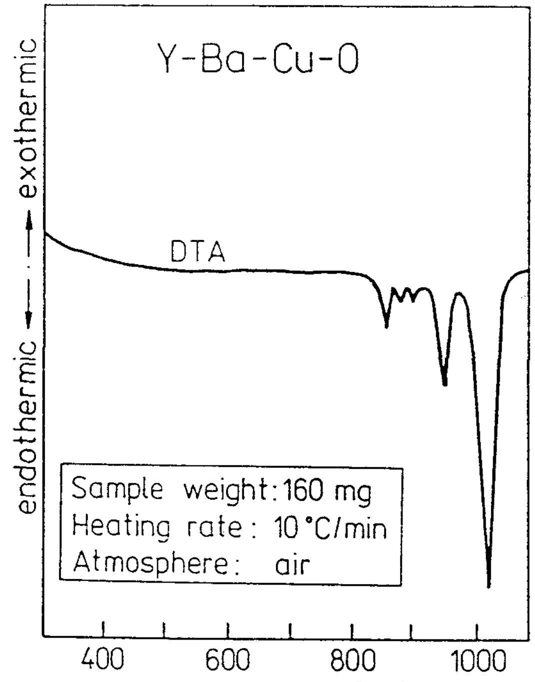

Fig. 1 DTA graph for an Y–Ba–Cu–O powder after pyrolysis of the gel precursor at the temperature 530°C in oxygen during 1.5 h

was the first reaction in the described system. For this reason it was necessary to subject the powder to calcination.

The determine the most advantageous calcination conditions, i.e. temperature, type of atmosphere and duration, thermogravimetric investigations were performed in flowing oxygen and argon as well as in static air. The results of the $BaCO_3$ decomposition as percent content of barium carbonate as a function of temperature were illustrated in Fig. 2. Barium carbonate content was estimated from the weight changes of the sample with the assumption that only the '*123*' phase was formed. The deviation from stoichiometry in the oxygen sublattice '*x*' of the newly formed $YBa_2Cu_3O_{7-x}$ phase was estimated from the temperature dependence '*x*' on the partial pressure of oxygen [11]. It follows from Fig. 2 that the type of gas atmosphere had a great influence on the kinetics of $BaCO_3$ decomposition, and in consequence on the formation of the superconducting phase '*123*'. The $BaCO_3$ decomposition in argon at the partial pressure of oxygen equal to 10^{-2} atm was very intensive in the temperature range 800–850°C. In this range a 40% loss of $BaCO_3$ content was observed which is equivalent to the formation of 40% of the '*123*' phase. On the other hand, in the case of $BaCO_3$ decomposition in oxygen only 25% loss of $BaCO_3$ in the same temperature range was recorded. Still smaller, only 20% drop in $BaCO_3$ content was shown in static air in the above temperature range. So, it was evident that this process is the most intensive in argon and the slowest in static air. This fact was ascribed to carbon dioxide partial pressure in the reacting system. In static air the increase in CO_2 partial pressure due to the decomposition of $BaCO_3$ was intensive. Hence, in the sample heated up to 975°C in static air as high as 4% content of $BaCO_3$ was recorded. It has been found (Fig. 2) that the highest reaction yield at the lowest temperature can be achieved in argon ($pO_2 10^{-2}$ atm).

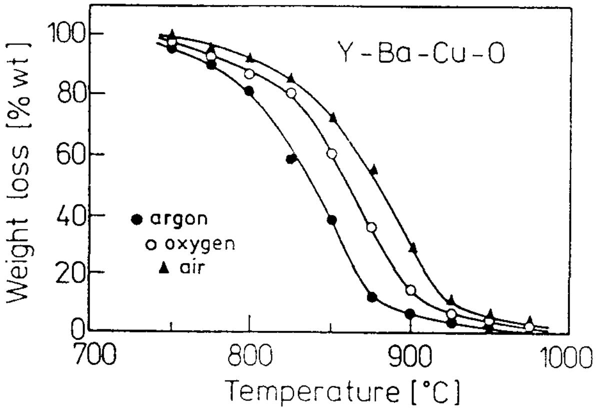

Fig. 2 $BaCO_3$ decomposition kinetics in argon, oxygen and static air estimated on the basis of TG

Table 1 Phase identification and *'123'* phase content in the Y–Ba–Cu–O calcinated powders

Calcination conditions		Identified phase					
		Atmosphere					
T / °C	Time / h	% *'123'*	Argon	% *'123'*	Oxygen	% *'123'*	Air
775	2	5	Y_2O_3 $BaCO_3$ CuO *'123'*-T		–		–
800	2	48	Y_2O_3 $BaCO_3$ CuO *'123'*-T		–		–
800	10	86	Y_2O_3 $BaCO_3$ CuO *'123'*-T Y_2BaCuO_5 $BaCuO_2$		–		–
825	2		–	35	Y_2O_3 $BaCO_3$ CuO *'123'*-T	17	Y_2O_3 $BaCO_3$ CuO *'123'*-T
850	2	84	Y_2O_3 $BaCO_3$ CuO *'123'*-O Y_2BaCuO_5	81	Y_2O_3 $BaCO_3$ CuO *'123'*-T Y_2BaCuO_5	67	Y_2O_3 $BaCO_3$ CuO *'123'*-T Y_2BaCuO_5
850	10	92	Y_2O_3-sl $BaCO_3$ CuO *'123'*-O Y_2BaCuO_5	87	Y_2O_3 $BaCO_3$ CuO *'123'*-O,T Y_2BaCuO_5 $BaCuO_2$	83	Y_2O_3 $BaCO_3$ CuO *'123'*-T,O Y_2BaCuO_5 $BaCuO_2$
850	25	98	$BaCO_3$ *'123'*-O Y_2BaCuO_5-sl $BaCuO_2$-sl		–		–

Table 1 Continued

Calcination conditions		Identified phase					
T / °C	Time / h	Atmosphere					
		%*'123'*	Argon	%*'123'*	Oxygen	%*'123'*	Air
875	2	56	*'123'*-O,T CuO Y_2BaCuO_5 $BaCuO_2$		–		–
900	2	30	*'123'*-T Y_2BaCuO_5 $BaCuO_2$ CuO	87	Y_2O_3 $BaCO_3$ CuO *'123'*-O,T Y_2BaCuO_5 $BaCuO_2$	88	Y_2O_3 $BaCO_3$ CuO *'123'*-T Y_2BaCuO_5 $BaCuO_2$
900	25		–	93	Y_2O_3 $BaCO_3$ *'123'*-O Y_2BaCuO_5 $BaCuO_2$	90	Y_2O_3 CuO $BaCO_3$ *'123'*-O,T $Y_2BaCuO5$ $BaCuO_2$
925	2		–	90	Y_2O_3 $BaCO_3$ CuO *'123'*-T, O Y_2BaCuO_5 $BaCuO_2$	90	Y_2O_3 $BaCO_3$ CuO *'123'*-T Y_2BaCuO_5 $BaCuO_2$
925	25		–	95	$BaCO_3$ *'123'*-O Y_2BaCuO_5 $BaCuO_2$	93	$BaCO_3$ *'123'*-O Y_2BaCuO_5 $BaCuO_2$
950	2		–	88	*'123'*-O CuO Y_2BaCuO_5 $BaCuO_2$	83	*'123'*-O,T Y_2BaCuO_5 $BaCuO_2$ CuO

The dominating variety of the *'123'* phase in the analyzed sample is underlined.

In oxygen or static air this process must be carried out at a considerably higher temperature which leads to the crystal growth of the '*123*' phase and in consequence favours the formation of phases, as confirmed by the X-ray phase analysis. The results are listed in Table 1. It has been found [12] that the '*123*' phase may exist both in the orthorhombic ('*123*'-O) and in the tetragonal, not superconducting, structure ('*123*'-T). These varieties with the general formula $YBa_2Cu_3O_{7-x}$ coexist in various quantities depending on the amount of oxygen in their composition. In the case of different texture of these phases it was not possible to determine exactly the fraction of each variety. The (020) and (200) reflexes of both phases, which intensities limited the phase composition, overlap [13]. It follows from the presented results (Table 1) that the greatest fraction 98% of the '*123*' tetragonal phase, with superconducting properties and with traces of $BaCO_3$, Y_2BaCuO_5 and $BaCuO_2$ was observed in the powder calcinated at 850°C for 25 h in argon. These results have been confirmed also by other researchers [14] who obtained the $YBa_2Cu_3O_{7-x}$ compound in high vacuum at 850°C. In the powder calcinated in the same atmosphere at 800°C for 10 h, only 40% of the '*123*' phase was reported, however with predominantly tetragonal structure. As it follows from Table 1, prolonged time of thermal treatment led to increased proportion of the '*123*' phase, whereas temperature rise at first raises the concentration of the '*123*' phase, and subsequently decreases it as a result of decomposition according to the equation [15]:

$$2YBa_2Cu_3O_{7-x} \rightarrow Y_2BaCuO_5+3BaCuO_2+2CuO \text{ (liquid)}$$

Generally, lower contents of the superconducting phase '*123*' in the powders prepared in oxygen and static air were observed in comparison to the powder calcinated in argon, with the oxygen partial pressure not lower than 10^{-2} atm. The requirement concerning the partial pressure of oxygen is important from the point of view of thermodynamic stability of the superconducting '*123*' phase [16], otherwise this phase would decompose according to the above equation.

To verify the influence of the powder calcination conditions on their superconducting properties magnetic susceptibility was measured as a function of temperature. Figure 3 shows the results of these measurements. Three types of powders were selected. They were calcinated for 15 h in oxygen, at 925°C, in argon at 850°C, and in static air at 925°C. They were characterized by the highest content of the '*123*' phase with minimal amount of the remaining ones. In the Fig. 3, showing the curves $\chi'=f(T)$ two principal courses can be observed, differing in the critical temperature $T_{c\chi}$, the range of the phase transition $\Delta T_{c\chi}$, and the value of the absolute magnetic susceptibility $\chi'_{4.2K}$. The highest critical temperature $T_{c\chi'}=91.5$ K was recorded for a sample calcinated in argon, while a sample calcinated in air showed the lowest value $T_{c\chi'}=90.2$ K. In the case of the sample calcinated in oxygen $T_{c\chi'}$ was equal to 90.6 K. The powder calcinated in argon attained the lowest negative value of susceptibility $\chi'_{4.2K}$ = $25\cdot10^{-3}$ cm^3/g. The values of magnetic susceptibility of powders calcinated in air and in oxygen were $\chi'_{4.2K} = 18\cdot10^{-3}$ and $19\cdot10^{-3}$ cm^3/g, respectively. X-ray analysis (Table 1) has revealed the highest content of the '*123*' phase in powder calcinated in argon, for which also the highest value of the parameter $\chi'_{4.2K}$ was recorded. Considerable differences in the range of diamagnetic phase transition were also observed, the consequence of which are rather high values of the $\Delta T_{c\chi'}$ parameter. The value of the $\Delta T_{c\chi'}$ parameter for the powder calcinated in argon was 27 K, whereas for the powder calcinated in air and in oxygen it was equal to 23 and 41 K, respectively. The reason for these differences should be looked for in the varying phase composition and in the complex microstructure of the above discussed powders, which are due to the presence of both intergranular and intragranular links in these powders [17, 18].

Considering the effect of the calcination conditions on the superconducting properties of the powders in the Y–Ba–Cu–O system, it can be said that the most favourable parameters determining the state of superconductivity have been obtained for powders calcinated in the atmosphere of argon (pO_2= 10^{-2} atm), at the temperature of 850°C for 25 h. Accordingly, it appears possible, when using this type of polycrystalline powders, to obtain single-phase superconducting bulk samples of highly advantageous physico-chemical parameters [4, 5, 19].

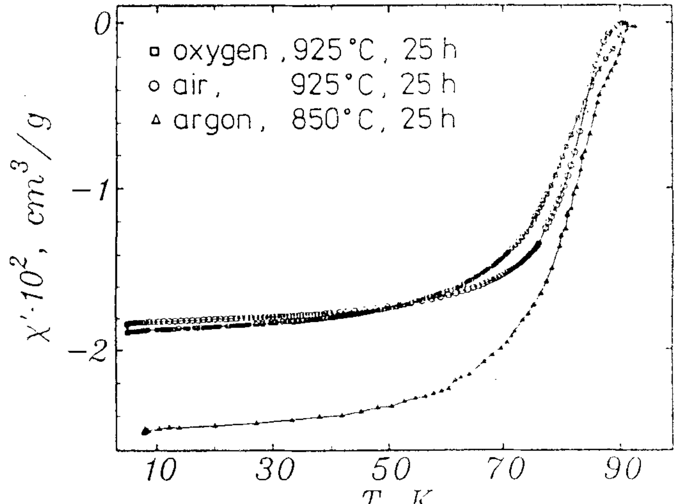

Fig. 3 Temperature dependence of magnetic susceptibility of the superconducting powders, after calcination in argon, oxygen and air and sintering at 925°C in oxygen for 24 h

Conclusions

The described results led us to the following conclusions:

1. The decomposition kinetics of $BaCO_3$ determines the formation of the superconducting $YBa_2Cu_3O_{7-x}$ compound.

2. The conditions of calcination, i.e. temperature, duration and type of atmosphere, have a significant influence on the $BaCO_3$ decomposition yield.

3. The powder calcinated in argon ($pO_2=10^{-2}$ atm) at 850°C for 25 h has the highest content of the superconducting phase and the most advantageous superconduction parameters.

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Zusammenfassung — Eine kurze Übersicht über die theoretischen Möglichkeiten der Bestimmung von energetischen und thermodynamischen Eigenschaften von chemischen Substanzen in gasförmigen und kondensierten (festen und flüssigen) Phasen wird gegeben. Die Überlegungen umfassen quantenchemische Methoden, die die Auswertung von energetischen Größen und statistischen thermodynamischen Abhängigkeiten ermöglichen, die für die Bestimmung anderer thermodynamischer Charakteristika erforderlich sind. Mögliche Anwendungen dieser Methoden werden ebenfalls diskutiert.