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Processing of porous structures of $YBa_2Cu_3O_{7-\delta}$ High-temperature superconductor

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Technological aspects of fabrication of the $YBa_2Cu_3O_{7-\delta}$ ceramics with preparation of open pores are presented. The highest porosity of the sample with open pores and suitable mechanical properties was performed using $C_{12}H_{22}O_{11}$ (sugar sucrose) as the supplementary phase.

Key words: *$YBa_2Cu_3O_{7-\delta}$; open porous structure*

1. Introduction

The search for applications of superconductive ceramics is mainly focused on two groups of materials: thin films and bulk ceramics. The main aim of this research to assure their proper use and to optimize parameters such as: critical current, critical magnetic field and critical temperature [1–4]. Superconductive ceramics can also be interesting material for other practical applications. Materials with porous structure can be used, for example, as gas filters [5] or as composites with superconductive matrices.

Despite many papers concerning the syntheses of $YBa_2Cu_3O_{7-\delta}$ [3, 4, 6–8], fabrication of open-pore superconductive ceramics is not well known yet [9, 10]. Therefore, various technological aspects of fabrication of $YBa_2Cu_3O_{7-\delta}$ open-pore ceramics have been studied. The basic problem is using an adequate supplementary filler in order to obtain a homogeneous localization of free spaces. Filling should not destroy the superconductive properties. It should also enable fabrication of samples with good mechanical properties. Various materials being used as supplementary phases, for example: wax, graphite or polyurethane foams, the best results were obtained using the crystalline sucrose as a filler.

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2. Experimental

2.1. Sintering granules of $YBa_2Cu_3O_{7-\delta}$

During the initial stage of this research, in order to obtain an open-pore structure, granules of $YBa_2Cu_3O_{7-\delta}$ were sintered so as to preserve pores that had been formed between not pressed granules. Superconductive $YBa_2Cu_3O_{7-\delta}$ material was prepared using the standard method of powders sintering. It was then ground and separated into three fractions: 0.2–0.4 mm; 0.4–0.63 mm and 0.63–0.8 mm. The sintering proceeded in the temperature range from 940 to 1100 °C and the time of sintering changed from 10 min to 3 h. The best results were obtained after sintering at 940 °C for 3 h (Fig. 1)

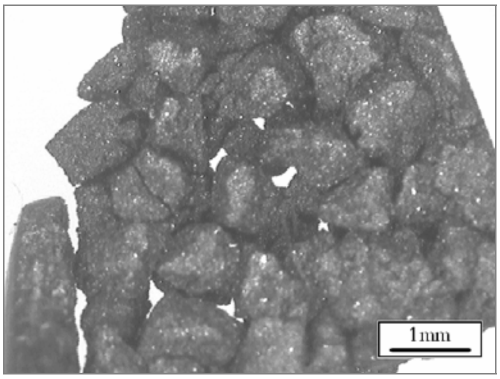

Fig. 1. Sample obtained by mixing $YBa_2Cu_3O_{7-\delta}$ granules of the size of 0.63– 0.8 mm, not pressed and sintered at 950 °C by 3h

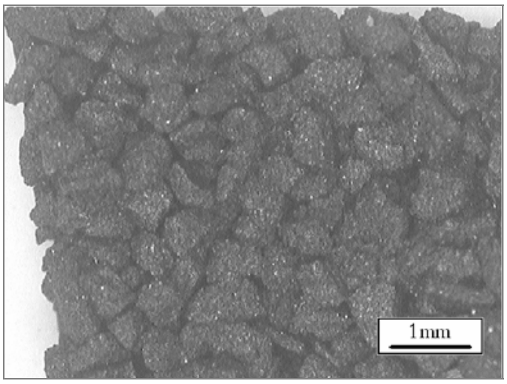

Fig. 2. Sample obtained by sintering $YBa_2Cu_3O_{7-\delta}$ granules filled with wax and slightly pressed

Generally, the obtained samples were either mechanically weak or containing a molten matrix. Therefore, the method was not reproducible. In order to improve the mechanical properties of the samples, it was modified by filling free spaces between granules in the matrix with liquid wax. After solidification of the filler, the sample was pressed and sintered to obtain intergranular bindings. The wax filler made possible a tight pressing of the granules without losing empty spaces between them. This resulted in fluidisation of the wax under high pressure and its outflow from the matrix. Nevertheless, weak pressing of the granules allowed one to obtain samples with open pores (Fig. 2). Unfortunately, they were not mechanically stable.

2.2. Fabrication of the $YBa_2Cu_3O_{7-\delta}$ porous ceramics by using poly(pyrrole imide) foams

Another way to obtain porous structure of the $YBa_2Cu_3O_{7-\delta}$ ceramics was described in [9,10]. Poly(pyrrolone imide) (PPI) foams were used as porous structure replicas. The authors presented two methods of preparing the porous structure. The first method consisted in a complete filling of the PPI foams, then they obtained negatives of the foams. The other method consisted in covering the structure of the PPI foams with $YBa_2Cu_3O_{7-\delta}$, then they obtained replica of PPI foams. Both methods required mixing of very finely ground superconductive with a liquid in order to obtain a suspension of an optimum viscosity. The next stage for both methods is burning out PPI and sintering $YBa_2Cu_3O_{7-\delta}$. In the present work, this stage (a slow heating) was carried out to ca. 400 °C. It should inhibit burning of PPI foam. Then the sample was sintered at 935 °C for 24 h. The difference between the methods described above consists in choosing a proper viscosity of the suspension and the method of filling with the foam. In the case of fabricating replica, a moderate viscosity of the suspension should be chosen in order to provide open pores in the soaked foam samples (Fig. 3). In the case of applying the foam as the supplementary filler, use of a thick suspension of $YBa_2Cu_3O_{7-\delta}$ was required to fill all free spaces within the foam.

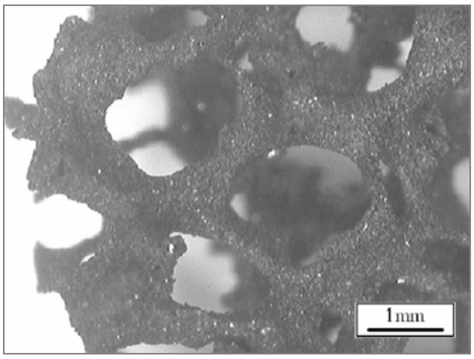

Fig. 3. A porous sample obtained by burning out PPI foams covered with $YBa_2Cu_3O_{7-\delta}$ suspension

The critical point of such technique of fabrication of open-pore ceramics was the preparation of the $YBa_2Cu_3O_{7-\delta}$ suspension of appropriate viscosity and also depositing a small amount of the suspension on the foam by soaking it. In order to obtain the required viscosity, the following liquids were applied: methanol, water, glycerine or their mixtures. Despite many attempts, the obtained samples were neither reproducible enough nor mechanically resistant, mainly due to the lack of pressing the $YBa_2Cu_3O_{7-\delta}$ ceramic before sintering them. Therefore the obtained samples were not suitable for a further material research.

2.3. Mixture of the $YBa_2Cu_3O_{7-\delta}$ granules and crystalline sucrose

The basic disadvantage of the previously described methods of preparation of open-pore structures was insufficient pressing of the samples or not pressing them before the sintering stage. Because of this, the samples exhibited poor mechanical properties. In order to avoid such problems, a method consisting in mixing granules of the filler with granules of $YBa_2Cu_3O_{7-\delta}$ was elaborated. Such material was produced by the first method and additionally very strongly pressed before sintering the samples. The best results were obtained when applying the crystalline sucrose as a filler.

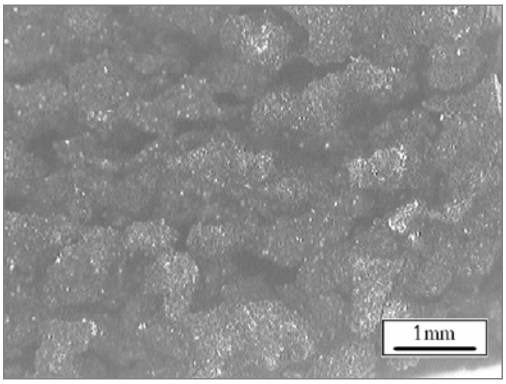

Fig. 4. The outer side of the porous sample $YBa_2Cu_3O_{7-\delta}$ and sucrose granules pressed at 700 MPa sintered at 935 °C by 36 h and oxidized at 475 °C by 36 h

In order to open pores, the filler was added in the amount necessary to obtain 50% and 60% volume fraction. Using such an amount of the filler assured the connection between granules of the filler and existence of open-pore system after sintering the mixture. The granules with the same size range were mixed. The mixtures were pressed up to 700MPa, slowly heated to 400 °C and sintered at 935 °C for 36 h. The method turned out to be well reproducible and gave the samples of good quality (Fig. 4).

2.4. XRD and *R*(*T*) measurements

X-ray diffraction (XRD) patterns were recorded with an X'Pert MRD (Philips) difractometer using CuKα radiation (2θ range of 20–65°). Finally, electrical characterization $R(T)$ were carried out using a standard four probe geometry (Ag paste to Ag electrodes deposited onto the samples).

3. Results and discussion

The best results were obtained with the method using mixed granules of $YBa_2Cu_3O_{7-\delta}$ and a filler. It allowed to press the mixture very tight and thereby to obtain suitable connections between granules of $YBa_2Cu_3O_{7-\delta}$. The crystalline sucrose turned out to be the best filler, which allowed us to obtain the material having good mechanical resistance, containing 60 vol. % of the pores. It, was characterized by the average density of about 2.76 g/cm^3 and the size of pores dependent on the size of the used granules. In order to analyse the quality of the samples, XRD and $R(T)$ measurements were performed.

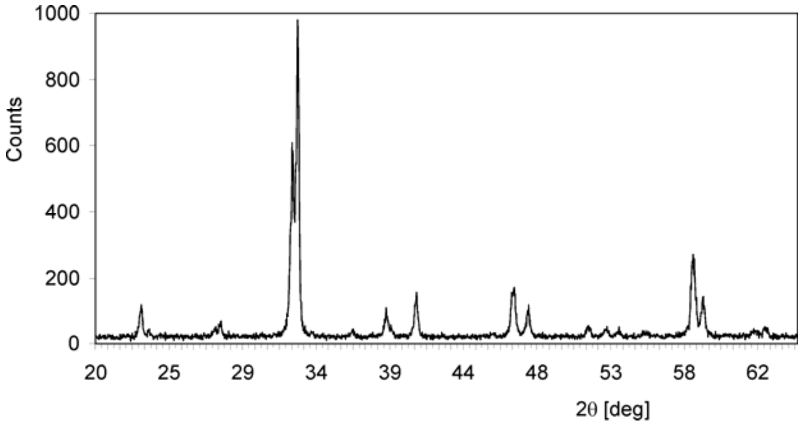

Fig. 5. XRD pattern for standard $YBa_2Cu_3O_{7-\delta}$

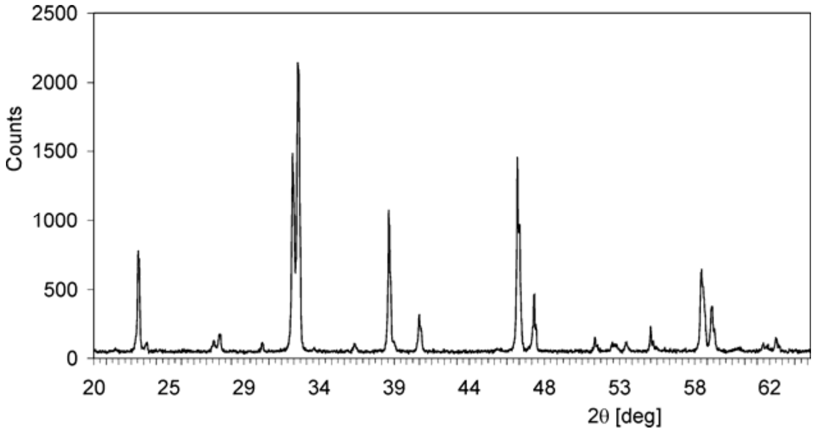

Fig. 6. XRD pattern for the $YBa_2Cu_3O_{7-\delta}$ after sintering with sugar

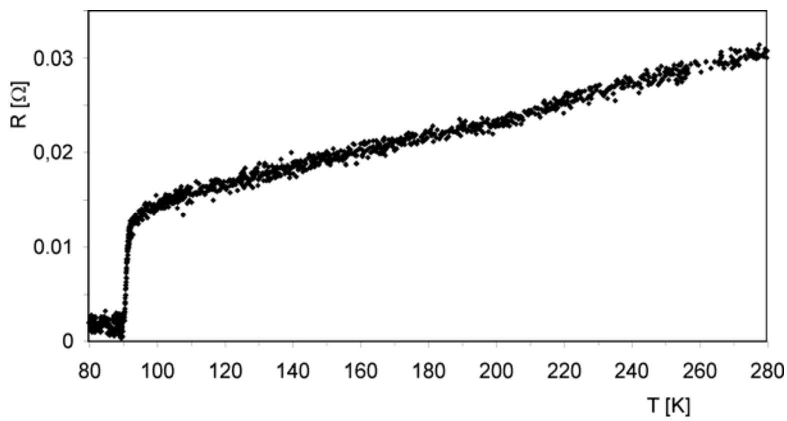

Fig. 7. *R–T* plot for a superconductive sample having open pores filled with Iron and fixed with wax

Figures 5 and 6 present the XRD patterns for a reference sample and the sample after sintering with sucrose and oxidation at 475 °C for 36 h. The X-ray analysis revealed absence of remaining sucrose filler: the samples were burned out completely. Moreover, the $R(T)$ dependence points to the metallic nature of the material above the transition temperature and a narrow (2–3 K) transition to superconductivity at 91 K (Fig. 7).

4. Conclusion

The method of producing the porous $YBa_2Cu_3O_{7-\delta}$ ceramics consisting in using granules of supplementary materials as fillers, gave the best results in the case of crystalline sucrose. The obtained materials have good superconductive and mechanical properties. Therefore such a technique is suitable for obtaining materials applicable in a material research.

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