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Combination of MCA and SHS for Material Synthesis

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Abstract – The combination of mechano-chemical activation (MCA)and Self-propagating High-temperature Synthesis (SHS) has widened the technical possibilities for both methods. For YBCO systems the investigation showed that a short-term MCA of initial powders before SHS leads to single-phase and ultra-fine products. A new technique for preparation ultra-fine high-temperature superconductors (HTS) of YBCO composition with a grain size d <1 m is developed using combination of MCA and SHS. The specific feature of the technique is formation of the $YBa_2Cu_3O_{7-}$ crystalline lattice directly from an X-ray amorphous state arising as a result of mechanical activation of the original oxide mixture. The technique allows the stage of formation of any intermediate reaction products to be ruled out. X-ray and magnetic studies of ultra-fine high temperature superconductors are carried out. Dimension effects associated with the microstructure peculiarities are revealed. A considerable enhancement of inter-grain critical currents is found to take place in the ultra-fine samples.

Key words : mechano-chemical activation (MCA), Self-propagating High-temperature Synthesis (SHS), YBCO, HTS

I. INTRODUCTION

Mechano-chemistry and its synthesis are in wide use as experimental for the production of highly dispersed powders. However, from a technological point of view, mechanical activation possesses a lot of problems, which cannot be easily solved. The biggest problem is the low productivity of the techniques currently available, as well as the contamination of the end products caused by abrasion of the grinding media. The energy consumption should also be taken into consideration in some large scale processes. SHS is energy-saving method and can be applied to the large-scale production for complex oxides. Nevertheless, this method includes a combustion stage which requires very high temperatures. As a result, final products can be obtained only in the form of dense sintered or solidified products when SHS exceeds the melting point of reagents and/or products. To transform such products into commercially interesting powders, one needs to use milling as an unavoidable step. The grinding leads to further contamination

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and to additional energy consumption. Another disadvantage of SHS is a relatively high temperature gradient near the combustion surface which leads to a non-uniform phase composition of the obtained products.

Since the discovery of high-temperature super-conductivity an enormous number of papers devoted to the synthesis of the cuprate superconductors has been published [1,2]. In all cuprate superconductors the critical temperature depends onthe oxygen content, which can be adjusted with the temperature and the oxygen partial pressure during heat treatment. The conditions during powder synthesis are therefore of crucial importance for the resulting physical properties of superconductor wires and bulk material. It has been shown that fine-grained ceramic high-temperature superconductors (HTS) prepared using mechano-chemical methods at the initial synthesis stage possessed a number of advantages over coarse superconductors, namely, particularly high chemical purity, perfect homogeneity, high density (up to 97 % of single crystal), critical currents an order greater than in coarse HTS (both inter-and inside crystalline), much higher first critical fields, and so on [3,4]. The minimum size of HTS grains possessing optimal superconductor characteristics (Tc and rhombic distortion degree) was about 2 m. The well-known ceramic technology was incapable of producing finer grains, because the time needed to form the HTS crystalline lattice due to diffusion through the crystalline lattice of intermediate compounds turned out long enough to produce grains of size > 1 m. The use in the ceramic technology of low temperatures (<930℃) and short sintering times (<8 h) results in an incompletely arranged orthorhombic lattice, i.e. in a lower rhombic distortion degree and, hence, in lower Tc .

The objective of this work is to extend the range of particle sizes toward ultra fine grains (<1m) retaining the optimal superconductivity parameters at a high level. These samples are interesting because they can both furnish information about the effect of structure non-homogeneity of different scale on the HTS properties and permit one to answer the question: what is the minimum size to which HTS grain may be reduced provided that it still remains a superconductor with Tc>90 K?

We propose a new procedure for preparing ultra fine HTS whose specific feature is formation of the HTS crystalline

lattice directly from the X-ray amorphous state arising as a result of mechanical activation of the original components. The prepared ultra fine samples were examined by X-ray technique, analyzed for oxygen content (by the iodometric titration technique), and subjected to magnetic measurements to demonstrate the existence and specificity of the dimension effects at d < 1 m.

II. EXPERIMENTAL PART

Mechanical activation method applied in various works implies different types of mechanical impact. At the same time, as an analysis of the literature data shows, the result of this impact depends heavily on how the method is applied. The most popular approach is the use of a planetary mill. In this work mechanical treatment was performed in the ball planetary mill (AGO-2)in which particles impacted by balls experience multiple contacts and are deformed.

The volume of the mill drums was 250 cm3, the ball diameter was 5 mm, the ball load was 200 g and the weight portion of powder treated was 10 g. In order to avoid oxidation of the metals, all the experiments on mechanical activation were carried out in an argon atmosphere. The X-ray phase analysis was performed with a DRON-3M diffractometer with CuKα radiation. Electron microscopic studies were carried out using the JSM-T20 electron microscope and the high-resolution microscopes JEM-2010 and JEM-400. As a result, powder is not only dispersed but, according to X-ray phase analysis, is partially or completely converted into amorphous phase. The mean power spent in the apparatus amount up to 20 W/h, the local energy release rate at the instant of ball impact is at least three orders of magnitude higher. The mechanical energy absorbed by powder (dose) varies during experiment from 1 to 10 kJ/g dose. According to the X-ray analysis data, no iron yield of milling was detected, because of copper-plated balls were used. A sample activated mechanically was subjected to cold pressing to make pellets. Y_2O_3, BaO_2, CuO were used as starting reagents, and then samples annealed at T=850℃ for 2, 12, and 36 h and also at T=900℃for 1, 6, 12 h, respectively in a tubular furnace of the SUOL type. The phase composition was controlled by X-ray analysis.

III. RESULT AND DISCUSSION

A high exo-thermal effect of reaction and a strong Arrhenius-type temperature dependence of the reaction rate of decisive importance are for the feasibility of SHS processes. For diffusion-controlled processes, to which SHS also belong, another important parameter is the disperse state of the initial components, including the uniformity of their mixing and surface area of contacts between components.

Benefits offered by mechanical activation in preparing fine dispersed materials are well recognized. However, as the result of many studies, in which this procedure is applied to HTS materials, show, this method sometimes may not produce appreciable positive effect. Thus, the use of mechanical processing to crush a ready-made material leads to undesirable effects changing the oxygen content and Tc value.

The electron microscopic investigation of the products of the mechanical activation in a ball mill demonstrated that after activation for 30 s the initial particles consist of agglomerates of various shapes and sizes. Fig. 1a shows microphotograph of the cross section of the agglomerate. An increase of the activation time to 3 min causes a drastic change to the morphology of the product particles (Fig.1b).

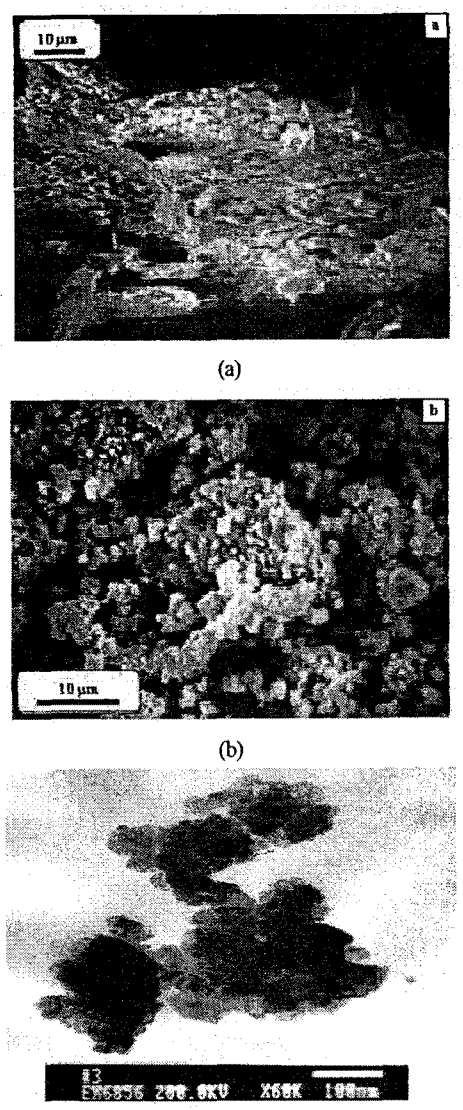


Fig.1. Microphotographs of a cross section cleavage of the initial powders after mechanical activation for 30 s (a), 2 min (b), 4 min (c)

Whenever mechanical activation is employed at an early synthesis stage, of

great importance is the proper choice of the original components. Barium carbonate $BaCO_3$ 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" Y_2BaCuO_5 phase, or proceeds concurrently through the "blue" Y_2BaCuO_5 and "green" Y_2BaCuO_5 phase. Transition of the green phase to $YBa_2Cu_3O_x$ is known to be hindered, therefore high values of T_{sint} and t_{sint} are required to form the end product.

The mechanism changes drastically when barium dioxide BaO_2 is chosen as the starting material. Melting at low temperature T=450℃, this compound easily becomes amorphous in the course of grinding and enters into reaction with CuO producing cuprates and leaving unchanged Y_2O_3, which can hardly be made amorphous. Hence, $YBa_2Cu_3O_x$ is produced via the following reaction

$$4BaCuO_2 + Y_2O_3 + 2CuO = 2\,YBa_2Cu_3O_x + kO_2,$$

in which participation of the green phase in synthesis is completely ruled out. This reaction pathway not only provides the highest phase homogeneity, but significantly reduces the time and lowers the temperature of synthesis of the desired compound.

It is the way how fine ceramic $YBa_2Cu_3O_x$ samples with the minimum grain size of about 2 m were prepared. The next step in further reducing T_{sint} and t_{sint}, which is realized in this work, consists in precluding formation of intermediate reaction products. For this purpose, a mixture of the starting reagents Y_2O_3, CuO, and BaO_2 taken in a desired ratio was processed mechanically in a vibration mill and then placed directly in a hot furnace at T=850~900℃ in the form of powder (to provide easy oxygen evolution during $YBa_2Cu_3O_x$ synthesis). Diffraction patterns taken after 15-min annealing showed only peaks pertaining to the final product, which indicates that the end product is predominantly formed directly from the amorphous mixture of starting reagents.

We succeeded in the performing SHS in the sample compacted from powder after mechano-chemical treatment [5]. Subsequent mechano-chemical activation homogenizes the product and leads to the formation of a homogeneous superconductor material.

Parameters of a unit cell, oxygen content

According to the X-ray analysis, all samples annealed at 850 and 900℃ are strictly single-phase and correspond to a well crystallized compound with orthorhombic symmetry. The measured oxygen content does not differ from the standard value of x = 6.8 - 6.9 inherent in fine-grained samples.

Mechanism of grain growth

Being low-melting compounds, copper oxide and barium peroxide form readily the amorphous phase in the course of mechanical activation, therefore in the ternary Y_2O_3-CuO-BaO_2 system they interact first, and only later on the product of their interaction reacts with Y_2O_3. In this interaction way which changed the mechanism of $YBa_2Cu_3O_x$ formation to the more efficient reaction involving "no green phase". Interaction between the components in this case proceeds apparently via a mechanism similar to homogeneous nucleation, rather than via the diffusion-controlled mechanism. However the rate-limiting process still remains cation and anion ordering. Therefore annealing for a few hours is needed to form the long-range crystalline structure.

Correlation between the degree of amorphous conversion in the course of mechanical treatment and melting point is genuine and not-surprising, because these two processes (melting and mechanical activation) involve rupture of the bonds between atoms in the crystalline unit, i.e. cell destruction.

IV. CONCLUSION

1. The above results suggest that the powder procedure with mechanical activation proposed in the work enables one synthesize orthorhombic YBCO compound directly from a mixture of starting reagents in the X-ray amorphous state.

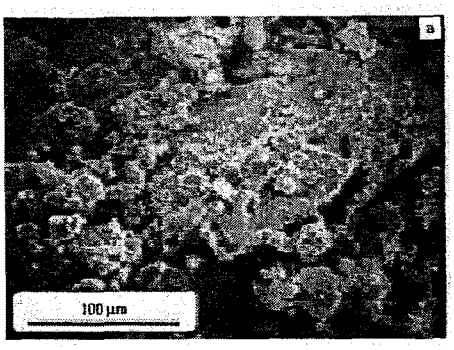
2. Owing to this the synthesis temperature and time can substantially be reduced, which results in very fine final product particles and retains the parameters optimal for superconductivity (rhombic distortion degree, oxygen content, Tc

value). The minimum grain size d in the samples studied was 0.4 m.

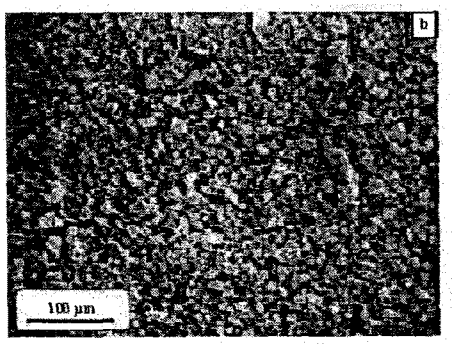
3. Varying annealing times and temperature one can synthesize samples with a controlled grain size ranging between 1 and 100 m, which facilitated performing investigations into the "microstructure-property" interrelation as applied to this particular compound and allowed the range of some physical characteristics to be appreciably extended.

4. The mechano-chemical approach becomes practicable only with high rates of promoted reactions, i.e., those that are not only thermodynamically allowed, but also give an energy gain. High rates of mechano-chemical processes result in final products, which are highly dispersed, and this can significantly influence the properties of the resultant material.

5. Our investigation shows that the combination of the SHS process with the mechanical activation of reagents could be rather attractive for technological applications of synthesizing materials.



(a)



(b)

Fig.2. Microphotograph of the YBCO SHS product (a) without mechanical activation, (b) with mechanical activation initial powders.

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