THE MORPHOLOGY OF SOME YBCO SUPERCONDUCTOR MATERIALS.

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Abstract
This work emphasizes our experimental tests and studies regarding microstructural characterization of YBCO materials. YBa$_2$Cu$_3$O$_{7-\delta}$ superconductor powder was made through ceramic method by solid state reaction with high purity oxides. The structural examination has offered the semnificative morphology details. By the optical microscope and SEM analyses is emphasized that presented crystallites with plate-like morphologie. The crystallites lend to the morphology for superconducting phases with high critical temperature (plate, poliedric).

1. INTRODUCTION
To achieve superconductor materials in the YBCO system the ceramic method is used, the reaction method in solid state. This method is broadly used to produce superconductor oxides, considering the less restrictive technological conditions.
To achieve superconductor materials by solid state reaction, powder mixtures of binary oxides, oxides and carbonates, oxides and nitrates are used [1, 2, 3, 4].

1.1 Ceramic method for YBCO compound
Within the studies and researches carried out to achieve YBCO-123 superconductor compound high purity Y$_2$O$_3$, BaCO$_3$, CuO powders were used.
Powders were homogenized and mechanically ground in an agate mechanical mill. In order to assure an improved homogeneity of the mixture several grinding/calcination cycles are implied, the technological parameters under which these were carried out are presented in table 1.

Table 1 Grinding / calcination cycles for the production YBCO compound

<table>
<thead>
<tr>
<th>Heat no.</th>
<th>Grinding h</th>
<th>Calcination °C/h</th>
<th>Atm</th>
<th>Grinding / calcination cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>840/4</td>
<td>air</td>
<td>3 + final grinding</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>840/4</td>
<td>air</td>
<td>4 + final grinding</td>
</tr>
</tbody>
</table>

The mixed powders were pressed in 11mm diameter with height between 1 to 2 mm samples at 10 tf/cm$^2$. The sintering process that practically led to the manufacturing of these superconductor product was carried out at 925°C in oxygen, for several sintering times (12 h, 20 h, and 50 h respectively).
Table 2 show YBCO samples achieved for to the sintered time specification.
Table 2 The technologicals parameters for the production YBCO compound

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Heat no.</th>
<th>Pressing force, tf/cm²</th>
<th>Heat treatment °C/h</th>
<th>Atm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>10</td>
<td>925/12</td>
<td>O₂</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>10</td>
<td>925/20</td>
<td>O₂</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>10</td>
<td>925/50</td>
<td>O₂</td>
</tr>
</tbody>
</table>

2. RESULTS AND DISCUSSIONS
2.1 Microscopy studies and researches
The assessment was carried out on NU - 2 ZEISS type microscope at magnifications up to 600×, and NEOPHOT 32 ZEISS microscope for magnifications up to 1000×.
The microstructure was analyzed on ground and polished surfaces of the samples to correctly examine the size and morphology of the phases.
Figure 1 shows the microstructure of YBCO compounds, sample no 2 and 3 in table 2. Comparing the images, a growth of the polyhedral phase is noticed at the sample sintered for 50h (sample 3) against that sintered for 20h (sample 2).

Sample 2, 300x  Sample 3, 300x

Sample 2, 1000x  Sample 3, 1000x

Figure 1 Microstructure of sintered YBCO samples, 925°C in oxygen

A number of pores trapped inside the grains are noticed. The pores are up to ~ 10 µm…15 µm and uniformly scattered. The temperature plateau leads to crystal growth and bonding as well as the complete of partial eradication of pores. Pore volume decreases both due to the effect of the material superficial stress and the pore migration towards the surface.
In sample 2 YBCO, the grains are plate-like, strongly anisotropic and in a wide range distribution: their length may exceed 100 µm while their width is between 5 µm … 20 µm.
Grain orientation is not affected by the sintering time, however, long sintering times may lead to a slight increase in grain size (grain width up to 25 µm … 30 µm for a sintering time of 50 h, figure 1). The presence of secondary phases can also be noticed at the edges of the grains, even if X-ray diffraction at samples YBa₂Cu₃O₇₋δ show an orthorhombic structure, [5]. For longer sintering times, 50 h against 20 h, the secondary phase share (black phase) decreases notably.

2.2 Microscopy studies and researches by qualitative analysis
Phase assessment of YBCO compounds was carried out on Buehler Omnimet image analyzer. The computerized image analysis was carried out on a YBCO sample, pressed at 10 tf/cm², sintered at 925°C, for 50 h in oxygen (sample 3, table 2). Five randomly selected fields were analyzed. Four distinct phases were noticed. The phases are: plate-like crystals, counting around 87% of the analyzed fields, the rest being identified as pores.

2.3 Electron microscope studies and researches by SEM analysis
The most significant test results carried out on by SEM analysis, on the initial powder samples and in the intermediary YBCO ceramics production stages are presented below. SEM analyses were performed on a TESLA BS 301 microscope. The images achieved by electron scanning analysis in figure 2 show the initial morphology of the powders used as raw material, and the material crystals as powders after sintering.

Figure 2 Microstructure of YBCO compound during the manufacturing process
Yttrium oxide powder (figure 2a) has an irregular morphology, fang-like particles that have needle aspect. Their sizes are between 2 µm and 20 µm. The barium carbonate powder (figure 2b) has a more uniform aspect, round particles, others as rod-like. Their sizes are below micron sizes. Copper oxide powder (figure 2c) has a spheroidal towards cubic morphology, and sizes between 2 µm to 4 µm. The large spheroidal particles after mixing, sintering and grinding is noticed. Their sizes increase (~ 10 µm), and their morphology tend to a more regular and polyhedral aspect and the facets are somehow rounded, (figure 2d) The crystal morphology after pressing and sintering for YBCO compound (sample 1, table 2) is presented in figure 3.

The fracture surface of the sample shows a random distribution of the polyhedral particles, of these large crystals (~ 80 x 18 µm), or small (~ 23 x 13 µm), with edges and round facets.

3. CONCLUSION
Analyzing the grinding process, for the YBCO compounds, it has been noticed that at insufficient grinding (e.g. hand grinding), the necessary homogeneity to achieve high quality samples was not accomplished. Hence, samples manufactured as described showed a green pigmentation on the surface, pigments representing Cu particles that had not reacted with Y and Ba oxides. A slight greenish colour of the surface samples was noticed, showing a rather great portion of BaCu2 semiconductor phase compared to Y2BaCuO5 which transforms in YBa2Cu3O7-δ at 920°C. The powder particles have a irregular aspect and are gathered.

The samples used in the SEM analyses were identically prepared as those used for the image analyses. The images show crystals under a polyhedral aspect, specific to 123 YBCO phase. The polyhedral crystals have a particular morphology, polygonal pores on the facets suggesting crystal formation by the interaction of several plate-like crystals, on various directions.

At the corners of the grains the presence of several secondary phases is noticed, even if X-ray diffraction show YBa2Cu3O7-δ samples having orthorhombic structure.

The quantitative analyses on the phases of YBCO compounds were carried out on a Buehler Omnimet image analyzer.

The examined samples were mechanically ground and polished on a special cloth, using alumina and then diamond paste. However, during the survey, a perfect polished surface was not always achieved, i.e. without scratches and a good flatness on the entire surface. Five randomly selected fields were analyzed per sample in order to comprise a large surface for...
analysis. Three distinctive phases were noticed for the YBCO compounds. The phases are plate-like crystals, in a considerably share of around 87% of the analyzed field area. The rest could be considered as pores. By correlating the analyses of the optical, qualitative and quantitative microscopy we may conclude that the plate-like crystals are of 123 superconductor phase.

REFERENCES