SINTERING OF \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) CERAMICS IN A TEMPERATURE FIELD WITH A CONSTANT GRADIENT

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As a result of studying the sintering of ceramic material \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) in a temperature field with a constant gradient the possibility of rapid mass transfer with participation of a liquid phase is established. Its formation provides rapid sintering and radial shrinkage in the high-temperature region. Redistribution and crystallization of the liquid in the low-temperature region causes ceramic swelling. The effects described are also accompanied by a change in material phase composition in a direction parallel to the temperature gradient.

Interest in the compound \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) is due to its superconductivity in the nitrogen temperature region [1]. The history of its discovery and methods for preparing this compound are well known [2, 3]. Currently the effort of researchers is directed toward studying properties, improved methods for preparing \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \), and also solving problems connected with using its unique properties in technology. It is possible to separate two basic problems: to increase the superconducting transition, temperature and to increase the critical electric current density bounding the superconducting condition. The solution of the second problem is connected with improving the ceramic structural state. In this connection it is important to study sintering of the original homogenized powder which is a definitive step in preparing compacted ceramic material.

As a rule sintering is performed in an isothermal schedule at 900-950°C. However, the low thermal conductivity of the compound \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) and also the unevenness of the temperature field under actual conditions causes presence of local temperature gradients which in turn cause a whole number of undesirable phenomena which worsen the superconducting properties of the material obtained. In particular this relates to the phenomena of decomposition of the basic superconducting phase into a series of associated phases, local segregation of individual components, and appearance of a eutectic which is characterized by a different melting temperature. In view of this it is of interest to study sintering of ceramic \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) in a specially created and variable temperature field with a constant gradient. The importance of this temperature gradient has been mentioned previously [4, 5] although it has not been studied in detail. In particular the transfer mechanism for a substance with nonisothermal ceramic sintering, the role of the liquid phase in this process, and changes in phase composition and structure are questions which remain unresolved. The aim of this work is to overcome these omissions.

Powder corresponding to the composition of superconducting phase \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) was prepared by solid-phase chemical reaction in a mixture of powders \( \text{Y}_2\text{O}_3 \), \( \text{BaCO}_3 \) and \( \text{CuO} \) at 900°C for 30 h. After each ten hours of annealing the powder which is a reaction product was ground mechanically for 1 h. The degree of its homogenization was monitored by an x-ray method. This made it possible to establish that the synthesized powder corresponds to the \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) phase and that it is single-phase within the limits of experimental error (\( \approx 2\% \)). Homogenized powder was sieved through a screen with a mesh size of 50 \( \mu \text{m} \). Specimens for study in the form of cylinders 10 mm in diameter and 20-30 mm high were prepared by compaction under a pressure of 150 MPa. The relative density of compacts in the original condition was 55-60%.

The prepared specimens were annealed in air in a vertically placed tubular furnace with a prescribed temperature gradient. In the area where specimens were placed the temperature was varied by a linear rule (it was varied at both ends of a specimen). The furnace heating rate was constant and it was 1 deg/sec\(^{-1} \); the annealing time was varied within the range from several minutes to ten hours.

Specimen dilation and also the change in their structural state were monitored by means of an optical microscope. X-ray microanalysis was used in order to study the phase composition of compacts.
Shown in Fig. 1 is a specimen sintered in a temperature field with a constant gradient for 2 h. The temperature at the specimen ends was kept constant and was 1020 and 790°C. Quantitative data about its relative dilation in a direction perpendicular to the temperature gradient are presented in Fig. 2. With a reduction in the lower temperature the region of the specimen corresponding to negative shrinkage (‘swelling’) shifts in the direction of the more heated end. However, its position always corresponds to the temperature range 960-840°C.

The structure of different areas of a specimen is presented in Fig. 3. The region corresponding to swelling is characterized by the presence of a large number of pores and a small grain size. In the region of the specimen immediately adjacent to the more heated end there are individual coarse pores and the grains are considerably larger in size. Close to the less heated end the specimen structure is almost indistinguishable from the original structure.

Given below is the phase composition of a sintered specimen:

<table>
<thead>
<tr>
<th>Temperature range, °C</th>
<th>Phases recorded</th>
</tr>
</thead>
<tbody>
<tr>
<td>790—840</td>
<td>( YBa_2Cu_3O_7-x )</td>
</tr>
<tr>
<td>840—880</td>
<td>( YBa_2Cu_3O_7-x ), CuO</td>
</tr>
<tr>
<td>880—960</td>
<td>( YBa_2Cu_3O_7-x ), ( YBa_2Cu_3O_5 ), BaCuO_2</td>
</tr>
<tr>
<td>960—1020</td>
<td>( Y_2BaCuO_5 ), BaCuO_2</td>
</tr>
</tbody>
</table>

As can be seen, the region of a specimen corresponding to swelling is enriched in copper and barium ions, but the region adjacent to the more heated end is conversely impoverished in them. All of these changes were only observed in the case when the temperature of the more heated specimen end exceeded 920°C. In order to explain the role of the force of gravity in an experiment we also performed the following control test. Two identical specimens were annealed under identical conditions with the sole difference that for one of them a higher temperature was maintained in the upper part of the furnace, and for the other it was maintained in the lower part. No differences between specimens were observed and consequently the role of the force of gravity is insignificant.

Thus, sintering of ceramic \( YBa_2Cu_3O_7-x \) in the presence of a temperature gradient is characterized by clearly expressed transfer of a substance in a direction parallel to the gradient, and it is accompanied by uneven shrinkage in a direction perpendicular to it (Fig. 1). In our opinion this effect is caused by development of a liquid phase in the region of the more heated specimen end and subsequent transport in a direction opposite to the temperature gradient.

The last conclusion is confirmed by the following experimental facts and control tests. First, the effect described only develops when the maximum specimen temperature is 920°C. According to the constitution diagram for the \( Y-Ba-Cu-O \) system this temperature corresponds to development of a liquid phase [6]. The liquid formed as a result of a thermocapillary effect spreads into the lower temperature region [7]. Second, the results of X-ray microanalysis indicate that the most probable reaction which describes the composition of the original phase with formation of liquid is as follows:

\[
2YBa_2Cu_3O_7-x \rightarrow Y_2BaCuO_5 + 3BaCuO_2 + 2CuO.
\]

The last conclusion is confirmed by the fact that the limiting temperatures which correspond to areas enriched in copper and barium are in good agreement with calculated temperatures which specify solidification of BaCuO_2 and CuO [8].

Third, the considerable positive shrinkage of a specimen in the radial direction observed in the higher temperature region corresponds to the liquid-phase sintering mechanism [9]. Consequently, specimen swelling is connected with jumps in