Structure and properties of YBCO before and after the short-term exposure of the plasma flow

A E Rabadanova¹, S Kh Gadzhimagomedov¹, D K Palchaev¹,
M H Gadzhiyev², G B Ragimkhanov¹, N A Demirov²

¹ Dagestan State University, Gadzhieva 43-A, Makhachkala, 367000, Russia
² Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13
Bldg 2, Moscow, 125412, Russia
E-mail: rabadanova.aida@mail.ru

Abstract. The results on the structure and electrical resistance of the porous YBa₂Cu₃O₇₋δ nanoceramics before and after plasma treatment are shown. It is shown that after exposure to high-enthalpy argon plasma flow, the structural, stoichiometrical and superconducting properties in the volume of this ceramics change slightly. An amorphous layer forms on the surface, the mechanical strength of the inter-granular bonds of which becomes higher than for the material in the bulk.

1. Introduction

Functional high-temperature superconducting materials, including nanostructured, based on YBa₂Cu₃O₇₋δ, are used in various branches of modern technology: electronics, computing, medicine, energy, transport, for photocatalysis, and others. In microcrystalline ceramic samples of YBa₂Cu₃O₇₋δ, as a result of a decrease in the inter-atomic interaction forces on contacts between superconducting grains, the critical current decreases by orders of magnitude. The strength of these contacts is also affected by thermal stresses associated with the formation of defects and pores in the sample during sintering of ceramics. When the material is nanostructured the strength of the material is further reduced. On the other hand, a decrease in the size of crystal grains reduces the effect of the occurrence of thermal stresses during sintering, and the presence of nanoscale structural defects effectively contributes to vortex pinning. Nanostructured ceramic materials are also characterized by a significant decrease in the critical current, however, the transition temperature to the superconductor state, which is detected as a decrease in electrical resistance in to physical zero and the Meissner effect, remains at about 90 K. Moreover, as shown in [7,8], the transition temperature to the superconducting state \( T_c \) for nanoceramics according to electrical resistivity data is higher than for microcrystalline ceramics. The values of the thermal power and the Hall effect, which are volumetric characteristics, are zero for superconductors. Therefore, superconducting nanostructured materials with low critical current density values can be used in practice to control (increase or decrease) the contact potential difference in hybrid systems implementing Seebeck, Pelte, Thomson and other effects. The strength of these materials can be enhanced by plasma processing of their surface. As is known [9,10], plasma treatment of HTSC ceramics leads to amorphization of the sample surface and a decrease in the fraction of defects in the intergranular boundaries.
This paper presents the results of studies of the structure and properties of nanostructured ceramics based on YBa$_2$Cu$_3$O$_{7-\delta}$ obtained using a new chemical technology \cite{7,11} before and after plasma exposure.

2. Results and discussion
The surface of a ceramic sample obtained from nanopowder by sintering at 920$^\circ$C for 1 hour was exposed to a high-energy plasma jet. The sample was exposed to a high-enthalpy plasma jet at a distance of 20 mm from the exit nozzle for $\sim$ 30 s formed by a direct-current plasma torch \cite{12} (250 A). The plasma gas was argon with a flow rate of 3 g/s. Analysis of the results of high-speed images and thermograms (figure 1) showed that in a short time of 30 s the temperature in the plasma jet epicenter reaches $\sim$ 1600 K, and the sample outside the epicenter heats up to 1400 K. Based on the calorimetric measurements, the heat flux created by the plasma was determined for different values of current, gas flow rates and distances from the outlet of the plasma torch nozzle. When changing the power of the plasma torch $P = 5 \div 10$ kW in argon and the distance from the nozzle exit 10 \div 30 mm, the plasma jet with a normal drop on the calorimeter provides a specific heat flux of 0.02 \div 1 kW/cm$^2$. For example, for an arc current of 250 A at a gas flow rate of 3 g/s and a distance of 20 mm from the sample, the specific heat flux was $q = 0.054$ kW/cm$^2$.

![Figure 1.](image)

Figure 1. The glow of the sample after 30 s of plasma exposure and its conversion to the temperature field.

Diffraction analysis, morphology and phase composition of the samples were studied on a PANalytical Empyrean series 2 diffractometer with a database PAN-ICSD and an ASPEX Express scanning electron microscope based on an Omega Max EDX detector, respectively. The crystallite size was determined by the Scherrer formula. The oxygen content ($\delta$) was also determined by Raman spectroscopy from the intensity ratio of the Raman shift line 500 cm$^{-1}$ and 340 cm$^{-1}$, obtained at Ntegra Spectra (NT-MDT) (Raman scattering mode).

Figure 2 shows fragments of diffraction patterns indicating the oxygen content and Raman spectra (CR) before and after exposure to the plasma of nanostructured YBCO ceramics. According to XRD analysis, the oxygen index of the surface of a sample of ceramics decreased from 6.9 to 6.6, and according to the Raman spectra refinement – from 6.9 to 6.7, respectively. The exposure to plasma flow also led to small changes in the sample density and the average crystallite size (from 3.5 g/cm$^3$ and 72 nm to 3.8 g/cm$^3$ and 74 nm, respectively). Influenced by the plasma flow on the surface of ceramics and investigated the structure and properties of this surface.
Figure 2. Diffractograms and Raman spectra of nanostructured YBCO ceramics, before – a), c) and after – b), d) plasma effects.

Figure 3. Morphology and elemental composition of nanostructured YBCO ceramics: before – a), c) and after – b), d) plasma effects.
Figure 4. Temperature dependences of the electrical resistance of nanostructured YBCO ceramics: before – a) and after – b) plasma exposure.

The morphology and elemental composition of nanostructured YBCO ceramics before (a) and after (b) exposure to plasma are shown in Figure 3. The exposure to plasma flow led to a small change in the density of the sample from 3.5 g/cm$^3$ to 3.8 g/cm$^3$. This is confirmed by studies of morphology (figure 3b). After exposure, the elemental composition is practically preserved (figure 3c, d).

Measurements of the electrical resistance of the samples were carried out using a standard 4-probe method using a Keithley 2002 digital multimeter on an automated installation. The results of the study of electrical resistance before and after plasma exposure are shown in figure 4.

It has been established that before and after exposure the temperature of the onset of the transition to the superconducting state ($T_{c,\text{onset}}$) of the samples did not change significantly (figure 4). However, the temperature dependence of the resistivity after exposure to plasma changed from metallic to semiconductor (figure 4). For the semiconductor stroke, the temperature coefficient of resistance (TCR) is 0.0018 K$^{-1}$ in the range of 300–150 K. TKR in the range of 150–95 K increased by more than 10 times.

The absolute values of electrical resistance turned out to be almost 2 times higher. This indicates a decrease in the oxygen stoichiometry index after exposure to plasma flow [9].

3. Conclusion
The impact of a high-enthalpy plasma jet ($q = 0.054$ kW/cm$^2$) on a ceramic sample at a distance of 20 mm for $\sim 30$ s resulted in insignificant changes in its structure and properties. The temperature in the epicenter of the plasma jet reached $\sim 1600$ K, and the sample outside the epicenter was heated to 1400 K. We observe a decrease in the oxygen index from 6.9 to 6.6 (according to XRD) and 6.7 (according to Raman spectra) and an increase in density from 3.5 g/cm$^3$ to 3.8 g/cm$^3$. Before and after exposure to $T_{c,\text{onset}}$ the beginning of the sample did not change significantly; however, the course of the temperature dependence of the electrical resistivity changed from metallic to semiconductor. TCR is equal to 0.0018 K$^{-1}$ in the range of 300–150 K. After exposure to TCR in the range of 150–95 K, it has increased more than 10 times, and the absolute values of electrical resistance – almost 2 times.
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