# EFFECT OF PULSED LASER PROCESSING ON PHASE COMPOSITION AND PROPERTIES OF SURFACE LAYERS OF YTTRIUM CERAMIC

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It is demonstrated that nanosecond laser processing of superconductive yttrium ceramic by pulses with energy density of 1.7-2.1 J/cm$^2$ permits an increase in critical current density in surface layers by three orders of magnitude.

The most important problem in contemporary development of high temperature superconductor materials is the search for methods of increasing critical current density. It has now been established that this requires elimination of the effect of grain boundaries, which can be achieved by fusing such boundaries or producing the semiconductor from a melt. However, remelting causes decomposition of the original compound and loss of oxygen, which then requires additional thermal processing to reestablish the structure of the high temperature superconductor material. In connection with this, the effect of short-term heating to the fusion point on the properties of high temperature superconductor materials is of special interest, since this technique produces only surface fusion of the grain boundaries, as a result of which recrystallization occurs upon an oriented substrate, the role of which is played by the unmelted portion of the grain. We will note that such a process is also realized in gas thermal and plasma deposition of powdered materials [1].

To accomplish rapid heating to the fusion point of the grain surface and rapid recrystallization of the melt in order to increase critical current density, concentrated energy pulses can be used, in the form of ion or electron beams or laser pulses. Use of nanosecond length electron beams for this purpose has proved successful [2]. However, because of the deep penetration of electrons into the material surface melting requires repeated action (up to 20 times) of the pulsed electron beam. The modified layer of the high temperature superconductor material is not oxidized in this process, which indicates that in the process of melt formation and rapid recrystallization of the surface region of superconductive ceramic materials oxygen loss does not occur [2]. In connection with this, it is of interest to study the action of laser pulses on high temperature superconductor materials, since the fusion depth in that case is significantly less than for electron beam processing, permitting modification of thinner layers.

We will note that pulsed laser annealing is widely used for formation of semiconductor structures and for the purpose of crystallization of amorphous, or recrystallization of finely dispersed polycrystalline compounds [3].

Results were presented in [4] on the use of this method for processing volume yttrium ceramic high temperature superconductor material with the goal of recrystallizing the surface layer. The laser processing was performed by pulses 1 msec in duration with an energy of 80 J, with subsequent high-temperature annealing of the ceramic to the point of saturation of the surface layer by oxygen. This caused the critical current density in the processed layer to increase by a factor of 20 times. Thus, it would be of interest to consider the action on high temperature superconductor materials of laser pulses shorter than those used in [4]. Some unique features of the action of laser radiation on the compound $YBa_2Cu_3O_{7-x}$ were described in [5], from which it follows that the energy density in the pulse sufficient for fusing the surface of the material lies within the limits 1-10 J/cm$^2$. Scanning electron microscopy revealed that at a pulse energy density of 5-10 J/cm$^2$ surface erosion occurs with expulsion of microdroplets, while at lower values fusion of crystallites occurs.

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TABLE 1. Critical Currents in $YBa_2Cu_3O_{7-x}$ Specimens Before and After Annealing

| Specimen number | Specimen thickness t, cm | Pulse energy density, $J/cm^2$ | Critical current before processing $I_{cr_1}$, A | Critical current after processing $I_{cr_2}$, A | Critical current density before processing $J_{cr_1}$, $A/cm^2$ | Critical current density after processing $J_{cr_2}$, $A/cm^2$ |
|---|---|---|---|---|---|---|
| 1 | 0,15 | 1,5 | 1,13 | 0,90 | 38 | 30 |
| 2 | 0,15 | 1,7 | 0,72 | 0,75 | 24 | $1{,}8\cdot10^4$ |
| 3 | 0,24 | 1,8 | 2,18 | 2,61 | 44 | $6{,}5\cdot10^4$ |
| 4 | 0,25 | 1,9 | 1,61 | 2,07 | 30 | $5{,}1\cdot10^4$ |
| 5 | 0,23 | 2,0 | 1,75 | 2,33 | 36 | $5{,}8\cdot10^4$ |
| 6 | 0,20 | 2,1 | 1,32 | 1,40 | 33 | $3{,}5\cdot10^4$ |
| 7 | 0,30 | 2,2 | 1,74 | 1,62 | 29 | 27 |
| 8 | 0,20 | 2,3 | 1,16 | 1,08 | 29 | 27 |
| 9 | 0,40 | 2,5 | 1,44 | 1,36 | 18 | 17 |
| 10 | 0,25 | 2,7 | 1,39 | 1,29 | 28 | 26 |
| 11 | 0,25 | 2,9 | 1,49 | 1,49 | 30 | 30 |
| 12 | 0,20 | 3,1 | 1,76 | 1,64 | 44 | 41 |
| 13 | 0,20 | 5,2 | 1,79 | 0,64 | 45 | 16 |
| 14 | 0,20 | 7,4 | 2,04 | 1,52 | 51 | 38 |

The present study investigated the structure and properties of high temperature superconductors of the composition $YBa_2Cu_3O_{7-x}$ processed by a single laser pulse at a wavelength of $\lambda = 1.06$ μm, duration 50 nsec, beam diameter 10 mm, and energy density of 1.5-7.4 $J/cm^2$, without subsequent high temperature annealing. The specimens to be studied were obtained by the standard solid state synthesis method. The original ingot, consisting of yttrium, barium, and copper nitrates, was subjected to preliminary annealing at a temperature of 750-800°C for 5 h. After grinding a three-step annealing was carried out at 940-945°C for 5 h with surface grinding between stages. Ceramic specimens were produced in the form of rings 10 mm in diameter, with inner diameter of 6 mm, and thickness as shown in Table 1, by pressing at a pressure of 2 kbar, annealing for 5 h at a temperature of 940-945°C in air and then cooled together with the furnace at a rate of ~3 deg/min. X-ray analysis of the superconductive ceramic produced revealed a single-phase composition (an orthorhombic $YBa_2Cu_3O_{7-x}$ phase). The oxygen content of the ceramic specimens, determined by iodometry [6], comprised 6.79-6.81 atoms per formal unit.

The temperature of transition to the superconductive state in the original specimens, as measured by both inductive and resistive four-probe methods, was $T_c \sim 90$ K. The critical current density flowing through the specimen at nitrogen temperature was measured by the contactless induction method [7]. To do this the ring-shaped ceramic specimen with a ferrite core placed in its inner hole was placed in a measurement cell between two coils — primary and secondary. An ac current was fed through the primary winding and the voltage induced in the secondary coil measured by an oscilloscope. The measurement cell was immersed in liquid nitrogen. In the case where the specimen was superconductive the output signal fell to the noise level. With increase in input current above some threshold value there appeared on the oscillogram abrupt spikes exceeding the noise level. The value of this threshold current was the critical current $I_{cr}$, which the superconductive ring could pass. The value of the total critical current $I_{cr}$ was calculated with the expression:

$$I_{cr} = i_1 n,$$

where $i_1$ is the critical current in the primary winding, while the critical current density $J_{cr}$ was determined from:

$$J_{cr} = \frac{I_{cr}}{td}.$$

Results of critical current measurements in the synthesized specimens processed by a laser pulse with 50 nsec duration and pulse energy density of 1.5-7.4 $J/cm^2$ are presented in Table 1.

As follows from Table 1, processing of the yttrium ceramic at an energy density of 1.7-2.1 $J/cm^2$ leads to an increase in the critical current value. This increase is caused by formation on the ceramic surface of a fused layer.

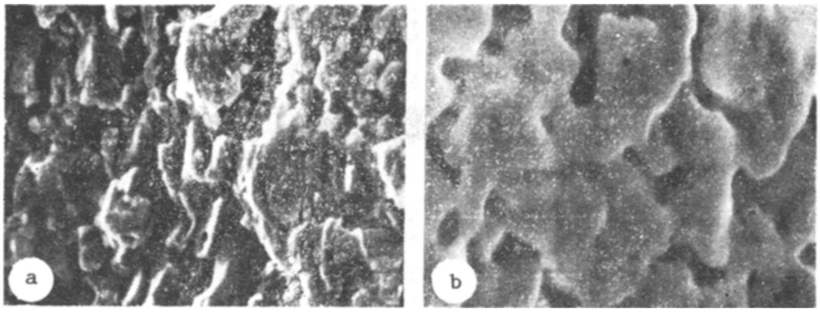

Fig. 1. Photomicrograph of ceramic specimen surface, ×2000: a) before processing; b) after pulsed laser processing with energy density of 2 J/cm$^2$.

The superconductor surfaces were studied with an RÉM-100 U scanning electron microscope at magnifications of 300-3000 times. Figure 1 shows photomicrographs of $YBa_2Cu_3O_{7-x}$ specimens processed by laser pulses with an energy density of 2.0 J/cm$^2$ which reflect the change in surface state due to laser processing. It is evident that laser action in this energy density range causes fusion of grains with formation of a continuous surface layer.

Processing by pulses with lower energy density leads to grain fusion without formation of a continuous layer, with a granular surface being formed. Over the energy density range used in the present study no surface erosion or cracking of the layer formed was observed. Apparently the efficiency of processing depends on the original density of the material as well as the size and orientation of the crystallites composing it.

It was established by profilometric measurements of the specimen surface that upon laser processing smoothing of surface roughness occurred. The mean deviation from the baseline of the original surface was 0.55-0.58 μm, while for the laser-processed surface this value decreased to 0.019-0.085 μm. The maximum height of projections and pits comprised 0.69-0.85 and 0.08-0.09 μm, respectively. Consequently, the action of laser pulses with the above parameters reduces the level of microroughness by approximately 10 times.

The thickness of the fused layer was determined by gradual removal of that layer by grinding the laser-processed specimens on an aluminum oxide plate with ongoing measurements of the critical current. Grinding was halted when the total critical current passing through the specimen returned to the value corresponding to the specimen unprocessed by the laser (decreased to its initial value). The decrease in mass caused by grinding was used to determine the thickness of the fused layer formed. For the yttrium ceramic specimens processed by a laser with pulse energy density of 1.7-2.1 J/cm$^2$, the surface layer thickness comprised 1.9-2.1 μm.

Studies of transverse sections of the laser-processed specimens with magnification up to 3000 times showed no structural changes at depths above 1-2 μm. It should be noted that in this case there is a large difference in the electron contrast of processed sections and the original structure, with the processed sections appearing brighter, indicating a change in their electrophysical characteristics. Therefore, studies were made of oblique sections of the laser-modified layer, cut at an angle of less than 1°. It was found that after processing the intermediate region between the ceramic volume and the fused layer consists of a clearly expressed continuous cellular structure, with cell dimensions several times the size of the original crystallites. We will also note that processing of the ceramic leads to a great increase in the durability of the surface with respect to mechanical abrasion.

It should be stated that in the case where there is an integral increase in the critical current through the specimen, at which the portion of the volume not recrystallized by the laser pulse switches to the normal nonsuperconducting state, all the additional current passing through the specimen at nitrogen temperature shifts into the recrystallized layer. Therefore, in calculating the critical current density it is necessary to consider the fact that the total current flows only through the volume of the surface current-carrying layer. As a consequence of this, for specimens Nos. 2-6 (see Table 1), for which there was an increase in total current after laser processing, the critical current density was calculated based on the cross section of the fused current-carrying layer with average thickness of 2 μm. As is evident from Table 1, for these specimens the critical current density in the

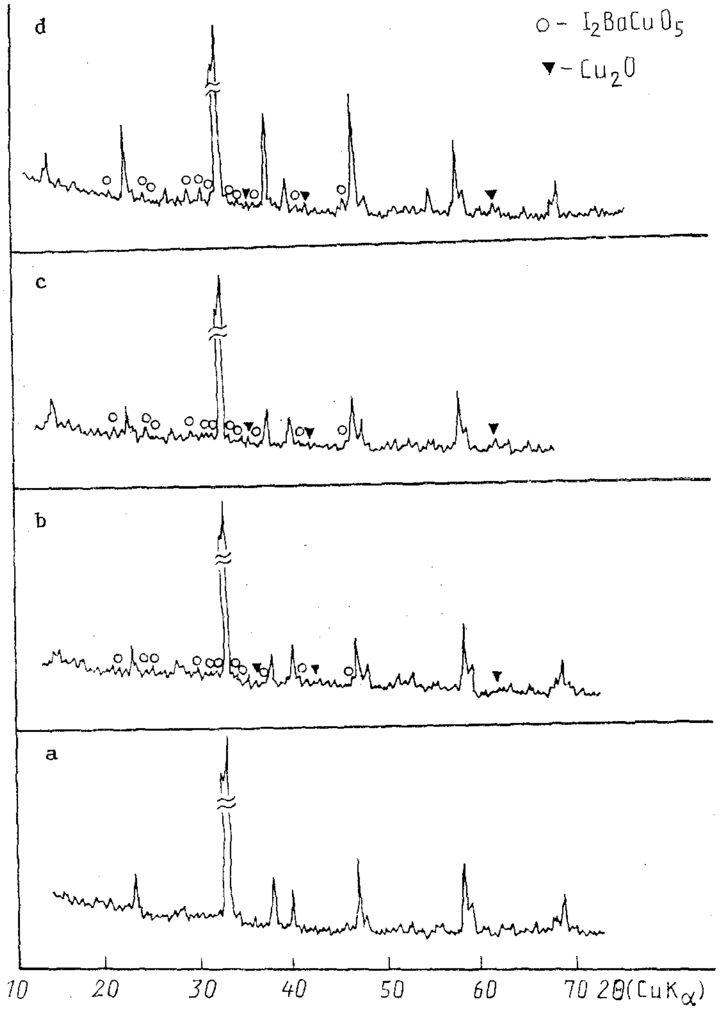

Fig. 2. Specimen roentgenograms after processing of volume ceramic by pulse with energy density of: a) 1.8 J/cm$^2$; b) 2.2; c) 2.6; d) 3.1. 2θ (CuK$_\alpha$), deg.

fused current-carrying layer lies in the range $1.8\cdot10^4$-$6.5\cdot10^4$ A/cm$^2$, which is approximately three orders of magnitude higher than the critical current density of the original volume specimens.

X-ray phase analysis was carried out on specimens in the form of tablets 10 mm in diameter, pressed at 2 kbar from the original mix, annealed under the conditions described above, and processed by laser pulses of various energy densities. Printouts obtained with a DRON-3 diffractometer using CuK$_\alpha$-radiation are shown in Fig. 2. It follows from comparison of the graphs that at a pulse energy density of 2.1 J/cm$^2$ the fused surface layer is an orthorhombic $YBa_2Cu_3O_{7-x}$ phase, showing practically no difference from the phase composition of the original volume ceramic (Fig. 2a). With increase in pulse energy density to 2.2 J/cm$^2$ new reflexes appear, characteristic of the phases $Y_2BaCuO_5$ and $Cu_2O$ (Fig. 2b), the intensity of which increases with further increase in pulse energy density (Fig. 2c, d). Consequently, for a pulse energy density above 2.1 J/cm$^2$ in the surface layer decomposition of the orthorhombic phase $YBa_2Cu_3O_{7-x}$ begins, accompanied by disappearance of the effect of increased critical current in the fused surface layer. Nor are critical current increases observed at energy densities less than 1.7 J/cm$^2$, because complete recrystallization of the surface film is not achieved at such energies.

The results obtained permit the following conclusions.

In the energy density range 1.7-2.1 J/cm$^2$ processing of a $YBa_2Cu_3O_{7-x}$ structure by a laser pulse of 50 nsec duration leads to formation of a surface layer of several μm thickness, which has an increased critical current value as compared to the original material. The layer thus created does not require subsequent saturation by oxygen. Thus, for nsec pulse processing grain fusion and rapid recrystallization of the melt are realized in the surface region of the high temperature superconductor material without change in phase composition, leading to a large increase in the number of contacts between ceramic grains, with resulting formation of a current-carrying surface layer having high critical current density values ($\sim 10^4$ A/cm$^2$) at nitrogen temperatures.

## NOTATION

$\lambda$, wavelength; $T_c$, transition temperature to superconductive state; $I_{cr}$, critical current; n, number of turns in primary winding; $J_{cr}$, critical current density; t, superconductive ring thickness; d, superconductive ring width.

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# METAL FUSION BY LASER RADIATION ACTION IN AN OXIDIZING MEDIUM

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Results are presented from a calculation of fusion of a massive zirconium plate under the action of laser radiation with consideration of simultaneous surface oxidation.

Interaction of concentrated heat fluxes with metals is found in various scientific and technological applications [1-3]. In [4, 5] the process of laser heating of a massive copper target in an oxidizing atmosphere was considered. In this situation an oxide film was formed on the irradiated metal surface, which leads to an intense change in the absorption capability of the target. In the models considered the temperatures were limited to values below the fusion point of copper [1-5]. In the present study the investigation of laser radiation interaction with a two layer oxide—metal system will be extended in temperature through the point of target fusion to the point of commencement of fusion of the zirconium dioxide layer using the example of zirconium.

The process studied can be described briefly as follows. Radiation from a $CO_2$-laser with wavelength $\lambda = 10.6$ µm and constant energy density falls on the surface of a massive metal target made of zirconium and is partially absorbed at a depth of the order of the skin layer. Since in metals the latter is much less than the laser radiation wavelength and the depth

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