EXPLOSIVE TREATMENT OF SHS END PRODUCTS (OF HIGH-TEMPERATURE SUPERCONDUCTORS)

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The problems of dynamic pressing of HTSC ceramics produced by the SHS method are considered. Curves are obtained for optimal modes of the explosive compaction of the HTSC by the scheme of a cylindrical explosive press. The effect of the amplitude of shock waves on HTSC properties is studied in the pressure range 20-500 kbar. The transition from an orthorhombic to a tetragonal phase is shown to occur at pressures over 300 kbar. Methods of producing composite materials and layered-type SHS HTSC ceramics/metal articles are developed.

As a rule, the end product of SHS processes is a porous ceramics. The practice, problems, and prospects of dynamic pressing of ceramic powders (irrespective of the method for their production) are well known [1]. Therefore, it is natural to anticipate rather good results also in an explosive treatment of a diversity of SHS materials. By way of example of this possibility of producing high-density materials, let us consider the explosive pressing of high-temperature superconductors (HTSC) synthesized by the SHS method.

Impressive achievements made in recent years in the HTSC area [2, 3] have fostered extensive investigations in all directions of the problem. In the technological aspect, the investigations proceed vigorously, following two main trends: 1) developing the economical procedures for producing the HTSC powders (the starting material) and 2) setting up the technological processes for manufacturing articles from the HTSC powders. It appears [4-6], that the SHS method is highly efficient for preparing HTSC powders (oxide ceramics) and more economical than furnace technologies. It allows the production of all HTSC known today, among them yttrium, bismuth, and thallium ceramics. In the absence of high pressures, the synthesis products are obtained in the form of brittle porous sinters and are not very convenient for practical applications. However, they can be readily ground, and the powder thus obtained can be pressed to a monolithic state using explosive-pressing methods. The explosive pressing combines in this case a shock-wave compaction of the synthesis products and a forming of articles (billets) therefrom. Benefits of the explosive pressing (no need for complicated equipment, record-breaking high pressures, etc.) are obvious. Therefore, it is not surprising that the first studies on the explosive pressing of HTSC powders, synthesized by a furnace technique, sprang up shortly after the HTSC phenomenon had been discovered [7-9]. The HTSC ceramics produced by the SHS method possesses a number of special features distinguishing it from that obtained by other means. In particular, it is fine-grained in structure (the grain size is about 1 μm) and characterized by the presence in its composition of a weakly bound oxygen, emerging from the synthesis nonequilibrium. These special features may affect the compaction process and the kinetics of phase transitions and chemical reactions proceeding on the grain surface by the action of the shock waves.

The problem solved in [10, 11] lay in producing a high-density homogeneous SHS HTSC ceramics shaped into an article of required geometry and having the necessary electrophysical properties (to suit the purpose). The HTSC homogeneity is, in this case, an essential requirement and, unless it is met, high operational characteristics of the articles are not generally attained. The problems one has to solve here are traditional for those regarding the explosive pressing of powders. Thus, for example, in manufacturing long articles from powders, the requirement that they should be homogeneous is customary. Figure 1 shows the simplest procedure of explosive pressing employed in this case. The initial powder is placed in a metal cylindrical container (a vial), which is, in turn, surrounded by a layer of the explosive. On detonation initiation, a detonation wave, slipping along the

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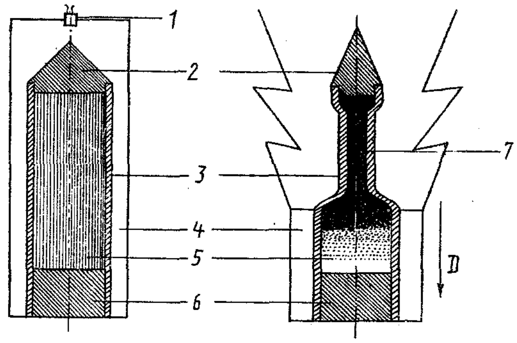

Fig. 1. Pressing of powders using a cylindrical explosive press: 1) electric detonator; 2) upper plug; 3) metal vial; 4) explosive initial powder; 6) lower plug; 7) high-density product.

cylinder generatrix, generates in the upper part of the charge. The detonation products, whose pressure amounts to tens and even thousands of kilobars, compress the container at a high rate, with the resulting formation in the powder of a powder-pressing conic shock wave, converging to the center. Obtaining a homogeneous pressed article with such a procedure of explosive pressing necessitates a regular mode of shock wave reflection in the central part of the sample. This is one of the central problems with this version of the explosive treatment of SHS products.

Fedorov and Gordopolov [10] performed experiments on the yttrium ceramics Y_{123}, synthesized using the SHS method, preground (the fraction size is smaller than 100 μm), and compacted to a density of 3.6 g/cm^3. The cylindrical explosive press sketched in Fig. 1 was used. Copper served as the vial material (some experiments also tested stainless steel). The vial diameter and wall thickness were selected such that their ratio remained constant to avoid a difference in deformation energies of the shells. Vials 15, 20, and 25 mm in diameter and with wall thicknesses of 1.5, 2, and 2.5 mm, respectively, were used. One of the basic parameters of the process is, in this case, the pressure on the front of the detonation wave, which was varied over a range of 10-100 kbar by altering the type of explosive used. As the explosive, the experiments used the ammonite 6 ZhV and its mixtures with barium niter, as well as trinitrotoluene, hexogen, and their mixtures in various proportions and of various densities. The pressure on the detonation wave front is determined by the detonation rate from the formula $P = 2.5\rho D^2$, where P is the peak pressure (kbar), ρ is the density of the explosive (g/cm^3), and D is the detonation rate (m/sec). The detonation rate was recorded in the experiments with the aid of electron sensors.

The pressure in the explosion product is not the only parameter of the process governing the quality of pressed articles. A prominent part is also played by the "loading history" of the sample (i.e., by the time dependence of the pressure when the shock and expansion waves pass through the sample); by the physicomechanical characteristics of the powder particles and by the initial porosity of the powder; by the material of which the vial is manufactured, by its wall thickness, etc. However, the peak pressure of the explosion products and the time of action of high pressures, which is indirectly characterized by the mass ratio of the explosive and compacted powder, with other conditions of this multiparametric process being unchanged, are of the greatest importance. By varying the above two parameters, we may establish the curve of optimal modes for the explosive compaction (Fig. 2a). The curve connects experimental points corresponding to the tests which realized regular modes of shock wave reflection. The region of the experimental parameters at which the sample overpressing is observed lies over the curve, and the region with the sample underpressing lies under it. Figure 2b gives the densities of homogeneous pressed samples conforming to the curve of optimal modes. As is evident from the figure, the maximal relative density of the pressed samples homogeneous over the cross section that is attainable with this experimental procedure is about 90% of the theoretical density of yttrium ceramics. The obtained samples demonstrated the Meissner effect at the liquid nitrogen temperature (77 K); however, they did not conduct the transport current without subsequent thermal treatment. The recovery of the current superconductivity necessitates post-annealing.

Another procedure of the explosive loading of yttrium SHS HTSC ceramics was undertaken in [11]. It differs from the one depicted in Fig. 1 in that a metal rod is arranged coaxially in the central part of the vial. In this case, a higher final density of the pressed samples is attained (up to 97% of the theoretical density of yttrium ceramics). With all the modes of the explosive treatment studied, the generation of the transport current in the pressed ceramics failed, whereas the recovery of the current

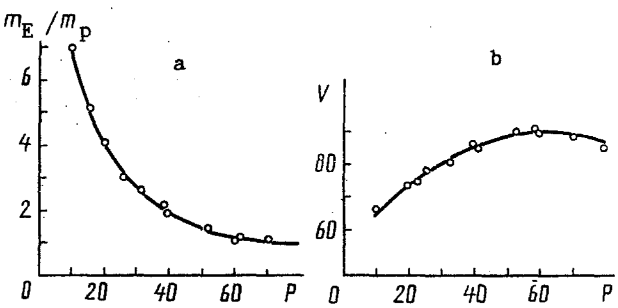

Fig. 2. Curve of optimal compaction modes for the HTSC ceramics according to the scheme of a cylindrical explosive press (a) and the corresponding densities (b) [m_e/m_p is the explosive-to-powder mass ratio, V is the relative density (in % of theoretical value); and P is the pressure, kbar].

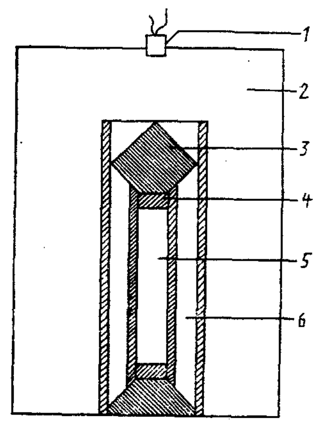

Fig. 3. HTSC pressing using a transmitting medium: 1) electric detonator; 2) explosive; 3) centering plug; 4) plug; 5) HTSC powder, 6) transmitting medium.

superconductivity called for post-annealing. To accomplish this procedure, the pressed sample was to be withdrawn from the metal shell (the deformed container). Such an operation appeared to be exceedingly arduous because the mechanical damage to the brittle ceramics was difficult to prevent during the withdrawal.

The withdrawal of the HTSC billet from the metal shell is facilitated considerably by using an explosive loading scheme illustrated in Fig. 3. In this case, the HTSC ceramics powder is placed into a thin-walled metal tube, and the loading is effected through a transmitting medium (water, oil, or glycerol). The HTSC sample is easier to remove from the thin-walled shell. Fedorov and Gordopolov [11] carried out an experimental run for exactly such a scheme. A steel vial of wall thickness 0.5 mm and diameter 25 mm, hermetically sealed by plugs at both ends, was used. The vial was positioned coaxially relative to the outer steel container of diameter 52 mm and wall thickness 2 mm, filled with water or glycerol. As the explosive, the ammonite 6ZhV and its mixtures with barium niter were used in ratios of 50/50 and 30/70, of various thicknesses. Here, the pressure was varied between 25 and 70 kbar. For the given pressing procedure, it has been possible to produce samples with a high degree of homogeneity and with a relative density of up to 90% of the theoretical density of yttrium ceramics. Experimental data on the modes of pressing of the HTSC ceramics using the above procedure are tabulated. Such a procedure is used, in particular, in fabricating electromagnetic screens. The pressed products were subjected to annealing. Samples were manufactured therefrom by a mechanical treatment for studying screening properties of the ceramics. Measurements of the screening numbers using inductive sensors revealed that their values approach theoretical.

TABLE 1. Experimental Data on Explosive Pressing of HTSC Ceramics Using a Transmitting Medium

Explosive	Charge thickness, μm	Real pressure on the front of the detonation wave, kbar	m_e/m_p, rel. units	Experimental result
Am 6ZhV	17,0	50	2,0	Underpressing
Density	22,0	60	2,8	»
0.8 g/cm^3	27,0	70	3,7	Regular mode
Am 6ZhV/Ba$(NO_3)_2$	17,0	30	2,5	Underpressing
50/50	19,5	30	3,1	Regular mode
Density	24,5	45	4,1	Overpressing
1.0 g/cm^3	29,5	60	5,3	»
Am 6ZhV/Ba$(NO_3)_2$	19,5	25	3,4	Underpressing
30/70	22,5	25	3,9	»
Density	27,0	40	5,2	Regular mode
1.1 g/cm^3	32,0	50	6,5	Overpressing

In accordance with the data of magnetometric measurements, the explosive loading is characterized by a displacement of the superconduction transition to a low-temperature region from 90-93 K at 20 kbar to 85-87 K at 250 kbar, with a transition width increasing up to 2-12 K. At pressures over 300 kbar, the orthorhombic phase converts to tetragonal. Electric measurements indicate the absence of the transport superconduction current in the temperature range above 77 K in all samples; here, the temperature dependence of the specific resistance on the temperature decreasing to 300 K is of semiconduction character. Measurements of the oxygen content using pulse reducing fusion and neutron activation analysis made it clear that the bound oxygen content of the samples treated by shock waves diminishes from 6.90 (formula units) at 20 kbar down to 6.75 at 500 kbar. The oxygen content of the HTSC ceramics is likely to alter in the shock wave front, since residual temperatures in the experiments were not higher than 250°C. To recover the superconducting properties, the samples were annealed in an atmosphere of air and oxygen. An oxygen saturation at temperatures 350-400°C over 20-40 h causes an augmentation of the oxygen content up to 6.95-6.99, an increase in T_c up to 90-95 K, and a decrease in the transition width down to 0.5-2 K (according to the data of magnetometric measurements). Electric measurements show the emergence of the transport superconduction current in the samples treated at pressures 70-300 kbar. The transport superconduction current appeared in all samples after preannealing in air at 820-850°C for 5-10 h with a subsequent saturation with oxygen at 350-400°C.

We also devised methods of producing composite materials and layered-type SHS HTSC ceramics/metal articles using tailor-made containers and various loading schemes [12]. The methods are based on the fact that the container, deformed by the explosion, transforms to a metal die serving as the protection against mechanical damage, and the HTSC layer provides the required electrophysical properties. Using these methods and schemes, we produced articles and billets from yttrium HTSC ceramics for different purposes. Typical parameters of the articles are as follows: the temperature of the transition to a superconducting state is 93-95 K; the transition width is 1.2-1.5 K; the density of the critical current amounts to $1\text{-}2 \cdot 10^3$ A/cm^3 at 77 K in the absence of the magnetic field; and the density of the HTSC ceramics is 90-97% (of the theoretical value).

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