# CRITICAL PARAMETERS AND PHASE COMPOSITION OF YBCO CERAMICS DEFORMED AT DIFFERENT TEMPERATURES

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*Tape-like samples of* HTSC *ceramics based on* YBCO *system have been obtained by flatting(pressing) at different temperatures and power parameters according to the scheme "powder in a tube". Under different deformation conditions the peculiarities of the formation of phase composition and critical parameters of the oxide ceramics both in the as-deformed and the as-sintered ( 1200 K) states. Unlike earler studies, we have used the* Al-*bronze as a hermetic shell and deformation was realized at the liquid nitrogen temperatures. As a results, pressure and temperature ranges have been found which can be successfully used for plastic deformation to obtain improved critical parameters of* HTSC-*ceramics based on 123 system. Deformation scheme and modes as well as the material of hermetic shell used have shown the work to be perspective one in view of substitution of expensive silver for the* Al-*bronze.*

**Introduction.** One of the perspective methods of obtaining tapes and wires of HTSC materials is the deformation process according to the "powder in a tube " scheme. From the point of view of technology there exist a number of difficulties when obtaining extensive tapes and wires from the oxide ceramics prossessing high critical parameters, namely:

- loss of oxygen during the plastic deformation;
- a problem of ceramics sintering and saturation with the oxygen.

The most successive was the use of the noble-metal shells, mainly silver ones, since they do not practically interact with ceramics and let oxygen go through. For Y–Ba–Cu–O system the current density reaches $10^3$ A/cm$^2$ (the MTG method) at 77 K and 0 T [1 ]. Net high $I_c$ values are related to relatively low melting temperature for silver ( ~ 960 °C ) which disables the heat treatment of yttrium ceramics at higher temperatures. Thus, search for materials suitable for protictive shell possessing more higher melting temperature as well as good plasticity, neutrality to oxygen, etc., is actual. Recently, a number of works reported on using Cu for the protective shell [2 ].

Usually, plastic deformation of HTSC ceramics is realized at the room temperature. This results in increase of $\Delta T_c$ which is due to oxygen escape from the basal plane. So, we supposed that if plastic deformation of the oxide ceramics were realized at temperatures when oxygen losses most of its mobility, than probability for oxygen conservation in ceramic structure would be essentially higher than at the room-temperature deformation.That's why we deformed the ceramics placed in air-tight shell at the liquid-nitrogen temperatures.

The use of air-tight shell is necessary for oxygen returning to its positions after sintering for the safe of stoichiometry conservation. This work gives the investigation results obtained under plastic deformation of Y–Ba–Cu–O-based HTSC ceramics in the air-tight shell made of Al-bronze at 77 and 300 K and pressures up to 1,0 GPa.

**Experimental.** The stating material was HTSC-ceramic powder of $YBa_2Cu_3O_{7-x}$ composition, the primarily size of particles being 5...10 $\mu$m ( up to 90 % of the volume). To study the interaction of ceramics' oxygen with the shell at the sintering temperature 1250 K in one case the powder was saturated with oxygen up to the mean value of the oxygen index ~ 6.77 shown by the X–ray phase analysis resulting in the formation of two superconducting phases with $T_c \simeq 92$ K and

$T_c \simeq 60$ K of the most equal volume and total SC-phase content $\sim 70\%$. In the second case the mean oxygen index was about $\sim 6.9$ which has made it possible to obtain one-phase powder with $T_c \simeq 92$ K and phase content of about 80 %.

Preparation of samples to be deformed was as follows. The HTSC-powder was placed by slight pressing into a tube whose internal coating contained the Al-bronze. Then the powder was hermetically sealed. For all the samples weight of powder was the same and equaled 0.8 g. The internal and outer diameter of the tube was 4.2 and 6 mm, respectively.

The deformation by flattening was at pressures from 0.3 to 1.0 GPa and temperatures of 77 and 300 K. The samples were studied after the deformation followed by thermal treatment at 1250 K for 1 ... 2 hours and cooling at the rate of $\sim 2$ deg/min. The superconducting characteristics were determined by both the contact-free method by measuring the diamagnetic response, and the resistive measurements. The first method was used for both the measurement of characteristic temperatures of the metal-oxide superconducting transition, and, according to early developed technique [3], the percentage of the superconducting phase of HTSC-materials. The resistive measurement, including the registration of resistance temperature dependence, critical current of samples and their current-voltage characteristics, were performed by the four-phobe technique with both d.c. and a.c. (400 Hz).

The X-ray phase analysis was performed using a diffractometer of the DRON-3 type, the microstructure of samples was studied using a NEOPHOT-32 microscope.

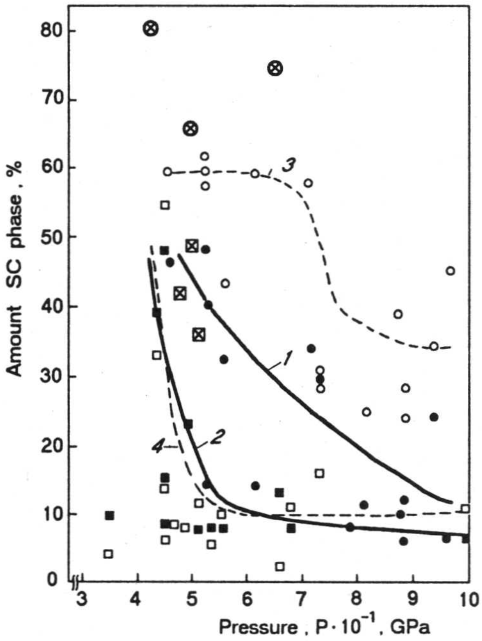

**Fig.** Influence of deformation temperature and pressure as well as $Ag_2O$ addition on phase composition of *Y*-ceramic : samples deformed at : $T$ = 77 K: ● — deformation; ○ — deformation + sintering; ⊗ — additions of $Ag_2O$ + deformation + sintering; $T$ = 300 K: ■ — deformation; □ — deformation + sintering; ⊠ — additions of $Ag_2O$ + deformation + sintering

**Results and discussion.** Figure shows the dependences of superconducting phase (SC) portion change in ceramics 123 determined by measuring the diamagnetic response in the magnetic field on plastic deformation conditions: temperature and pressure. In Fig., curves *1* and *2* show superconducting phase content in samples after 77 and 300 K deformation. As it was supposed, deforming at the nitrogen temperatures (curve *1*) in pressure range up to 1.0 GPa makes it possible to conserve a higher level of SC phase as compared to deformation under the room temperature. At the same time, it is seen that pressure level in the 0.45 ... 0.5 GPa range is favourable of conserve an essential quantity of SC phase in samples deformed both at low and room temperatures (curve *1*, *2*). However, deformation at pressures higher than 0.5 GPa and at room temperature results in sudden decrease ( > 5 times) of the superconducting phase in $YBa_2Cu_3O_{7-x}$ ceramic samples and further its content do not practically change up to pressures ~ 1.0 GPa and persists at the level ~ 9 ... 10% by conductor volume. At the same time, under the low-temperature deformation we did not observe such an abrupt fall of SC phase amount ( at $P > 0.5 \ldots 0.6$ GPa), though its content decreases, and at pressures ~ 1.0 GPa the amount of SC phase in samples after the low-temperature deforming approximately corresponds to composition of samples deformed under the room temperature.

Decrease in SC phase volume in case of samples pressed at $T = 300$ K is accompanied by smearing of the curve of transition to SC state though we did not notice an essential change of the temperature of SC transition onset ($T_c$ on) depending on pressure and temperature of deformation.

The presented results show that during deformation at various pressures the redistribution of oxygen in the basal plane of YBCO compound and its displacement, most probably, to pores of sample occur.

After the low-temperature deformation the relationship between the low- and high-temperature SC phases in the two-phase system remains unchanged in total pressure range speaking of sufficiently uniform displacement of oxygen from the volume of granules.

Usually, in case of shells which do not contain noble metals in the mode of ceramic sintering at 930 ... 950 °C for 1 ... 2 hours the oxygen processes in the shell due to oxygen of ceramics are so intensive that superconductivity either disappears or remains in slight amount.

When using the aluminium-based bronze shell we supposed that bronze would be poorly oxidized the same as aluminium, still possessing more higher strength and melting temperature.

Sintering of samples done after pressing at 77 and 300 K (Fig. curves *3* and *4*, respectively) influences the YBCO-ceramics differently. If sintering at 1250 K of samples deformed at $T = 300$ K did not practically influence the phase composition of SC ceramics, then in samples pressed at 77 K the annealing resulted in essential increase of the SC phase. Thus, at $P \sim 0.45 \ldots 0.7$ GPa ($T = 77$ K) the superconducting phase volume amounted ~ 60% corresponding to ~ 80 ... 90% of ceramics initial composition. Samples deformed at higher pressures ~ 0.8 ... 1.0 GPa and $T = 77$ K after sintering contained ~ 30 ... 40 % of SC phase, and at the same pressures but after the room-temperature deformation the SC phase content was at ~ 10% level.

Increase of the superconducting phase content in oxide superconductor indicates, firstly, that air-tightness of the shell was not damaged under the deformation and most of oxigen remained in pores of ceramics and secondly, there were no intense oxidation processes in the shell.

It is known that partial loss of oxygen can be restored by introduction of oxygen donors like $Ag_2O$ into ceramics. In Fig. the dots are plotted reflecting the volume fraction of SC phase in samples after deformation and sintering in the case, when they contained the argentum oxide in amount of 10 %. The studies confirmed the early found regularity : at the nitrogen temperatures the volume of SC phase in ceramic samples is higher than after the room-temperature deformation. The SC phase amounted values at the level of 70 ... 80% .

The study of optical microstructure of samples deformed at different pressures and temperatures has shown that pressure increase results in smaller size of separate grains, decrease of dimension of pores, i.e. a finer-grained structure is formed with relatively unform distribution of structure elements though volume of the sample. Vortex-like structures appear in the structure of deformed and sintering samples.

The results of X–ray investigation of phase composition have shown that practically all the samples are not the one-phase ones. The main phase are — 123 ($YBa_2Cu_3O_{7-x}$) and 2115 ($Y_2BaCuO_5$). Total volume of superconducting phase in the range of optimum deformation pressures (0.45 ... 0.55 GPa) equaled 90 ... 95% , the oxygen index measured up to 6.7 ... 6.9 . Texture was detected at samples deformed at pressures > 0.7 GPa. With the increase of deformation pressure the content of 123 phase decreases, another phases, apart from 2115, appear. Data on determining the phase composition and oxygen index show that the more oxygen is contained in this phase ( here we mean both tetragonal and orthorhombic modifications).

The temperature of transformation to the superconducting state measured by the resistive method was 91 ... 92 K practically for all the samples. In different samples the zero resistance was observed at 80 ... 86 K. At samples deformed under the optimal conditions the critical current density was ~ 2000 $A/cm^2$ at 4.2 K in zero magnetic field.

**Conclusion.** The obtained results have shown that the aluminium-bronze protective shell rather reliable prevents oxygen loss in the ceramics making it possible to restore the superconducting properties at ceramics sintering temperatures.

To conserve the SC phase in a large amount it is preferable to perform plastic deformation at the nitrogen temperatures (as compared to the room-temperature one). The subsequent sintering at 1250 K practically (80 ... 90% ) restores volume of the super conducting phase up to the initial one. Partial loss of oxygen can be restored by addition of respective oxygen donors ( e.g. $Ag_2O$ ).

1. *Salama K., Selvamanickam V., Gao L., and Sun K.*, Appl. Phys. Lett. 54, 2352 (1989).
2. *Sekine H., Inoue K., Maeda H., Numata K.*, J. Appl. Phys. 66, 2762 (1989).
3. *Mikheenko P., Kusovlev Yu., and Malyshev E.*, Sov. JTP 60, 104 (1990).