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Structural variations in high-temperature superconductive $YBa_2Cu_3O_{7-\delta}$ ceramic samples under high pressure–high temperature conditions

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Structural variations in $YBa_2Cu_3O_{7-\delta}$ samples treated under high pressure as a function of the technological parameters of the process (pressure, temperature, time and material with which the samples were in contact), oxygen content of the structure, and dimensions of twinning domains of the starting samples, have been investigated.

1. Introduction

The present work presents the results of an investigation of the structural variations of $YBa_2Cu_3O_{7-\delta}$ samples treated under high quasi-hydrostatic pressures (1–5 GPa) up to 1500 °C.

It is well known that $YBa_2Cu_3O_{7-\delta}$ samples, prepared by the traditional method of solid-phase synthesis, have a low density as well as a low level of mechanical properties. Using different methods of pressure treatment (hot-pressing, intermediate densification at room temperature followed by thermal annealing, hot isostatic pressing (HIPing) in an oxygen atmosphere, etc.), these characteristics can be improved. An effective method to increase density up to the theoretical one as well as the microhardness and Young's modulus, is the thermal treatment under high pressure [1, 2]. As opposed to hot pressing [3], when the pressure does not exceed 0.5 GPa, in the case of high-pressure conditions (5 GPa; when the sample is in contact with ZrO_2) the stoichiometric $YBa_2Cu_3O_7$ is preserved up to 1200 °C, i.e. oxygen does not leave the structure. This makes it possible in a comparatively short time period to produce high-density ceramics with a high level of superconductive properties and essentially improved mechanical characteristics. In addition, there is no need for further annealing for oxygen saturation of the structure, as in the case of hot pressing.

Under high pressure, the samples containing $YBa_2Cu_3O_{7+\delta}$ ($\delta > 0$) phase, superstoichiometric with respect to oxygen, were also synthesized [4].

The present work reports comprehensive studies of structural variations under high pressure–high temperature conditions. It also considers transformations in $YBa_2Cu_3O_7$ in contact with ZrO_2 or BN which are utilized as insulators.

2. Experimental procedure

The initial $YBa_2Cu_3O_{7-\delta}$ samples were produced by the traditional solid-phase synthesis. Their density was not less than 4.8 $g\,cm^{-3}$, the temperature of transition to the superconducting state, T_c, and the width of the transition interval, ΔT_c, were 93 K and 1.5–2 K, respectively.

High quasi-hydrostatic pressure (1–5 GPa) and temperature (900–1500 °C) were created in the recessed anvil-type apparatus (Fig. 1). After applying pressure, the samples were heated by direct conduction of the current through a graphite heater. The values of pressure and temperature were determined by indirect methods for which precalibration using reference points and thermocouples was performed. The accuracy of the pressure measurements in the 1–5 GPa region was ± 0.15 GPa, and that of the temperature measurements in the 900–1500 °C region was ± 20 °C. The samples were heated at a rate of about 1000 $°C\,min^{-1}$ and were cooled at a rate of about 400 $°C\,min^{-1}$. The material-insulator from the graphite heater was monoclinic ZrO_2 or hexagonal BN. For convenience, the rings and the tablets (Fig. 1) were pressed under a pressure of $P = 0.45$ GPa. The electrical resistance of the samples was determined by the four-probe method, as well as from the magnetic susceptibility measurements by the Faraday method.

Lattice parameters and phase composition were determined with the automated X-ray diffractometer (Model ADP-1) and scanning electron microscope Superprobe 733 (Jeol, Japan).

3. Results and discussion

The X-ray diffraction study shows that the thermal stability of the Y123 phase increases with compaction

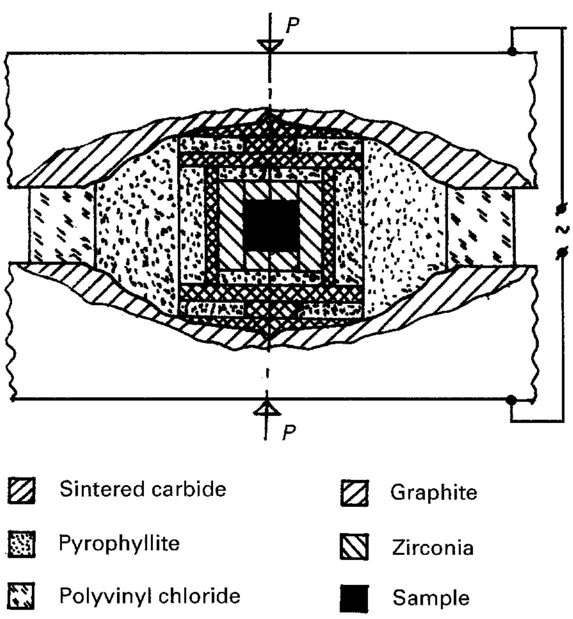

Figure 1 Schematic drawing of the recessed anvil-type high-pressure apparatus assembly.

pressure. In the case of contact of $YBa_2Cu_3O_x$ with ZrO_2 under a pressure of 1 GPa, Y123 phase decomposes even at 900 °C (holding time $\tau = 2$ h). But under a pressure of 5 GPa, the Y123 phase is present in the samples at 1470 °C ($\tau = 0.15$ h). Under a pressure of 2 GPa and temperature of 900 °C in ZrO_2, the Y123 phase remains in the stoichiometric $YBa_2Cu_3O_7$ (Fig. 2) (evidence of stoichiometric variation and decomposition to form a "green phase" beginning to appear only when $\tau \geqslant 5$ h).

When BN is used as an insulator material the picture changes essentially. When $P = 2$ GPa and $T = 900$ °C, then even with $\tau = 0.5$ h, an increase in the c-parameter up to 1.1684 nm is observed, which is conditioned by the decrease in oxygen content of the structure ($\delta = 0.12$) , and in the case when $\tau = 2$ h, a complete decomposition of the sample followed by copper oxide reduction to the metallic copper, takes place. After heating to 1200 °C under a pressure of 2 GPa for 10 min, a complete reduction of the samples to copper occurs. When $P = 5$ GPa (with the same temperature and time) at the centre of the sample the Y123 phase with $c = 1.1660$ nm ($\delta = 0$) is maintained, but on the surface of the sample, a copper layer 1–1.5 mm deep is observed.

A somewhat different characteristic of the transformations can be observed when the heating temperature of the $YBa_2Cu_3O_7$ samples (in contact with ZrO_2) under high-pressure conditions is higher than 900 °C. For these samples with fine-domain twinned structure, the size of the twinned domains is 15–30 nm. On heating the samples (fine-domain) of stoichiometric composition ($\delta = 0$) in the region 950–1470 °C ($P = 5$ GPa, $\tau = 0.15$ h), the following transformations take place: (a) oxygen enters the $YBa_2Cu_3O_7$ structure to form the non-superconductive superstoichiometric (with respect to oxygen) $YBa_2Cu_3O_{7+\delta}$ ($\delta > 0$) phase; (b) partial decomposition of the $YBa_2Cu_3O_7$ phase along the periphery of the sample. The appearance of the $YBa_2Cu_3O_{7+\delta}$ phase is evinced by the noticeable c-parameter decrease; moreover, a linear dependence of the c-parameter on temperature was observed [4]. With a certain δ value, the pseudocubic phase with $a = b = c/3$ forms.

Fig. 3 shows the structure of the above samples treated under $P = 5$ GPa, $T = 1470$ °C, $\tau = 0.15$ h in contact with ZrO_2. In the upper parts of Fig. 3a and b, a dense layer, A, 15 μm wide is easily observed which is the interaction zone with ZrO_2. The microprobe analysis shows the presence of three oxide phases in this zone (Fig. 3b): (a) the lightest formations include yttrium, zirconium, barium, copper and oxygen, (b) the darkest formations consist of zirconium, barium, copper and oxygen, and (c) the elongated grey formations are the residues of the $YBa_2Cu_3O_x$ phase.

At the interface between the surface layer, A, into which zirconium had diffused, and the bulk zone, B, of the sample, skeletal crystals of the Y_2BaCuO_5 "green phase" could be observed. In Fig. 3a these are the lightest inclusions along the A/B interface, while Fig. 3c and d show the distinct hexagonal and prismatic habits of Y_2BaCuO_5 crystals. Fig. 3c and d show micrographs of the surfaces which are perpendicular to that shown in Fig. 3a and b which were prepared by grinding away the surface layer, A, down to the Y_2BaCuO_5 crystal formation zone.

The bulk zone, B, consists of (see Fig. 3b): (a) $BaCuO_2$ (the darkest formations in the figure), (b) Y123 phase with the oxygen in excess, (the grey prevailing phase in the figure), the formations having an elongated form, and (c) the oxide phase with the approximate ratio Y:Ba:Cu:O = 3:2:1:X (the lightest inclusions in the grey phase). Thus, under a high pressure, the non-standard decomposition of Y123 phase occurs because under normal pressure the Y123 phase decomposes to form $BaCuO_2$, Y_2BaCuO_5 and CuO. ZrO_2, which is in contact with the sample, is the most likely oxygen source for the $YBa_2Cu_3O_{7+\delta}$ ($\delta > 0$) phase formation under a high pressure. However, the fact that when Y123 phase decomposes, oxygen is also liberated, must be taken into consideration.

When the treatment temperature was increased to 1500 °C ($P = 5$ GPa, $\tau = 0.15$ h) the Y123 phase was not observed in the samples.

Starting samples, which were assumed to have a coarse-domain twinned structure (1–2 μm) behaved differently than samples with a fine-domain structure under the same conditions. Therefore, under a pressure of 5 GPa ($\tau = 0.15$ h) the starting samples with the coarse-domain structure remained monophasic ($YBa_2Cu_3O_7$) even after heating up to 1200 °C, as was revealed by X-ray analysis. The difference in the behaviour between coarse- and fine-domain starting samples may be explained by the fact that a phase with finer twinned domains, because of the larger area of the interdomain boundaries, absorbs oxygen more intensively. The twinned (1 1 0) and (1 $\bar{1}$ 0) boundaries are the region of the Y123 crystal where oxygen can most probably be fixed to form the stable octahedral polyhedron CuO_6. The dimensions of the twinned domains of the starting samples are influenced by the synthesis conditions, and iron and copper impurities. Usually, the sizes of the domains decrease with increasing temperature. This may offer an explanation for both

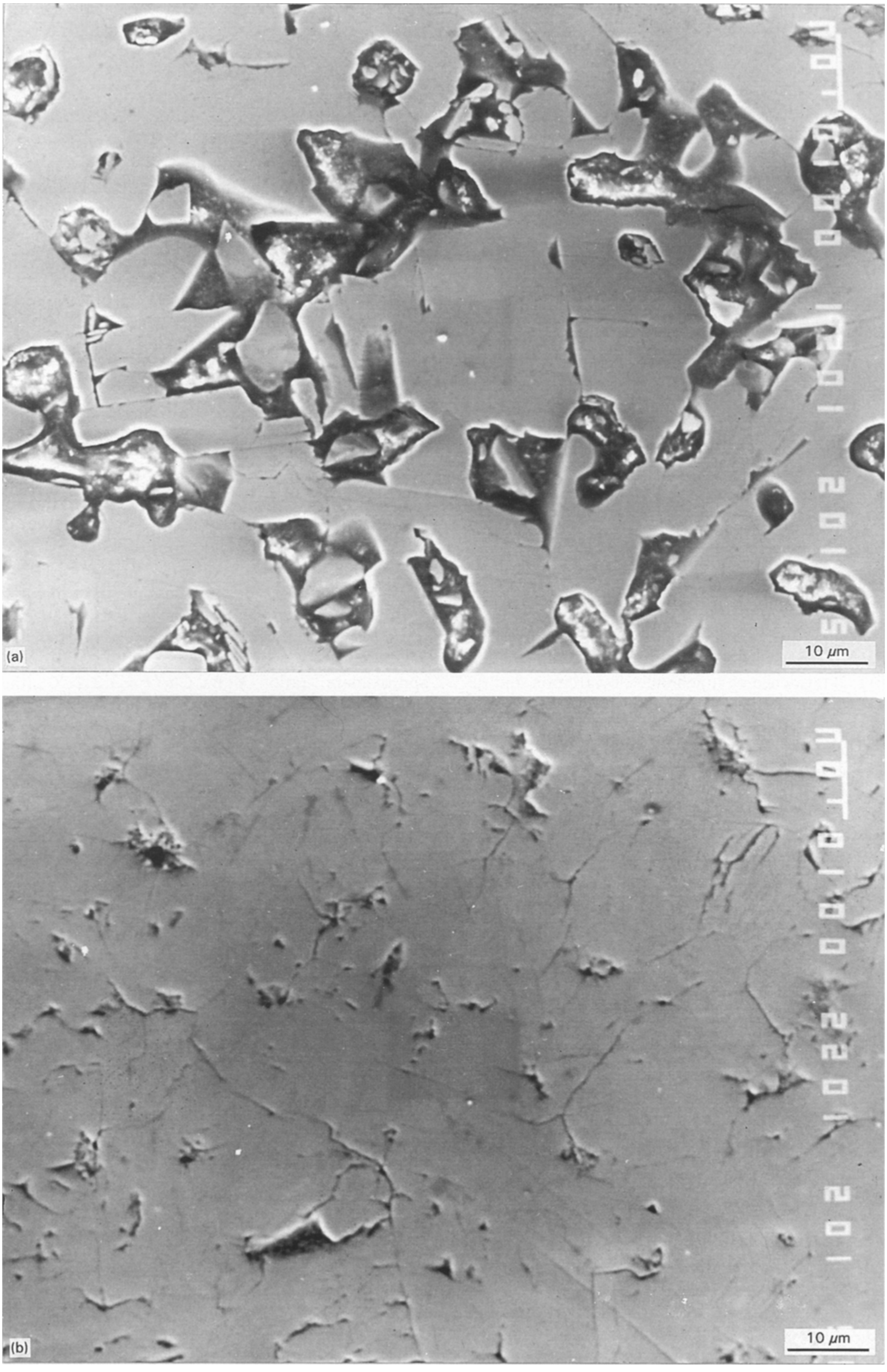

Figure 2 Y123 sample structure: (a) before treatment; (b) after treatment ($P = 2$ GPa, $T = 900\,^{\circ}\mathrm{C}$, $\tau = 0.5$ h, in contact with ZrO_2). The results of the X-ray and microprobe analyses confirm that only the $YBa_2Cu_3O_7$ phase is present in the samples before and after treatment.

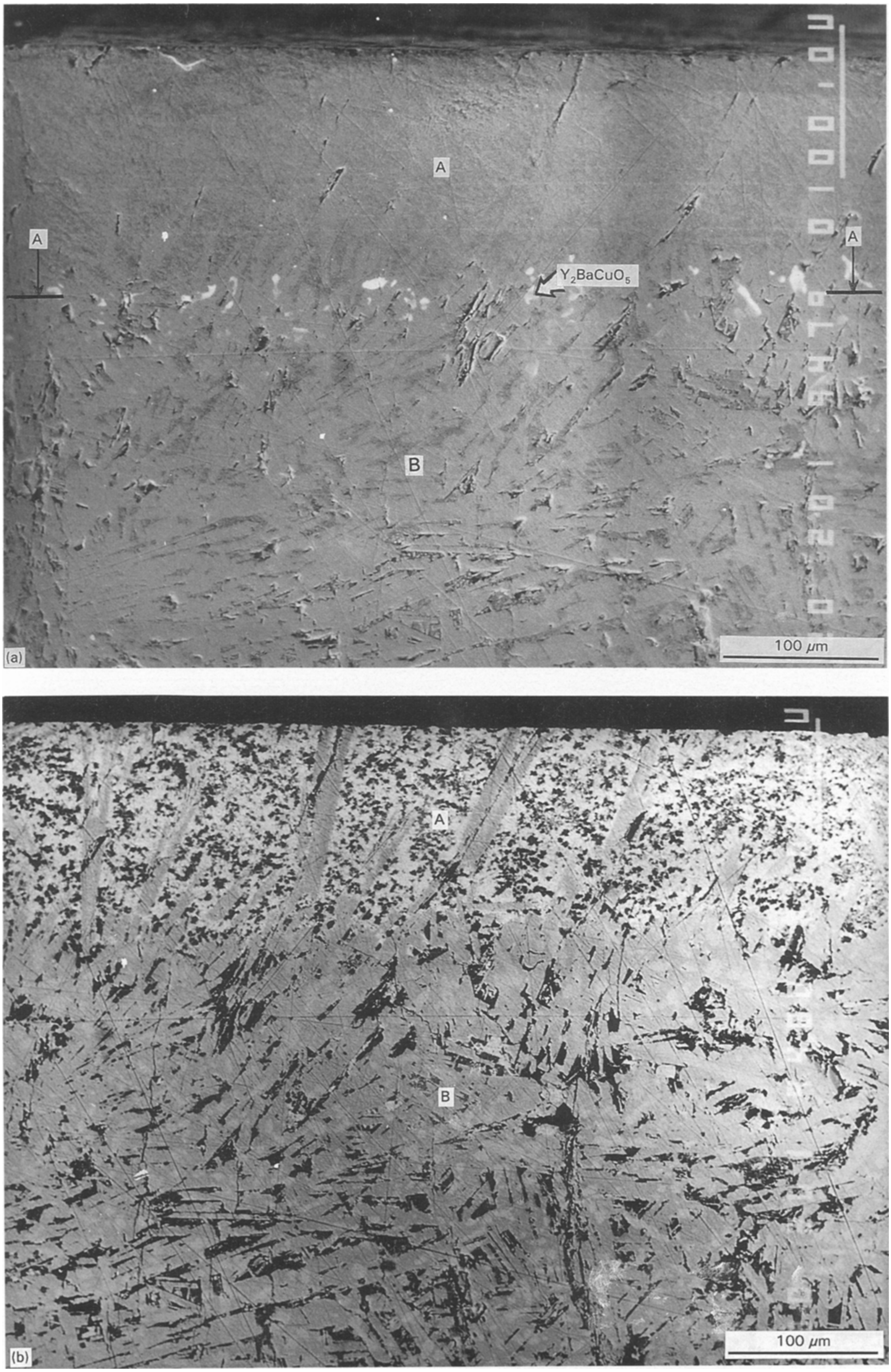

Figure 3 The structure of Y123 samples after treatment at $P = 5$ GPa, $T = 1470\,°\mathrm{C}$, $\tau = 0.15$ h in contact with ZrO_2. (a) secondary electron image (SEI); (b) COMPO (composition; the difference in lightness is caused by the middle atomic weight of the phase (Z)); (c) view from A–A (SEI), the peripheral part of the sample; (d) view from A–A (SEI), the central part of the sample.

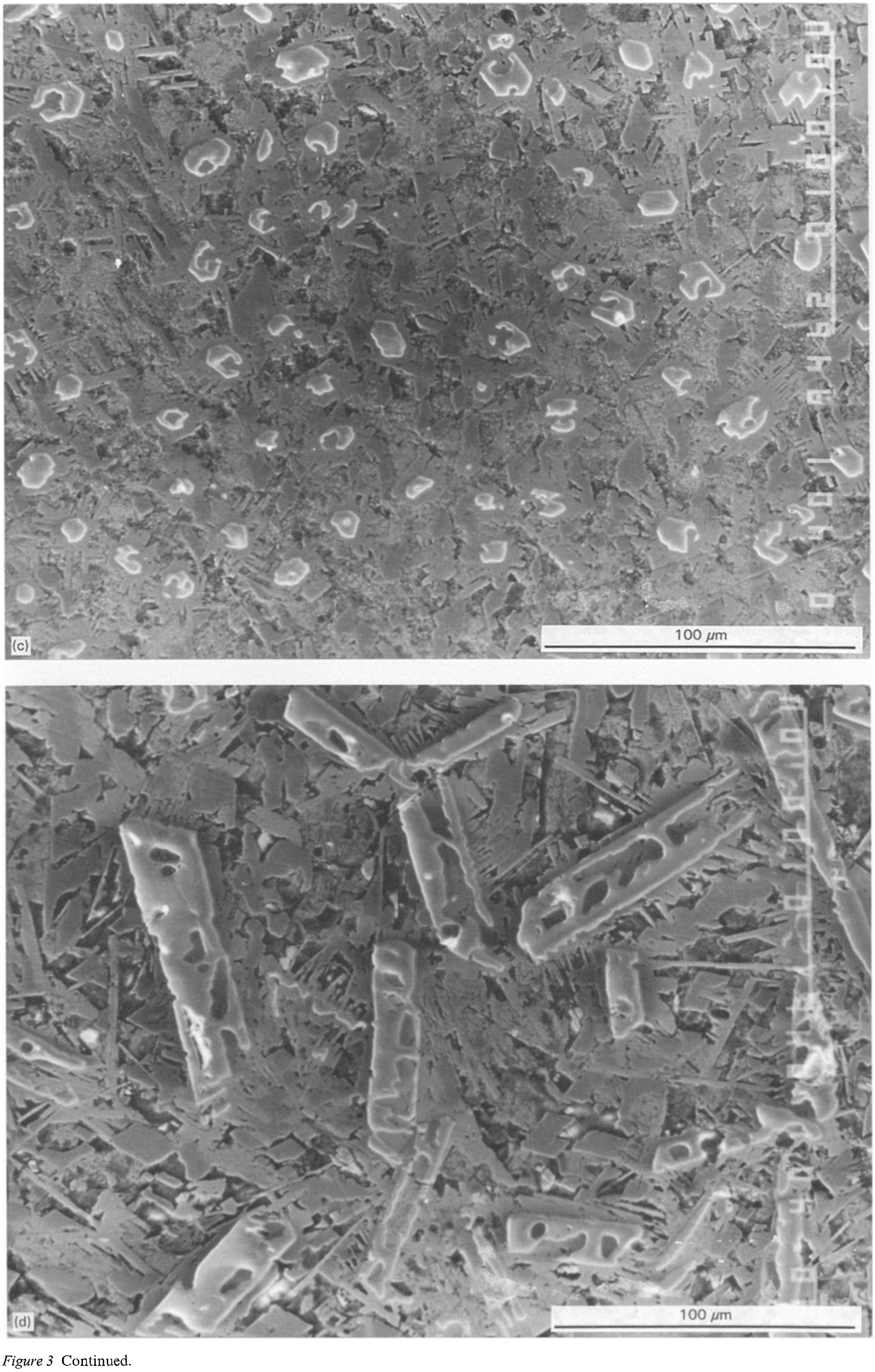

Figure 3 Continued.

TABLE I Transition temperatures into the superconductive state and oxygen deficiency of the treated samples

Sample	Treatment conditions			Transition temperature into the superconductive state, (K) based on measurements				Oxygen deficiency, δ		References
	P (GPa)	T (°C)	τ (h)	Resistive		Magnetic		Before treatment	After treatment	
				T_{c_1}	T_{c_2}	T_{c_1}	T_{c_2}			
1	2	900	0.15	92	88	107	99	0.0	0	[1]
2	2	900	2.00	93	91	90	75	0.0	0	[1]
3	5	1000	0.50	92	91	90	89	0.0	0	[2]
4	5	1200	0.15	90	5	90	65	0.0	0	[2]
5	5	1200	0.50	No transition		90	55	0.0	0	[2]
6	2	900	0.50	93	81	–	–	0.2	0	[2]
7	5	1000	0.50	93	86	–	–	0.2	0	[2]
8	5	1200	0.15	No transition		–	–	0.2	0	[2]
9	5	1200	0.50	No transition		–	–	0.2	0	[2]

the increase in the oxygen content of the samples with increasing synthesis temperature and the formation of a superstoichiometric phase with respect to oxygen.

The process of phase formation under a high pressure is also essentially influenced by the oxygen content of the starting samples. Thus, when $\delta = 0.2$, the decomposition processes proceed more intensively, than in samples with $\delta = 0$. At first, the samples with $\delta = 0.2$ (when in contact with ZrO_2, $T = 900\,°C$, $P = 2$–5 GPa, $\tau = 0.5$ h) are saturated with oxygen up to the stoichiometry $\delta = 0$, which is indicated by the c-lattice parameter decrease from 1.1693 nm to 1.1666 nm. On increasing the holding time up to $\tau = 1.5$–2 h (under $P = 2$ GPa, $T = 900\,°C$), the decomposition of the Y123 phase was observed to form $YBa_2Cu_4O_x$ (Y124), Y_2BaCuO_5, etc. An increase in pressure up to 5 GPa ($\tau = 2$ h, $T = 900\,°C$) results in maintaining the $YBa_2Cu_3O_7$ stoichiometry of the main phase, but such samples contain some impurities. When starting samples with $\delta = 0$ were used, after high-pressure treatment under the present conditions, no impurities were found in the samples (according to the X-ray analysis data).

We suppose that the samples do not become uniformly saturated with oxygen. This, to a greater extent, holds true for samples with $\delta = 0.2$ but not with $\delta = 0$. The non-uniform saturation results in a high local oxygen concentration as well as in the coexistence of phases with various δ. When the oxygen concentration exceeds 8 (by one formula unit), the Y123 phase appears to be unstable.

The starting samples Y123 with $\delta = 0$ and 0.2 with the coarse-domain structures after treatment at 5 GPa in contact with ZrO_2, remain in or acquire, the $YBa_2Cu_3O_7$ stoichiometry, even when they are heated up to 1200 °C. However, the superconducting properties vary both with δ of the starting samples and the treatment temperature, which is supported by the results of T_c measurements (see Table I). The increasing width of the temperature interval of the transition into the superconductive state of sample N 4, and the absence of the resistive superconducting transition of sample N 5, can be explained by the formation of a structural layer of $a_p 2^{1/2} = 0.56$ nm width (a_p is the parameter of a primitive perovskite cell) at the domain boundaries, which corresponds in composition to the superstoichiometric $YBa_2Cu_3O_{7+\delta}$ ($\delta > 0$) phase. This phase is not superconductive and it is not possible to determine its presence by standard methods of X-ray analysis. $YBa_2Cu_3O_{7+\delta}$ phase formation is associated with the local increase of oxygen concentration when it diffuses into the sample. The increase in the width of the superconductive transition interval of the samples produced from the starting samples with $\delta = 0.2$ (sample 7) in comparison with samples with $\delta = 0$ (sample 3), as well as the absence of superconductive transition in sample 8, whereas superconductive transition exists in sample 4 (samples 3 and 7, 4 and 8 were treated under similar conditions), can be explained by the presence of a large quantity of the decomposition phases, because the saturation of the starting samples ($\delta = 0.2$) with oxygen proceeds more irregularly and therefore is more intensive.

4. Conclusions

1. Changes in both structural characteristics and properties of Y123 ceramic samples depend on the pressure, treatment temperature, holding time, type of material which is in contact with the sample, starting oxygen content, and, probably, on the dimensions of the twinned domains.

2. The process of Y123 sample decomposition during heating to temperatures above 1000 °C under a high pressure proceeds differently from under normal pressure.

3. The $YBa_2Cu_3O_7$ stoichiometry and orthorhombic structure are stable on heating to 1200 °C (under 5 GPa). On heating to 1000 °C under 5 GPa, the transition temperature into the superconductive state can be 92 K with $\Delta T_c = 1$ K. The treated samples essentially surpass the starting one in density as well as in mechanical characteristics.

References

1. T. A. PRIKHNA, V. S. MELNIKOV, V.E. MOSHCHIL *et al.*, *Sov. J. Supercond.* **5** (1992) 666.
2. T. A. PRIKHNA, V. S. MELNIKOV, V.E. MOSHCHIL *et al.*, *Sov. J. Superhard Mater.*, to be published.
3. M. SIMON and A. C. D. CHAKLADER, *J. Canad. Ceram. Soc.* **58** (1) (1989) 52.
4. T. A. PRIKHNA, V. S. MELNIKOV, V. E. MOSHCHIL *et al.*, *Fiz. Tekh. Vysokikh Davlenii* 1 (1) (1991) 84 (in Russian).

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