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Plasma-enhanced fluorination of $YBa_2Cu_3O_{7-\delta}$ ceramics

Part I *Improvement of the superconducting properties*

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The radiofrequency plasma technique involving mixtures of $CF_4 + O_2$ gases has been applied to the surface treatment of high T_c superconducting oxides ($YBa_2Cu_3O_{7-\delta}$). Investigation of the various experimental parameters of the process has shown that the improvement of the critical current density, J_c, mainly depends on the inlet precursor composition $CF_4 + \tau\%O_2$, on the total pressure and on the reaction time. The presence of fluorine in the bulk of the ceramics has been observed from electron microprobe analysis, together with an increase of the "Cu^{3+}" content. The plasma-enhanced fluorination (PEF) treatment improves the superconducting properties of the materials: both values of the resistivity in the normal state and of the superconducting transition width are reduced and the critical transition temperature is improved by about 1 K.

1. Introduction

The discovery of high-temperature superconductors (HTSC) such as $YBa_2Cu_3O_{7-\delta}$(YBCO) has led to unprecedented activities, mainly because of the possible use of these materials for significant technological advancements. Unfortunately, the use of bulk HTSC has been hindered by their relatively low capacity for carrying high densities of electrical current, which is caused by a number of serious material problems such as grain-boundary weak links. Several processes have already been proposed to increase the critical current density, J_c. Melt-texturing of HTSC ceramics has been especially investigated using either a thermal gradient [1], a magnetic field [2] or a mechanical strain [3]. Other processes have been successfully developed to improve the intergranular properties, e.g. silver-doping or fluorination of $YBa_2Cu_3O_{7-\delta}$ ceramics.

It has been previously shown that a fluorination treatment by fluorine gas contributed to remove impurities from grain boundaries [4], and to protect the material against moist air [5]; in addition, the critical current density, J_c, was increased. Unfortunately, this process affords little industrial adaptibility due to drastic safety conditions.

On the other hand, plasma technologies are widely employed in etching [6] and polymerization [7] processes in microelectronics, especially using fluorocarbons precursors. Therefore, an original method, i.e. the radiofrequency plasma-enhanced fluorination (PEF) process can be substituted for the traditional fluorine gas fluorination treatment. This paper is devoted to the description of the PEF method and to the investigation of the influence of the various experimental parameters on the superconducting properties of the treated materials. Both fluorine-gas and PEF treatment mechanisms will be discussed in Part II, through detailed angle-resolved X-ray photoelectron spectroscopic analyses.

2. Experimental procedure

2.1. Description of the plasma equipment

The experiments were carried out in a S.E. 80 Barrel-Plasma Technology System. The apparatus is schematically shown in Fig. 1. The plasma, obtained from a $CF_4 + \tau\%O_2$ ($0 \leqslant \tau \leqslant 50$) mixture, was excited by a radiofrequency (r.f.) source at 13.56 MHz. The reactor consisted of two aluminium barrel electrodes which were coated with alumina (Al_2O_3). The inner electrode on which the sample was placed was connected to the r.f. source and the outer one was grounded. A primary vacuum was obtained by a 40 $m^3 h^{-1}$ Edwards E2M40-type pump equipped with a liquid-nitrogen condenser which trapped the residual gases.

The gas mixture was introduced in the upper part of the reactor and then dissociated by electron impacts occurring between the two electrodes. Neutral species and radicals diffused from this plasma zone to the centre of the reactor where they reacted with the

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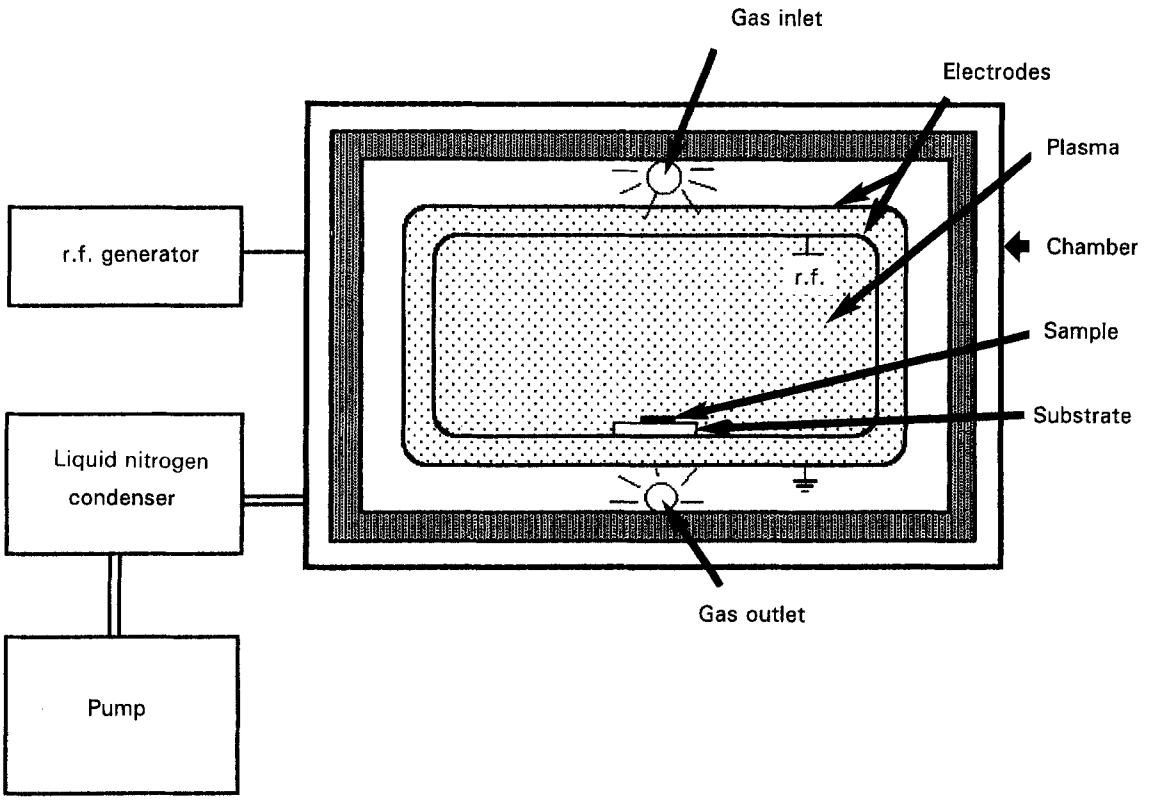

Figure 1 Schematic view of the plasma apparatus.

$YBa_2Cu_3O_{7-\delta}$ ceramics. In addition the barrel chamber was fitted with a thermostatically controlled heating jacket and a temperature lower than 100 °C was maintained during the PEF process. Several experimental parameters could be adjusted from this system: the inlet precursor composition $CF_4 + \tau\%O_2$ ($0 \leqslant \tau \leqslant 50$); the total pressure, p; the CF_4 gas flow, Q_{CF_4}; the time of the treatment, t; and the r.f. power, P, up to 300 W.

2.2. Preparation of $YBa_2Cu_3O_{7-\delta}$ ceramics

The starting material was a stoichiometric 1:2:3 powder from Rhône–Poulenc Co. containing few residual carbonated species; the mean grain size was around 2 μm. The powder was pressed to pellets of $2 \times 2 \times 12\ mm^3$ dimension. These were heated to 920 °C for 2 h under an oxygen flow and slowly cooled under oxygen to achieve the optimum oxidation and to hinder the formation of cracks. A microstructural and compositional characterization of these ceramics obtained by solid-state sintering was primarily required to clarify the influence of the PEF treatment on the superconducting properties. From the observations by scanning electron microscopy, the $YBa_2Cu_3O_{7-\delta}$ ceramics consisted of homogeneous grains of around 3 μm diameter and of an interconnected porosity with a compacity of about 0.88 (Fig. 2). However, an amorphous layer at the gas/solid interface was observed by transmission electron microscopy which could be probably ascribed to the presence of $(CO_3)^{2-}$ species [8]. On the other hand, no intergranular phase was observed at the grain boundaries.

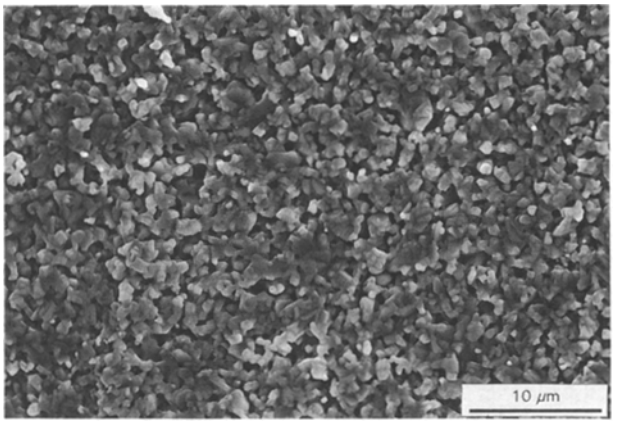

Figure 2 Typical microstructure of an $YBa_2Cu_3O_{7-\delta}$ ceramic obtained by solid state sintering at 920 °C.

2.3. Characterization techniques

After PEF treatments, the ceramics were systematically characterized using various techniques:

(i) electron microprobe analysis (EMPA) on polished fractures of pellets by a Camebax-type equipment in order to evaluate the profile and the amount of fluorine inside the ceramics. Standard samples were $YBa_2Cu_3O_7$ and BaF_2 crystals;

(ii) chemical analysis of the oxidation state of copper in the bulk pellet by Mohr-salt titration in order to obtain the mean deviation, δ, from the 1:2:3 stoichiometry in the compound $YBa_2Cu_3O_{7-\delta}$ [9];

(iii) a.c. susceptibility measurement to evaluate the critical current density, $J_{c(a.c.)}$. The temperature dependence of $J_{c(a.c.)}$ was plotted from this measurement, the $J_{c(a.c.)}$ values being deduced from the Bean

model [10]. The applied magnetic field amplitudes ranged from 0.1–10 Oe, and the used frequency was 333 Hz. The temperature dependence of the a.c. susceptibility of a superconducting ceramic generally showed two steps in both real part and imaginary part. The one for $T < 89$ K, corresponds to the intergranular contribution and the other one, for $89 < T < 91$ K, to the intragranular contribution. However in the imaginary part, no peak was observed in the higher temperature range, because of a too small size of grains. Therefore, these curves furnished mainly information on the intergranular contribution (Fig. 3).

3. Influence of PEF experimental parameters on the superconducting properties of $YBa_2Cu_3O_{7-\delta}$ ceramics

The different parameters which can be adjusted during the PEF experiments are reviewed, and their influence on the superconducting properties of the materials after treatment is discussed here. The optimization of the experimental conditions has been achieved to get best critical current densities.

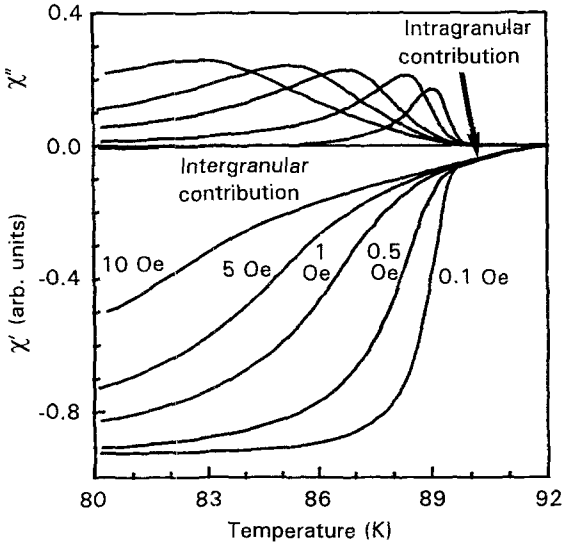

Figure 3 Temperature dependence of a.c. susceptibility of an $YBa_2Cu_3O_{7-\delta}$ ceramic obtained by solid state sintering at 920 °C.

3.1. Loading effect

It is first necessary to take into account the loading effect, which is related to the number and the area of samples which are simultaneously treated during one experiment [11]. This phenomenon has been clearly observed in the case of pellets with an area of about 80 mm^2 exposed to the plasma; the $J_{c(a.c.)}$ values actually depend strongly on the number of samples which are treated in a same batch, as shown in Fig. 4.

The mean amount of fluorine contained in the treated sample has been evaluated by EMPA. This amount decreases with increasing number of samples because of the increasing rate of consumption of fluorine with respect to the rate of supply (Fig. 4b). In fact, this loading effect can be explained simply: as the number of simultaneously treated samples increases, the partial pressure of active species (atomic fluorine) per surface unit decreases and so decreases the fluorine content of the ceramics. Therefore, the plasma treatment was realized for a short duration time ($t = 30$ min) on only one $YBa_2Cu_3O_{7-\delta}$ pellet with a constant area (1 cm^2) corresponding to a constant loading effect.

3.2. Influence of the inlet precursor composition

We have been primarily interested in the influence of addition of oxygen to the CF_4 precursor, because these mixtures have been proved to be most efficient in plasma etching processes. Plumb and Ryan [12] have developed a kinetic model which describes the main chemical reactions occurring in a CF_4 plasma containing different percentages of oxygen. According to

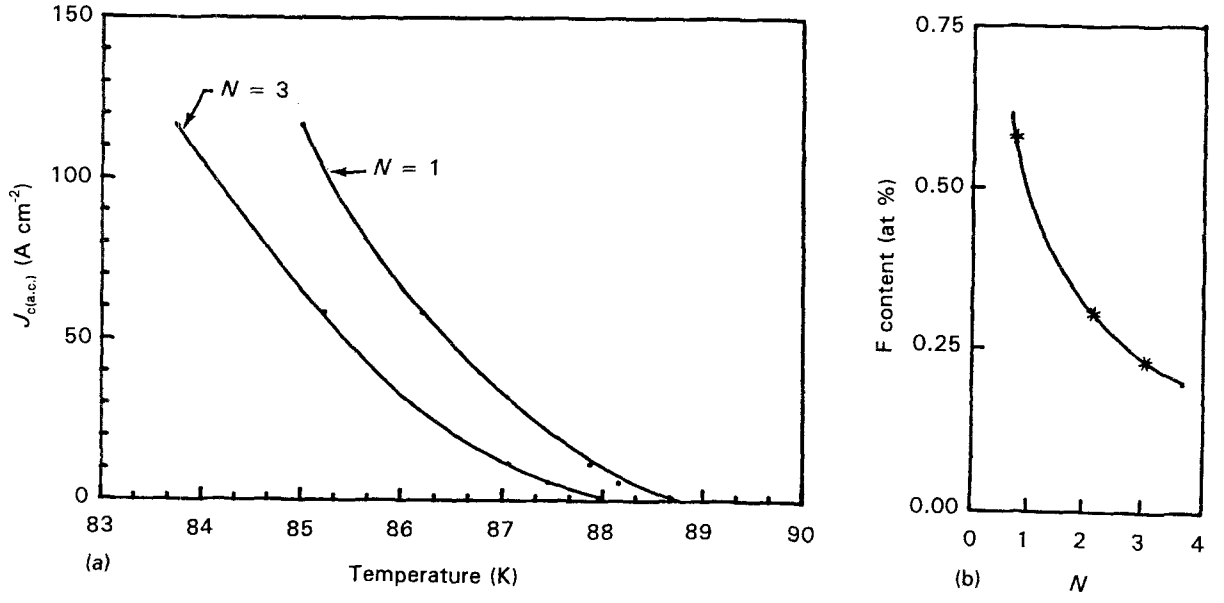

Figure 4 Influence of the loading effect for N samples: (a) on the temperature dependence of $J_{c(a.c.)}$; (b) on the fluorine content (at %) of the sample (experimental conditions: CF_4 + 25% O_2, $Q_{CF_4} = 15.4$ $cm^3 s^{-1}$; $P = 100$ W; $p = 56$ mtorr, $t = 30$ min).

these authors, when adding oxygen to a CF_4 plasma, additional radical reactions occur, which yield the formation of atomic fluorine

$$CF_3 + O \rightarrow COF_2 + F \quad (1)$$

$$CF_2 + O \rightarrow COF + F \quad (2)$$

$$CF_2 + O \rightarrow CO + F_2 \quad (3)$$

$$COF + O \rightarrow CO_2 + F \quad (4)$$

The amounts of atomic fluorine and oxygen which are formed inside $CF_4 + O_2$ plasmas have been evaluated using actinometric optical emission spectroscopy [13, 14]. Inside the plasma, the fluorine content reaches a maximum value for an addition of 25%–30% O_2 to CF_4, as seen in Fig. 5.

The analytical data corresponding to different gas mixtures are given in Table I. The mean amount of fluorine has been obtained from EMPA on the polished fractures of treated pellets and the "Cu^{3+}" content of bulk samples has been deduced from Mohr-salt titration.

As shown in Table I, the fluorine content of treated ceramics reaches a maximum value for an addition of 25% O_2 to the CF_4 plasma, which corresponds to the maximum amount of atomic fluorine present in the plasma. This result can be easily understood considering the Knudsen flux of atomic fluorine, ϕ_F, given by the relation

$$\phi_F = \frac{N_F}{4}(8kT/\pi m)^{1/2} \quad (5)$$

in which N_F is the atomic fluorine density, and kT is the thermal energy. If N_F is increased inside the plasma, then ϕ_F and, consequently, the fluorine content of the $YBa_2Cu_3O_{7-\delta}$ ceramic are improved, as shown in Table I. On the other hand, although the "Cu^{3+}" content also increases when the sample is treated in a pure CF_4 plasma the corresponding amount is not as large as that obtained after the addition of oxygen.

Concerning the influence of the addition of oxygen to a CF_4 plasma on the critical current density, we have observed that the most efficient result also corresponds to a CF_4 + 25% O_2 mixture, as shown in Fig. 6.

In the absence of oxygen (i.e. in pure CF_4 plasma), or for higher oxygen contents (CF_4 + 50% O_2 plasma), the optimal efficiency of the treatment is not reached, which would imply that atomic fluorine is the active species during the PEF process and may be responsible for the oxidation of the $YBa_2Cu_3O_{7-\delta}$ ceramics.

3.3. Influence of the total pressure

The total pressure inside the reactor may vary over the 50–400 mtorr range. We have observed that an increase of the pressure is disadvantageous to the temperature dependence of $J_{c(a.c.)}$ as seen in Fig. 7. Simultaneously, the fluorine content inside the treated

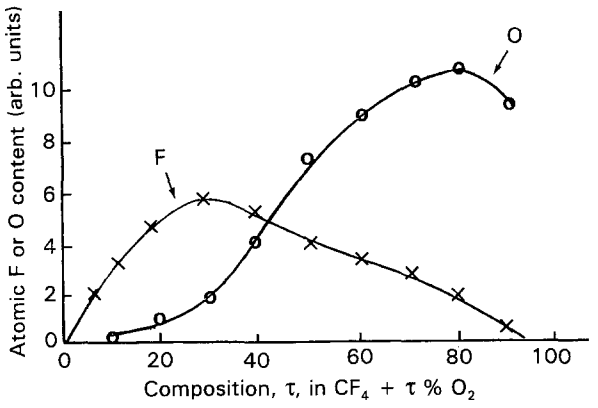

Figure 5 Influence of addition of oxygen to a CF_4 plasma on the atomic fluorine and oxygen contents.

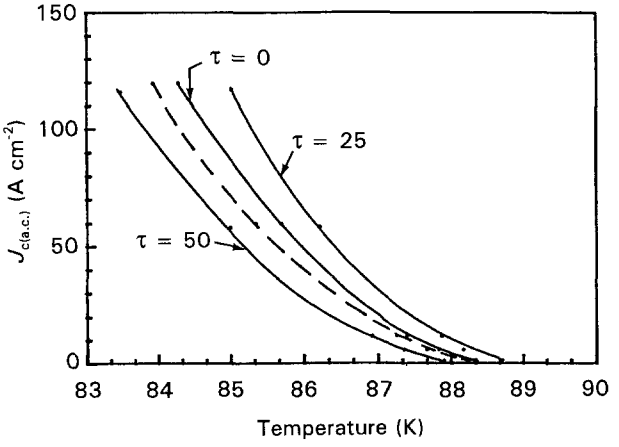

Figure 6 Influence of addition of oxygen to CF_4 precursor on the temperature dependence of $J_{c(a.c.)}$ (experimental conditions: $Q_{CF_4} = 15.4\ cm^3\ s^{-1}$, $P = 100$ W, $p = 70$ mtorr, $t = 30$ min, (---) untreated).

TABLE I Fluorine and "Cu^{3+}" contents of samples treated in different $CF_4 + O_2$ plasmas (experimental conditions: $Q_{CF_4} = 15.4\ cm^3\ s^{-1}$; $P = 100$ W; $p = 70$ mtorr; $t = 30$ min)

	$YBa_2Cu_3O_{7-\delta}$ ceramic			
	Untreated	Pure CF_4 treated	CF_4 + 25% O_2 treated	CF_4 + 50% O_2 treated
Fluorine content (at %)	0	0.27	0.50	0.26
F mol (per YBCO mol)	0	0.035	0.065	0.034
"Cu^{3+}" mol (per YBCO mol)	0.42	0.50	0.60	0.54

$YBa_2Cu_3O_{7-\delta}$ ceramic decreases as the total pressure is increased, as shown in Table II.

This result can be explained by a decrease of the production factor of atomic fluorine, P_F, inside the plasma. P_F depends on the electron density, n_e, on the neutral species density, N_o, and on the rate coefficient for dissociation, k_d, by the following relation

$$P_F = n_e N_o k_d \quad (6)$$

which can be alternatively written

$$P_F = n_e N_o \int_{\varepsilon_0}^{\infty} \left(\frac{2\varepsilon}{m}\right)^{1/2} \sigma_d(\varepsilon) f_e(\varepsilon) d\varepsilon \quad (7)$$

where m is the electron mass, σ_d the cross-section for dissociation, ε the electron energy, and $f_e(\varepsilon)$ the electron energy distribution function [15]. k_d, N_o and n_e depend on the total pressure. As the pressure is increased, n_e and k_d drop, as schematically shown in Fig. 8. Consequently, P_F(Eqn. 6) decreases as the pressure is increased. The subsequent reduction of the flow rate, ϕ_F, according to Equation 5, results in a decrease of the fluorine content inside the $YBa_2Cu_3O_{7-\delta}$ ceramics.

3.4. Influence of the inlet gas flow, Q_{CF_4}

The inlet gas flow, Q_{CF_4}, injected into the reactor may vary over the 15–125 $cm^3 s^{-1}$ range. We have not observed any noticeable change of temperature dependence of $J_{c(a.c.)}$ when the flow is increased (Fig. 9). Similarly, the fluorine content inside the $YBa_2Cu_3O_{7-\delta}$ ceramic is not affected by an increase of the flow as shown in Table III.

This result can be explained by a compensation effect between the increase of the flow and the increase of the total pressure inside the reactor. In the case of a diffusing flow, the neutral species density, N_o, depends on the inlet gas flow of CF_4 by the following reaction [16, 17]

$$Q_{CF_4} = N_o\left(k_d n_e + \frac{1}{t_r}\right)V \quad (8)$$

where k_d is the rate coefficient for dissociation, t_r the residence time, and V the volume of the reactor. Although the production factor of atomic fluorine (P_F) should increase with the inlet flow of CF_4(Q_{CF_4}), the consequent increase of the total pressure (see Section 3.3) compensates this effect.

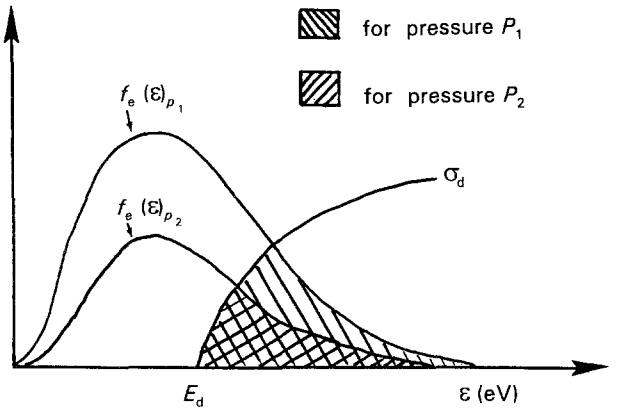

Figure 8 Schematized distributions showing the influence of the total pressure on the collision probability ($p_2 > p_1$).

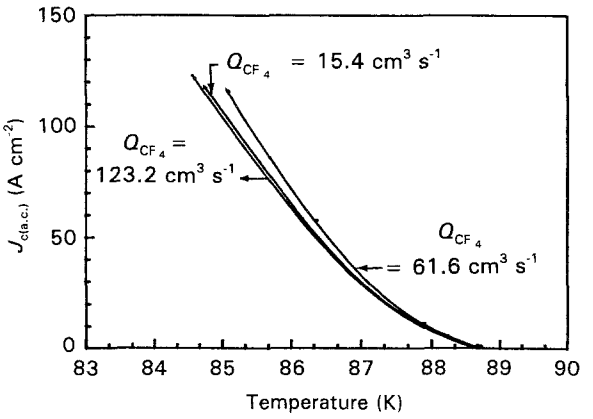

Figure 9 Influence of the inlet flow Q_{CF_4} on the temperature dependence of $J_{c(a.c.)}$ (experimental conditions: $CF_4 + 25\%O_2$, P = 100 W, t = 30 min, the total pressure depending on the inlet flow Q_{CF_4}).

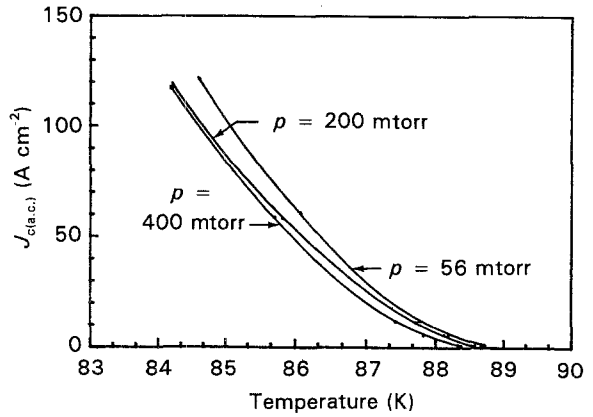

Figure 7 Influence of total pressure on the temperature dependence of $J_{c(a.c.)}$ (experimental conditions: $CF_4 + 25\%O_2$, Q_{CF_4} = 15.4 $cm^3 s^{-1}$, P = 100 W, t = 30 min).

TABLE II Influence of the total pressure on the fluorine content of $YBa_2Cu_3O_{7-\delta}$ ceramics

	Total pressure (mtorr)		
	56	200	400
Fluorine content (at %)	0.44	0.27	0.27
F mol (per YBCO mol)	0.057	0.035	0.035

3.5. Influence of the reaction time

The PEF treatment time also affects the temperature dependence of $J_{c(a.c.)}$ (Fig. 10). For reaction times up to 60 min, $J_{c(a.c.)}$ values are strongly improved by the plasma treatment. On the other hand, these values are reduced for reaction times above 60 min and the fluorine content inside the $YBa_2Cu_3O_{7-\delta}$ ceramic decreases simultaneously (Table IV).

It has been shown that the temperature of the sample increases during the experiment (up to about 100 °C). From Table IV, it appears that the higher the temperature, the lower is the fluorine content inside

TABLE III Dependence of the fluorine content on the inlet gas flow

	Inlet flow, Q_{CF_4} ($cm^3 s^{-1}$)		
	15.4	61.6	123.2
Total pressure (mtorr)	56	225	415
Fluorine content (at %)	0.44	0.50	0.38

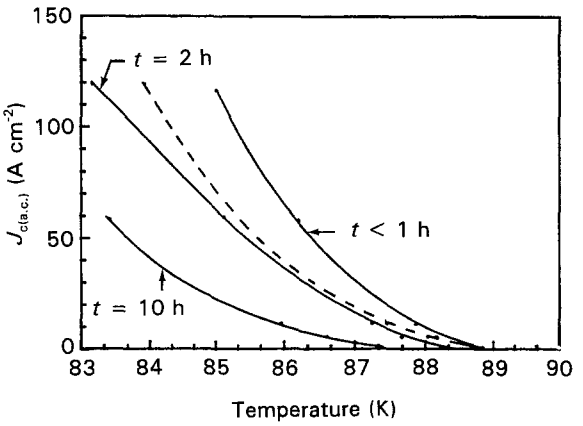

Figure 10 Influence of the reaction time on $J_{c(a.c.)}$ of $YBa_2Cu_3O_{7-\delta}$ ceramics (experimental conditions: $CF_4 + 25\%O_2$, $Q_{CF_4} = 15.4\ cm^3\ s^{-1}$, $P = 100$ W, $p = 56$ mtorr, (- - -) untreated).

TABLE IV Dependence of the fluorine content on the PEF reaction time

	PEF reaction time (h)				
	0.25	0.5	1	2	10
Fluorine content (at %)	0.38	0.44	0.42	0.35	0.13
F mol (per YBCO mol)	0.049	0.057	0.054	0.045	0.017

the $YBa_2Cu_3O_{7-\delta}$ ceramic. This peculiar behaviour which corresponds to an apparently negative activation energy has been observed because the overall kinetics could be regulated by the adsorption-desorption equilibrium of the active species. This process, which is usually exothermic, can become the bottleneck of the reaction at higher temperature [18]. However, another assumption can be proposed: when adding oxygen to CF_4, a radical reaction occurs which yields the formation of CO_2 (see Section 3.2). These species could alter the $YBa_2Cu_3O_{7-\delta}$ ceramic at the surface of the grains and consequently could limit the formation of fluorine species with a corresponding decrease of $J_{c(a.c.)}$ values.

3.6. Influence of the radio frequency power

We have not detected any change of the temperature dependence of $J_{c(a.c.)}$ on the power of the generator in the 50–300 W range, which would imply that the fluorination is limited by surface reactions.

4. Superconducting properties of PEF-treated $YBa_2Cu_3O_{7-\delta}$ ceramics

Taking into account the concluding results of the previous sections, the following optimized conditions can be established for one sample of 1 cm^2 external surface: inlet precursor composition, $CF_4 + 25\%\ O_2$; inlet CF_4 gas flow, $Q_{CF_4} \sim 60\ cm^3\ s^{-1}$; total pressure, $p = 225$ mtorr; reaction time, $t = 30$ min; r.f. power, $50 \leqslant P \leqslant 300$ W. These conditions correspond to the best $J_{c(a.c.)}$ values obtained for PEF-treated $YBa_2Cu_3O_{7-\delta}$ ceramics as shown in Fig. 11. The improvement of the superconducting properties is also supported by the temperature dependence of the electrical resistivity (Fig. 12).

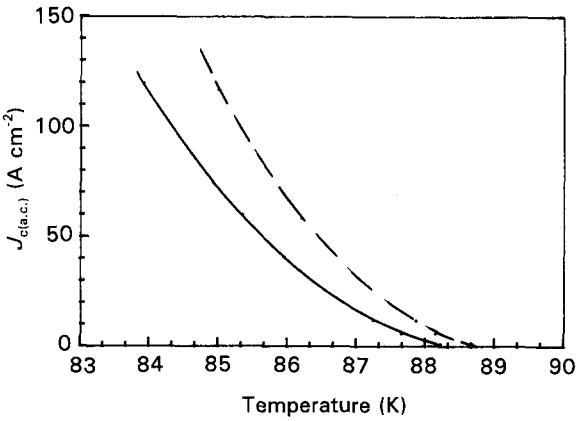

Figure 11 Temperature dependence of $J_{c(a.c.)}$ of a $YBa_2Cu_3O_{7-\delta}$ ceramic (——) before and (- - -) after plasma treatment under optimized conditions.

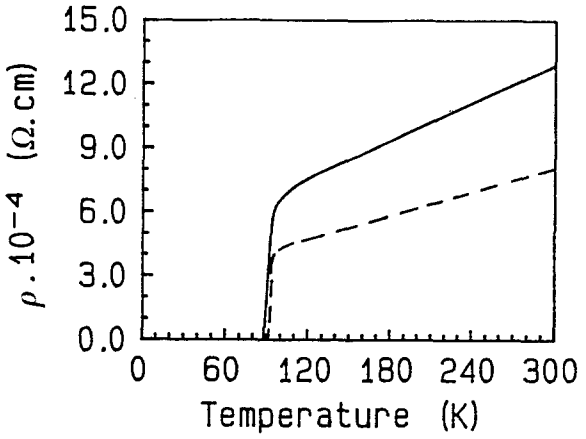

Figure 12 Temperature dependence of resistivity of $YBa_2Cu_3O_{7-\delta}$ ceramics (——) before and (- - -) after plasma treatment under optimized conditions.

TABLE V Comparison of the superconducting characteristics of YBCO ceramics before and after the plasma treatment

	Before plasma treatment	After plasma treatment
ΔT_c(K)	3.6	2.1
ρ_{o300K}(Ω cm)	13×10^{-4}	8×10^{-4}
T_c(K)	90.8	92

From Table V, it is clear that the PEF treatment reduces both the value of the resistivity in the normal state and the transition width, ΔT_c, and simultaneously improves the critical transition temperature by about 1 K.

Finally the improvement of the critical current density of a PEF-treated $YBa_2Cu_3O_{7-\delta}$ ceramic has been confirmed by a direct method involving pulsed currents under 2 $\mu V\,cm^{-1}$. The J_c value obtained by this method can be compared with that of a fluorine-gas treated $YBa_2Cu_3O_{7-\delta}$ ceramic: J_c (direct method at 77 K), 375 $A\,cm^{-2}$ (for untreated sample), 420 $A\,cm^{-2}$ (for fluorine-gas treatment), 480 $A\,cm^{-2}$ (for optimized PEF treatment).

5. Conclusion

We had previously shown that the superconducting properties of an $YBa_2Cu_3O_{7-\delta}$ ceramic could be improved by a fluorine-gas treatment. In the present work, we have succeeded in gaining an additional improvement through a new technique: the r.f. plasma-enhanced fluorination (PEF) treatment. An average fluorine content of 0.5 at % has been detected by EMPA, in the bulk of the $YBa_2Cu_3O_{7-\delta}$ ceramics. On the other hand, both "Cu^{3+}" content and the critical temperature are simultaneously improved. The atomic fluorine produced inside the fluorinated plasma is probably the species responsible for the oxidation of the material. The influence of the various experimental parameters has been systematically investigated. From these results we can conclude that the improvement of $J_{c(a.c.)}$ depends mainly on the three parameters: inlet precursor composition $CF_4 + \tau\% O_2$; total pressure; reaction time. The improvement of the critical current density of an $YBa_2Cu_3O_{7-\delta}$ ceramic by the PEF treatment has been confirmed by a direct pulsed method.

It seems preferable to relate the optimal superconducting properties to a certain Cu^{3+} content rather than to a particular O/F ratio, because a gradient of fluorine content is observed between the surface of the grains and their inner part (see Part II of this work). Before treatment, the oxygen content of the ceramics has been shown by Mohr-salt titrations to be around 6.75 [9]. The effect of PEF would correspond to an increase of the anion rate up to 6.83, which is the content required for optimized superconducting properties (T_c and J_c) [9].

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