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Abnormal oxidation behavior of $YBa_2Cu_3O_{7-\delta}$ ceramics

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Abstract The influence of sample thickness and cooling rate on the oxidation kinetics of dense small grain $YBa_2Cu_3O_{7-\delta}$ ceramics is presented. The oxidation behavior is strongly dependent on the phase type exhibited by the material. At high temperature, in the tetragonal phase, the oxygen stoichiometry of the ceramic core is dependent on the diffusion length and isothermal treatments improve the overall. Value increase in the sample thickness decreases the oxygen content. At low temperature, in the orthorhombic phase, the oxidation during cooling becomes very fast and the sample thickness is not observed to be a limiting parameter. An ultrasonic determination of Young's modulus as a function of temperature shows that this behavior cannot be related to the formation of microcracks. The improvement in oxidation observed in this temperature range is considered as characteristic of a very fast diffusion of oxygen along the grain boundaries, which is enhanced below the tetragonal to orthorhombic transition by the stresses resulting from anisotropic thermal contraction.

Introduction

The relation between oxygen stoichiometry, the tetragonal to orthorhombic transition and the superconducting properties of $YBa_2Cu_3O_{7-\delta}$ is well established [1, 2]. In equilibrium conditions, the variations of oxygen stoichiometry with temperature and oxygen partial pressure reported for powder and single crystals are in good agreement [3–6]. The best superconducting properties are observed for orthorhombic material with a low value of *d*, and consequently the ceramic preparation process generally involves an oxidation step.

The slow oxidation kinetics observed during isothermal treatment of ceramics with open porosity (5–15%) is usually considered as a consequence of the sample thickness or of the presence of intergranular phase [7] or residual carbon [8]. Some authors [9, 10] observed a very fast oxidation during cooling of ceramics with little open porosity (0–7%) and grains smaller than 1 μm, a size for which microcracks are supposed not to be formed [11–13]. This behavior suggests that oxidation of $YBa_2Cu_3O_{7-\delta}$ ceramics could be enhanced in non-isothermal conditions. The purpose of the present work is to follow the respective influences of cooling rate and sample thickness on the oxidation kinetics of $YBa_2Cu_3O_{7-\delta}$ ceramics with small grains and controlled impurity content.

Experimental

Ceramic preparation

Ceramics were prepared from a $YBa_2Cu_3O_{7-\delta}$ Rhône-Poulenc powder (NBK-25) (YBaCuO) with a $YBa_{2.01}Cu_{3.03}$ cation composition. Uniaxially pressed pellets (green relative density = 0.55) were sintered in flowing air at 895 °C for 12 h. Heating and cooling rates were 3 °C min^{-1}. The relative density of the as sintered cylinders, with 10.36 or 21 mm diameter, was 0.86 ± 0.015. The average grain size

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was between 1 µm and 2 µm. The thickness of the sintered samples was in the range 0.70–2.10 mm. The carbon content of the ceramics, evaluated using a previously described method [14], was less than 490 ppm for all samples.

Thermogravimetric study of the ceramic oxidation kinetics during cooling

The variation of YBaCuO sample mass versus temperature was studied using a SETARAM B85 thermogravimetric apparatus. The total pressure of the oxygen atmosphere surrounding the sample was $2{\cdot}10^4$ Pa. The oxygen flow was constant and equal to 0.1 L min^{-1}. In such conditions the mass was measured with a precision of ±1 µg.

The characteristics of the studied samples were the following:

- A-sample : ceramic with 2.05 mm thickness, 10.36 mm diameter and 937 mg mass;
- B-sample : ceramic with 1.23 mm thickness, 10.36 mm diameter and 570 mg mass;
- C-sample : ceramic with 0.70 mm thickness, 10.36 mm diameter and 317 mg mass;
- D-sample : 146 mg of an agglomerated powder obtained by grinding of a B ceramic.

Each sample, placed in an alumina vessel, was heated at 3 °C min^{-1} up to 885 °C and maintained for 6 h at this temperature. The corresponding mass, m_{885}, practically time independent ($\Delta m/m_{885}$ = 1.2 10^{-5} h^{-1}), was taken as a reference. Mass changes, due to oxygen uptake, were then recorded during cooling at different rates.

Ultrasonic characterization of Young's modulus change during heat treatment

In equilibrium conditions, the tetragonal to orthorhombic phase transition occurs at 670 °C for $p_{\text{O}_2} = 2 \cdot 10^4$ Pa [15]. During cooling from 885 down to 300 °C, whatever the temperature at which such a transition occurs, the anisotropic variation of lattice parameters and thermal expansion coefficients a_a, a_b, and a_c may lead to microcracks [16].

The representative macroscopic value of Young's modulus for a ceramic material is very sensitive to microstructural changes, such as the phase transformation or microcrack formation [17]. An ultrasonic pulse-echo technique was used to follow its evolution during heat treatment in flowing oxygen. Experiments were performed on rectangular bars (21 × 1.48 × 2.07 mm^3) cut from the 21 mm diameter cylinders. Continuous ultrasonic measurements were made using a 260 kHz transducer during the thermal cycle, which corresponded to heating at 3 °C min^{-1} from 25 up to 885 °C, followed by a 6 h hold and cooling down to 450 °C at 3 °C min^{-1}. Ultrasonic pulses were transmitted to samples by tungsten and alumina wave guides to protect the transducer [18]. The experimental situation refers to the ''long bar'' mode for which Young's modulus, E, is given by

$$E = \rho V_\text{L}^2$$

where ρ is the bar density (≈ 5,600 kg m^{-3} at the end of the treatment) and V_L the ultrasonic wave velocity.

Oxygen uptake during cooling

Influence of cooling rate

Evolution of the relative masses of C-ceramic and D-powder observed during cooling from 885 down to 300 °C at 1 and 3 °C min^{-1} is reported in Fig. 1. The oxidation kinetics of the powder are practically the same for both cooling rates (Fig. 1b). For the thinnest ceramic (e = 0.70 mm), the sample mass depends on the cooling rate (Fig. 1a); between 670 °C and 450 °C, a higher average oxygen content is obtained with the slowest cooling rate. Below 450 °C, the oxygen deficit acts as an oxidation accelerator ; at 300 °C, the oxygen content is slightly higher for ceramic cooled with the fastest rate.

In an attempt to improve the oxidation of thick ceramics, some cooling treatments at 3 °C min^{-1} were interrupted by successive holds at 640 °C for 10 h, 510 °C for 10 h and 400 °C for 8 h. Figure 2 shows the influence of these intermediate isothermal treatments on the mass change of a thick A ceramic. Between 640 °C and 400 °C, the average oxygen content is really enhanced when the cooling is interrupted by successive holds. The behavior observed at lower temperature is unusual; the sample cooled without any intermediate holds exhibits the highest oxygen uptake.

Influence of sample thickness

Mass changes of A, B, C ceramics and D powder were studied, in an oxygen pressure of $2{\cdot}10^4$ Pa, during a treatment corresponding to a cooling from 885 °C to 300 °C at 3 °C min^{-1}. The respective thickness of A, B and C ceramics were 2.05, 1.23, and 0.70 mm. The evolution of the average oxygen content, $7 - \delta$, versus temperature is reported in Fig. 3 for the four samples. The $7 - \delta$ value used as a reference for $p_{\text{O}_2} = 2 \cdot 10^4$ Pa and T = 885 °C is 6.27 [4]. The average oxygen content is higher for powder than for ceramics. The oxygen uptake observed for the powder cooled at 3 °C min^{-1} is not far from what would be obtained in equilibrium conditions.

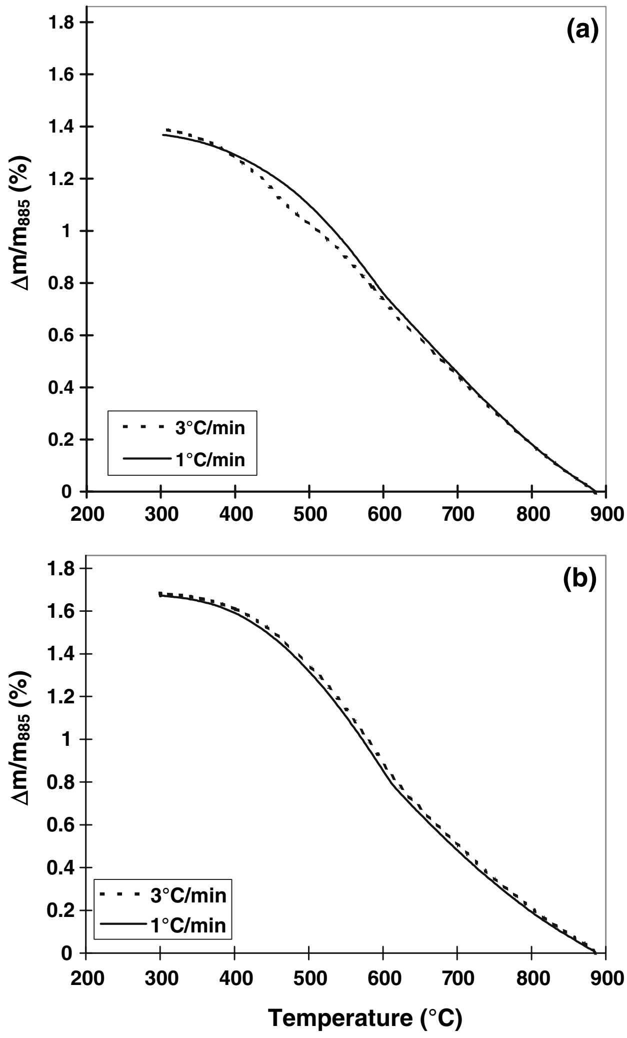

Fig. 1 Influence of cooling rate on the evolution of the relative mass of C-ceramic (**a**) and D-powder (**b**) during cooling at 1 and 3 °C min^{-1}. $p_{O_2} = 2 \cdot 10^4$ Pa

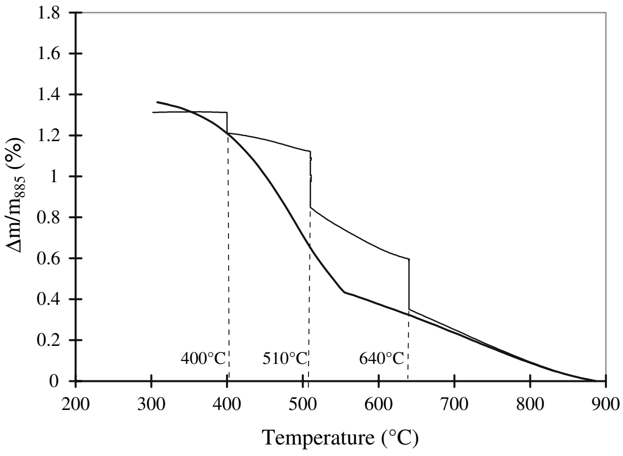

Fig. 2 Influence of intermediate holds at 640, 510 and 400 °C during cooling at 3 °C min^{-1} on the evolution of the relative mass of a A ceramic (e = 2.05 mm). $p_{O_2} = 2 \cdot 10^4$ Pa

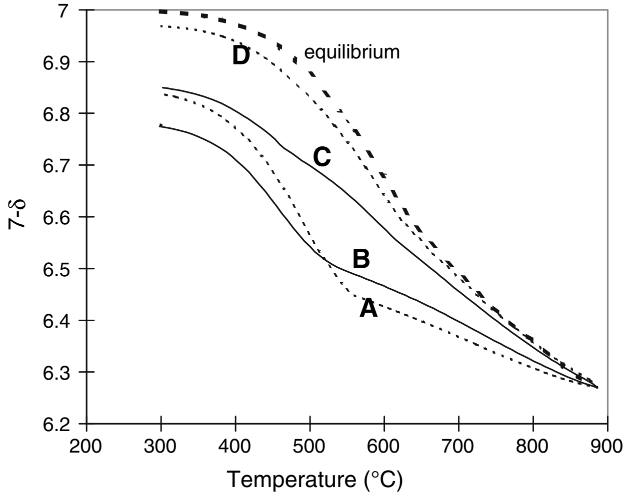

Fig. 3 Evolution of the average oxygen stoichiometry of A, B, C ceramics and D powder during cooling at 3 °C min^{-1} in an oxygen pressure of $2{\cdot}10^4$ Pa

The influence of ceramic thickness on the oxygen uptake during cooling depends on temperature range (Fig. 3). For $T \geq 550$ °C; the oxygen uptake is slower when the sample are thick. For $T < 500$ °C, the behavior is different ; the oxidation rate increases with the samples thickness. The difference between the average oxygen content of thick (A) and thin (C) ceramics decreases strongly with temperature.

Evolution of Young's modulus

The influence of temperature on Young's modulus of an YBaCuO bar heated and cooled at 3 °C min^{-1} in oxygen is presented in Fig. 4. The strong increase of Young's modulus observed between 655 °C and 570 °C during cooling has been previously reported an explained as characteristic of a progressive tetragonal to orthorhombic phase transition [17]. The evolution observed below 570 °C can be

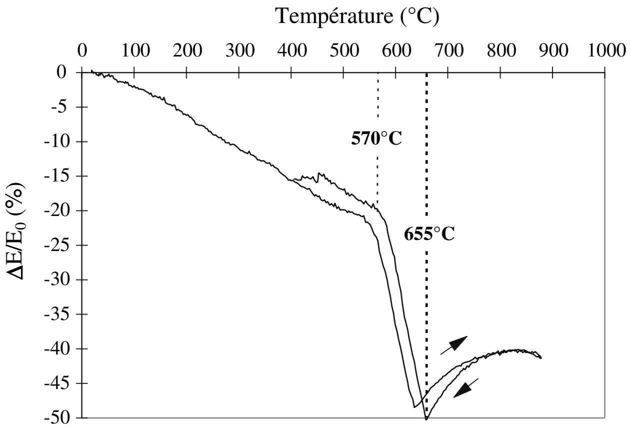

Fig. 4 Evolution of the Young's modulus of an YBaCuO ceramic during heat treatment in oxygen

associated with the stiffening of the solid due to thermal contraction and to a progressive oxidation of the orthorhombic phase during cooling at 3 °C min^{-1} [17]. Below 640 °C, Young's modulus values are slightly higher during cooling. As the ceramic was previously sintered and cooled in air, this can be explained by an increase in oxygen content of the sample during cooling compared to the heating cycle.

Discussion

Oxidation behavior of YBaCuO ceramics

At each temperature, the yield, Y, of the oxidation during cooling performed after a 6 h hold at 885 °C can be expressed by $Y = (x_{\mathrm{exp}}(T) - 6.27)/(x_{\mathrm{equ}}(T) - 6.27)$, where x_{exp} and x_{equ} are the $7 - \delta$ values at T, respectively, in the experimental conditions and in the equilibrium state [4]. The evolution of Y during cooling at 3 °C min^{-1}, versus temperature, is presented in Fig. 5 for the four samples.

For powder D, the diffusion path length is of the order of the grain size and the oxidation yield Y is always between 0.9 and 1. The behavior of the ceramic samples is more complex. Above 670 °C, which is the tetragonal to orthorhombic transition temperature in $p_{\mathrm{O}_2} = 2 \cdot 10^4$ Pa [16]), Y is practically temperature independent for the thick A (2.05 mm) and B (1.23 mm) samples. Below 670 °C, Y decreases until a temperature $T(Y_{\mathrm{min}})$ is achieved. $T(Y_{\mathrm{min}})$ equals 555, 520 and 480 °C, respectively, for the 2.05, 1.23 and 0.70 mm thick samples and hence decreases for the thinner samples. The progressive phase transition detected between 655 °C and 570 °C during the Young's modulus measurements in pure oxygen of a 1.48 mm thick ceramic suggests that the behavior observed in this temperature range is associated with a progressive tetragonal to orthorhombic transformation. For T lower than $T(Y_{\mathrm{min}})$, Y increases with the sample thickness and hence with a larger difference from the equilibrium composition.

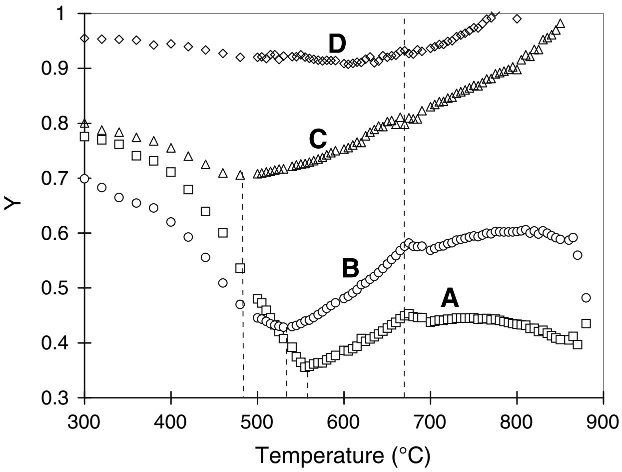

Fig. 5 Oxidation yield, Y, versus temperature for different samples cooled at 3 °C min^{-1} from 885 °C ($p_{\mathrm{O}_2} = 2 \cdot 10^4$ Pa)

When the tetragonal phase is stable, at temperature above 670 °C, the evolution of the average oxygen content of the ceramics during cooling, at a constant rate, is characteristic of an oxidation process controlled by diffusion from the surface of the sample to its core. At a given temperature, thick ceramic samples have a longer diffusion path and hence the average $7 - \delta$ value is decreased. The increase of the oxidation rate with the sample thickness, observed between $T(Y_{\mathrm{min}})$ and 380 °C, could be associated with a bulk oxygen chemical diffusion coefficient, D, which becomes significantly higher for the orthorhombic form of YBaCuO than for the tetragonal one. This would then allow the oxygen deficient regions to rapidly absorb a part of the missing oxygen. Such an effect would be enhanced for the thickest samples which present higher deficits. Results reported in literature [19–21] do not indicate such a diffusion coefficient change. At the phase transition, only a weak modification in D is observed, the sign of which depends on the authors.

Influence of the phase change on oxygen transfer in YBaCuO ceramics

The results of resistivity measurements [13, 22–23] performed during cooling have lead authors to consider that the oxidation of the ceramic with small orthorhombic grains may occur in two steps corresponding, respectively, to a very fast oxidation of the grain periphery and to a slower diffusion of oxygen inside the grains. Such a conclusion would imply that a fast oxygen transfer from the surrounding atmosphere towards the core of the sample, via the grain interfaces, can exist in orthorhombic YBaCuO ceramics.

Taking into account the value of bulk diffusion coefficient, D, given in the literature for orthorhombic YBaCuO [19–21, 24], it is possible to calculate the evolution with time, t, of the average oxygen content, $x = 7 - \delta$, of a spherical grain of radius, r, using the following equation [25]:

$$\frac{x(T,t) - x_s(T)}{x_s(T) - x_0(T,t)} = 2x \sum_n (-1)^n \exp\left(-D(T)\pi^2 n^2 \frac{t}{a^2}\right)$$

where $x(T,t)$, $x_S(T)$ and $x_0(T)$ are the oxygen stoichiometry at a given temperature T, respectively, at the grain center at time t, at the grain surface at time $t = 0$ and at the grain center at $t = 0$. $x_S(T)$ corresponds to the $7 - \delta$ value in equilibrium conditions at T. Calculations were performed using $D = 10^{-7}$ cm^2 s^{-1} [24], the lowest value given in the literature for the bulk oxygen diffusion coefficient along the (001) plan of YBaCuO and $x_0(T) = 6.27$, the average $7 - \delta$ value observed at the beginning of the cooling process. The evolution of the oxygen stoichiometry in the grain center, $x(T,t)$, versus time is shown in Fig. 6, for $T = 300$ °C, for two different r values.

The grain oxidation is very fast in such conditions : 0.06 and 6 s are respectively necessary for grains of 2 and 20 μm diameter to reach an oxygen stoichiometry above 6.97 in their center. Therefore, the oxygen diffusion from the surface of the grains towards their bulk cannot be considered as the limiting process for oxidation of small grain YBaCuO ceramics. In the same conditions, the oxidation of a 2 mm thick single crystal needs more than 16 h.

The formation of microcracks or a strong improvement of the grain boundary oxygen diffusion associated with the phase transition would promote the oxygen transfer from the surrounding atmosphere towards the grain surfaces in the core of the ceramic. The result would be a significant oxygen uptake, for A, B and C ceramics. The resulting fast decrease of the average relative difference from the oxygen content observed in equilibrium conditions would be greater for the thicker ceramic which exhibits a higher deficit. The tetragonal to orthorhombic transition is considered to be the origin for the formation of microcracks in dense ceramics when grains are larger than a critical value, in the range 1–4 μm, depending on the authors [26–29]. Although the average grain size is large enough (1–2 μm) to envisage the formation of microcracks, the following experimental results lead to the conclusion that such defects are unlikely in our ceramics:

(i) no upturn is observed in the Young's modulus values determined during the heating cycle in oxygen before the phase transition at 640 °C (Fig. 4). Such an upturn would be characteristic of the closing of microcracks [17]. Neither is a break and a subsequent decrease in Young's modulus observed in the cooling cycle below 640 °C, which would have been characteristic of crack opening. However, this latter observation is less significant since the cooling cycle data stops at 450 °C due to experimental difficulty with the coupling cement.

(ii) scanning electron microscopy observations did not reveal the presence of microcracks;

(iii) the critical current density measured at 77 K (835 A cm^2) is high for small grain ceramic and not affected by successive thermal cycles.

The phase transition is apparently not associated with the formation of microcracks in these small grain ceramics. The observed behavior for oxidation during cooling below the tetragonal to orthorhombic transition temperature can therefore be explained by a strong increase of the oxygen grain boundary diffusion acting as a short circuit path into the ceramic core. At low temperature, the total amount of oxygen carried from the sample surface towards the ceramic core, through grain boundaries, is enhanced by the an increase in the oxygen deficiency existing inside the sample and by the temperature change. The final oxygen uptake of the thickest ceramic (A) is lower when the cooling process at 3 °C min^{-1} is interrupted by successive holds at 640, 510 and 400 °C (Fig. 2) or when the cooling rate decreases (Fig. 1). Such behavior suggests that the oxygen gradient acts directly on the kinetics of grain boundary oxygen diffusion. Since the unit cell volume becomes progressively smaller with oxygen uptake and/or transition to the orthorhombic phase [29], the oxygen gradient should induce compressive and tensile stresses between outer oxygen rich regions and inner oxygen poor regions. These stresses probably act in a local manner to modify the grain boundary diffusion rate due to the anisotropic thermal contraction. Furthermore, not all the grain boundaries will necessarily act in the same way because the local stress gradient will depend on the misorientation between the grains.

Conclusions

The oxidation during cooling of YBaCuO small grain ceramics is strongly dependent on the nature of the phase. At high temperature, when the material symmetry is tetragonal, the average oxygen content is dependent on the diffusion path length: thicker ceramic samples give lower

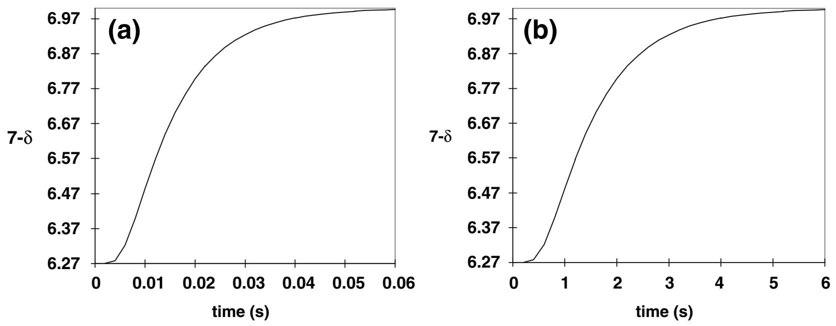

Fig. 6 Simulation of the evolution with time, at 300 °C in $p_{O_2} = 0.2$ bar, of the average oxygen stoichiometry $7 - \delta$ in the center of spherical YBaCuO grains previously quenched from 895 °C ($D = 10^{-7}$ cm^2 s^{-1}). (**a**) $r = 1$ μm and (**b**) $r = 10$ μm

oxygen contents. Isothermal treatments promote the oxygen uptake.

At low temperature, when the material symmetry is orthorhombic, the ceramic oxidation during cooling becomes significantly faster and the sample thickness is not apparently a limiting parameter. This behavior, which cannot be associated with the formation of microcracks in the studied ceramics, is characteristic of oxygen short circuit diffusion paths along the grain boundaries. This transfer, faster during cooling than during isothermal treatments, seems to be enhanced by the stresses resulting from differences in thermal contraction.

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