Influence of Al doping and oxygenation on the superconducting properties of TSMG YBCO bulks

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Abstract. YBCO bulk single-grain samples with the nominal composition $Y_{1.5}Ba_2(Cu_{1-x}Al_x)O_y$ were fabricated by the Top–Seeded Melt–Growth process. Aluminium was found to be a suitable chemical dopant in $Y_{1.5}Ba_2(Cu_{1-x}Al_x)O_y$ bulk superconductors, which introduces effective nanosized pinning centres. An increase of the critical current density, $J_c$, and the appearance of a peak effect were observed at intermediate magnetic fields below the critical temperature, $T_c$. A significant increase of the critical current density was observed in Al doped samples after high pressure oxygenation (16 MPa oxygen pressure) at 750 °C, i.e. by a factor of 3 compared to samples subjected to standard oxygenation at 400 °C at ambient oxygen pressure.

1. Introduction

It is well known that after the Top–Seeded Melt–Growth (TSMG) process, which is usually used for the production of $YBa_2Cu_3O_7$ / $Y_2BaCuO_5$ (further Y123/Y211 or YBCO) bulk superconductors, YBCO does not show superconducting properties. The increase of the oxygen content is necessary to obtain superconductivity in $YBa_2Cu_3O_7$ / $Y_2BaCuO_5$. Superconductivity appears when $\delta$ is lower than 0.5 ($\delta < 0.5$) and the oxygen amount of 7.0 – 6.8 per unit formula is considered to be optimal [1]. The superconducting and the mechanical properties of TSMG YBCO bulk superconductors strongly depend on the conditions of the oxygenation process, i.e. temperature, time of oxygenation, oxygen partial pressure etc.

Three basic types of cracks, $a/b$ – microcracks, $a/b$ – and $a/c$ – macrocracks, which are formed during the fabrication and oxygenation process, allow oxygen penetration into the structure of the Y123 phase [2]. On the other hand, these cracks have some negative influences on the properties of TSMG YBCO bulks, e.g. a decrease of the sample cross section, an increase of the number of inhomogeneities, a decrease of the hardness of the samples, etc.

The High – Pressure High – Temperature oxygenation (HPO) process [3] seems to be promising for increasing the oxygen content in the Y123 phase in very short time and to obtain samples without $a/b$ – and $a/c$ – macrocracks [4]. In the case of HPO, high oxygen pressure is not the main condition for effective oxygenation, but high temperature. The rate of oxygen diffusion into YBCO bulks and the oxygenation time strongly depend on temperature [5]. In order to use high temperature oxygenation (above 500 °C) oxygen pressure has to be applied to abide by the equilibrium line in the oxygen partial pressure - temperature diagram [6].

Recently, the successful substitution of Cu by Al atoms in YBCO bulk superconductors was reported [7]. It was shown that the Al atoms substitute the Cu atoms in the CuO chains [8]. We report here
on the influence of HPO on the superconducting properties of Al–doped YBCO bulk superconductors in comparison with standard oxygenation (SO).

2. Experimental details

YBCO bulk single–grain superconductors were fabricated by the TSMG process. Oxide powders $\text{YBa}_2\text{Cu}_3\text{O}_7 + 0.25\text{Y}_2\text{O}_3 + 0.5$ wt.\%$\text{CeO}_2 + \text{addition of Al}_2\text{O}_3$ in concentration determined by $x$ in $\text{YBa}_2(\text{Cu}_{1-x}\text{Al}_x)_3\text{O}_{7-\delta}$ were milled and pressed into cylindrical pellets of 20 mm diameter. $\text{SmBa}_2\text{Cu}_3\text{O}_7$ (Sm123) seeds were used as nucleation centres for the growth process. The Al concentrations $x$ in $\text{YBa}_2(\text{Cu}_{1-x}\text{Al}_x)_3\text{O}_{7-\delta}$ were: 0.0025, 0.005, 0.01, 0.02 and 0.05. Small samples for oxygenation and magnetization measurements were cut from the $a$–growth sector of the bulks at a distance of 1 mm from the seed (top surface of the pellets). The samples were plate-shaped with dimensions $2 \times 2 \times 0.5$ mm$^3$, the smallest dimension was parallel to the $c$–axis of the crystal.

The small samples were oxygenated by two methods. The first was standard oxygenation, where the samples were slowly heated in a tubular furnace to 800 °C in flowing $\text{O}_2$ atmosphere and kept there for 2 hours, then slowly cooled to 400 °C and annealed there for 240 h. After annealing they were furnace cooled to room temperature. The second method of oxygenization was high pressure oxygenation, where the samples were oxygenated in a special high pressure vessel under an oxygen pressure of 16 MPa at 750 °C for 24 hours with progressively increasing oxygen pressure [3].

Magnetization measurements were done at a temperature of 77 K by a vibrating–sample magnetometer in magnetic fields of up to 5 T applied parallel to the $c$–axis of the crystal. The critical current density, $J_c$, was calculated from magnetization hysteresis loops using the modified Bean model [9]. The transition temperatures, $T_c$, were determined from the magnetic transition curves taken after zero–field cooling, as the mid–point of these curves in an applied external magnetic field of 2 mT.

3. Results and discussion

The critical current densities, $J_c$, for Al–doped and undoped YBCO superconductors at 77 K are shown in Figure 1(a) and Figure 1(b) for SO and HPO, respectively. The results on $J_c$ for the highest concentration of Al ($x = 0.05$) are not presented in the Figure, because $J_c$ is negligibly small for both SO and HPO. The clearest peak effect (PE) is found in the samples with the lowest concentration of Al ($x = 0.0025$) for both methods of oxygenation. A comparison of the critical temperatures is presented in Figure 2(a).

![Figure 1](image1.png)

Figure 1. Dependence of critical current densities, $J_c$, on magnetic field, $B$, at 77 K for $\text{YBa}_2(\text{Cu}_{1-x}\text{Al}_x)_3\text{O}_{7-\delta}$ after standard oxygenation (SO) (a) and after high pressure oxygenation (HPO) (b).
The critical current density at the lowest Al concentration ($x = 0.0025$) for SO (Figure 1(a)) is higher between 0.5 and 2 T in comparison to the undoped reference sample. Thus, the critical current density is improved by Al doping. However, Figure 1(b) clearly shows that $J_c$ at the lowest Al concentration ($x = 0.0025$) is more substantially improved by Al doping and HPO than in the case of SO. The $J_c$ peak for HPO is $5.3 \cdot 10^4$ A/cm$^2$ in contrast to $1.81 \cdot 10^4$ A/cm$^2$ in the case of SO, i.e. higher by a factor of about 3. Also, the peak field, $B_p$, where the secondary peak appears, is shifted to higher fields, from 0.89 T for SO to 1.37 T for HPO. With increasing Al concentration $J_c$ and $T_c$ decrease, confirming that the Cu atoms in the Y123 lattice are partially substituted. The lowest Al concentration does not essentially affect $T_c$. It remains above 90 K for both methods of oxygenation (Figure 2(a)) and is even higher for the HPO samples. The pronounced PE in undoped HPO (Figure 1(b)) could be ascribed to oxygen vacancies acting as pinning centres \[10\]. Therefore, the appearance of the PE in HPO samples could be caused by a combination of Al doping and oxygen vacancies.

The volume pinning force densities, $F_p = J_cB$, were analysed for the lowest concentration of Al ($x = 0.0025$) and for both methods of oxygenation through normalized pinning force densities, $F_n = F_p / F_{p,max}$. Figure 2(b) presents a comparison of $F_n$ as a function of reduced magnetic field, $b_{fp} = B/B_{max}$.

$F_{p,max}$ is the maximum volume pinning force density and $B_{max}$ is the corresponding maximum magnetic field. The reduced magnetic field can be also presented by other criteria, for instance $B_{max}$ can be replaced by the irreversibility field, $B_{irr}$ \[11\] or a field defined from a Kramer plot (the so-called Kramer field, $B_k$) \[12\].

The $F_n(b_{fp})$ curves were fitted by the following expression:

$$F_n(b_{fp}) = b_{fp}^{n+1} \exp \left[ (1 - b_{fp}) \frac{(m+1)}{n} \right]$$

where $m$ was set to 1 and only $n$ remains a free parameter which controls the position of the PE \[13\]. The value of the parameter $n$ was found to be equal to 1.36 and 1.76 for HPO and SO, respectively. The higher value of $n$ for the SO sample shows that the PE is closer to $B_{irr}$ and the PE on the $J_c(B)$ curve is narrower compared to the HPO sample, where the PE is observed to be broader and farther away from $B_{irr}$.

According to Figure 1(a), the SO sample at the lowest concentration of Al ($x = 0.0025$) has lower values of the peak field, $B_p$, and irreversibility field, $B_{irr}$, compared to the HPO sample with the same Al content (Figure 1(b)). These differences in $B_p$ and $B_{irr}$ indicate a better homogeneity of the Al distribution and accordingly stronger flux pinning in HPO samples, which cause an increase of $J_c$. The increase of $J_c$ by HPO was explained \[4\] by the elimination of $alc$ – oxygenation macrocracks during oxygenation.
The same results were obtained by microstructural examinations of the samples in a light microscope as in Ref. [4]. ac - oxygenation macrocracks are observed (Figure 3(a)) after SO, but not after HPO (Figure 3(b)). Due to the higher effective cross section, the overall or effective \( J_c \) is significantly increased [14]. ab - microcracks are present in the samples after both oxygenation methods (Figure 3(a,b)). Also, a higher density of twins and dislocations for effective flux pinning is observed after HPO [15]. Al does not form any secondary phase with Y, Ba, Cu or Ce in studied systems [7].

![Figure 3](image-url)

**Figure 3.** Micrographs with visible ac – oxygenation macrocracks (c – MAC) and ab – oxygenation macrocracks (ab – MAC) formed during SO (a) and only ab – oxygenation microcracks (ab – MIC) after HPO (b).

**Conclusions**

The influence of Al substitution and High – Pressure High – Temperature oxygenation on the superconducting and microstructural properties of \( \text{YBa}_2(\text{Cu}_{1-x}\text{Al}_x)\text{O}_{7-\delta} \) were studied. A pronounced peak effect is induced in the samples at lower Al concentrations. Critical current density in Al doped sample after HPO with the lowest concentration of Al (x = 0.0025) increases by a factor of about 3 compared with standard oxygenation. The HPO process is an effective method to obtain oxygenated samples free of macrocracks.

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