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Influence of precursors and synthetic conditions on carbon trapping and related superconducting properties in bulk YBCO

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The influences of starting precursors and conditions of densification on carbon retention in YBCO ceramics are investigated. It is shown that both the degree of densification and the kinetics of densification have strong effects on the carbon trapping behaviour. By controlling the densification kinetics, a highly sintered density can be achieved with low carbon trapping in YBCO ceramics. Moreover, one observes that even in a melt-textured sample, depending on the quality of the precursor powders and on the presintering conditions, the residual carbon content can still be high, and depression of the superconducting critical temperature, T_c, may still occur. From a systematic investigation and characterization, we have established a correlation between the superconducting transition characteristics and the residual carbon level. Such a correlation can be used as a guideline for the control of carbon content and the optimization of superconducting properties in YBCO materials.

1. Introduction

The 92 K $YBa_2Cu_3O_{7-x}$ superconductor is, so far, the most promising candidate for the application of magnetic levitation. From the engineering point of view, the superconducting properties of large-scale processed materials, including powdered, sintered or textured monoliths, should be carefully controlled. In this respect, the superconducting transition characteristics (T_c and transition width, ΔT_c) have been shown to influence strongly the intragrain critical current density and the irreversibility line of the materials. For instance, in melt-texturing processed quasi-crystalline samples, the way that the superconducting critical current density value J_c, depends on T_c follows a scaling law: $J_c = [1 - (T/T_c)^2]^n$. The n value has previously been fitted to two [1] using quench melt growth (QMG) processed samples. Taking into consideration the result, we can deduce that 1 K depression of T_c can result in about a 10% decrease in the J_c value. In fact, during the study of Sn doping in the melt-powder melt-growth (MPMG) processed Y-123 system, it was observed [2] that an increase of 1 K in T_c resulted in a 15% increase in the J_c value.

Concerning the factors that may deteriorate T_c, assuming no obvious cationic contamination, oxygen content may be one cause. But actually, experimental evidence shows that the difficulty in oxygenation is not the sole cause of the depression of T_c. In some cases, extensive oxygenation may turn out to be inefficient. Shaw *et al.* [3] demonstrated that the retention of carbon in densely sintered 123 ceramics is an important origin for the observed degradation of T_c. Maciejewski *et al.* [4] have shown that 123 materials often contain a remarkable amount of CO_2 that may induce a decrease of the orthorhombicity of the crystal structure. The recent investigations by Boulay *et al.* [5] on the substitution of the CO_3 group into the Y-123 system have shown the possibility of forming oxycarbonates in this system with substitution of CO_3 groups for (CuO) copper chains.

In the works mentioned above, studies were based on sintered ceramics. But the extent of carbon retention has not been examined in melt-processed Y-123, which is considered to be the most promising material for applications that require large current-carrying capability in high magnetic fields. The aim of the present work is to investigate the influences of different parameters, such as starting precursor, sintering conditions and methods of processing (such as sintering or melt-texturing), on the extent of carbon retention, as well as their related superconducting transition characteristics.

2. Experimental procedure

Two kinds of superconducting $YBa_2Cu_3O_{7-x}$ precursors were employed and studied in this work: denoted as Sr5 and SSC. Both stoichiometric Y-123 and Y-123 with 20% excess Y-211 were used as nominal compositions. The Y-211 powder was synthesized by the solid-state reaction method. In the case of platinum addition, 0.5 wt% PtO_2 powder was added into the precursor prior to pelletization and thermal treatment. The mixing of the powders was made using a “pulverisette” (Fritch^{TM}VI). Bars for sintering and melt-texturing were pressed by cold isostatic pressing (CIP) at 300 MPa. Typical dimensions of the bars were $50 \times 10 \times 10$ mm^3. The sintering was performed

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in an oxygen flowing tube furnace at different temperatures. Parts of the presintered samples were cut down and further melt-textured. The melt-texturing was performed by a melt-texture-growth (MTG) process using a temperature gradient ($G = 20\,^{\circ}\mathrm{C\,cm^{-1}}$) furnace. The carbon content was determined by a high temperature flashing method by measuring the released CO_2 with a spectrometer (CNRS-Lyon, Service Central d'Analyse). Some of the above samples were also analysed by a chemical solution method that showed good agreement with the first method. Prior to superconducting characterization, all samples were annealed in an oxygen flow between 600 and 350 °C for a period of 100 h. The superconducting transition ($T_{\mathrm{c,onset}}$ and transition width, ΔT_{c}) was determined from the temperature dependence of the magnetization measurement using either a Squid magnetometer (Quantum Design, Model MPMS) or an alternating current (a.c.) susceptometer (Lake Shore). All measurements were performed in zero field cooled (ZFC) mode under a magnetic field of 10 gauss.

3. Results and discussion

3.1. The characteristics of the powder precursors

Both precursors are almost single phases upon X-ray diffraction (XRD) analysis. Only weak peaks were identified as CuO for the precursor Sr5. Table I shows some characteristics of the precursors. It can be seen that although Sr5 has a relatively high carbon content, its T_{c} onset is only 2 K lower than that of SSC, which has a much lower carbon content. It seems that for these powder precursors, carbon does not have a strong influence on the superconducting transition temperature. The nature of the carbon absorption in these powders is not quite clear: it is either absorbed on the surface of the powder or substituted in the lattice structure. This point will be discussed later.

3.2. The sintered samples

The sintering behaviours of these two powders were monitored by shrinkage measurement during heating in an oxygen flow. Fig. 1a shows that, for a sintering schedule of heating up to 950 °C, 2 h soaking and ramped at $80\,^{\circ}\mathrm{C\,h^{-1}}$, their shrinkages are quite different. The Sr5 powder reaches 18% shrinkage, compared with its initial sample length, L_0; while that of SSC is about 12%. The shrinkage behaviours of the ceramics during sintering can be closely related to their densifications. For instance, in the case of the Sr5 powder, after sintering at 950 °C for 2 h, the relative density is almost 100%, while that of SSC is still less than 90%. Note that, for the Sr5 sample, the isothermal densification at 950 °C reaches almost constant values after 2 h soaking, while that of SSC continues (see inset in Fig. 1a). These different densification behaviours can be explained by taking into consideration the different starting particle sizes. Powder with a smaller particle size has a higher surface energy and correspondingly a larger driving force for densification. The superconducting transition characteristics were probed on the samples Sr5 and SSC after sintering at 950 °C for 24 h with subsequent oxygen annealing. The temperature dependence of the magnetization curves is shown in Fig. 2. We see that the $T_{\mathrm{c,onset}}$ of the Sr5 sample (curve a) was depressed to 80 K, with a very broad transition. In contrast, the SSC sample (curve b) has a $T_{\mathrm{c,onset}}$ at 92 K, which is the optimum value for the Y-123 system, and the transition width is very sharp. As both samples were annealed extensively in flowing oxygen at low temperature prior to measurement, the dramatic difference between their superconducting properties should be due to other

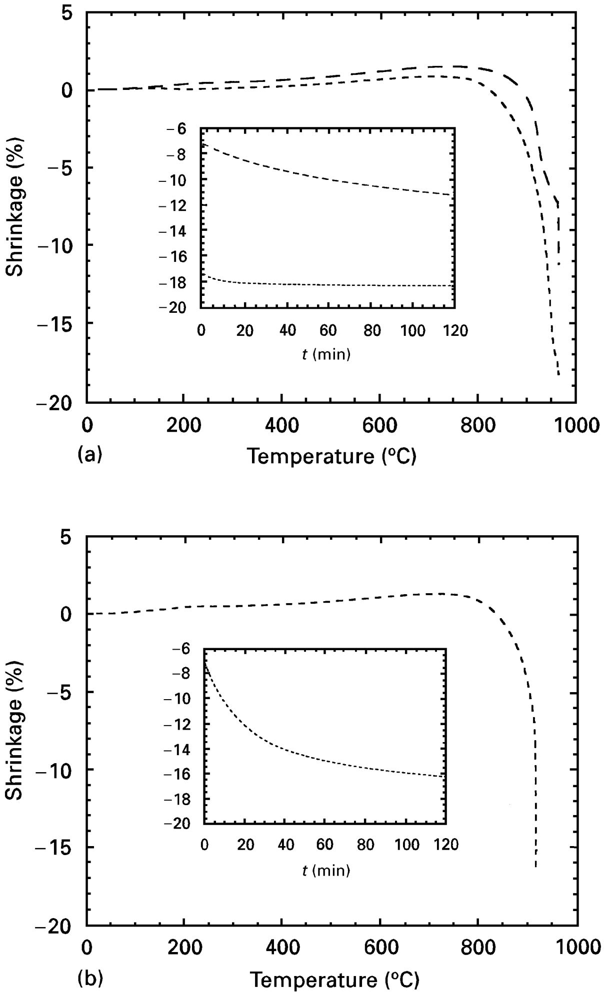

Figure 1 (a) Comparison of the shrinkage curves during heating and isothermal soaking at 950 °C for Sr5 (– – –) and SSC (- - -) powders. (b) Shrinkage curves of Sr5 during heating and isothermal soaking at 920 °C. The measurements were made in oxygen flow with a heating rate of $80\,^{\circ}\mathrm{C\,h^{-1}}$. The inset figures show the shrinkage of the samples during 950 and 920 °C soaking for (a) and (b), respectively.

TABLE I The chemical and physical characteristics of the two powders studied in this work: Sr5 and SSC

Precursor	Purity of XRD phase	Average particle size (μm)	T_{c} onset (K)	Carbon content (p.p.m.)
Sr5	123 + v.w. CuO	2.6	90	3000
SSC	Pure 123	7.5	92	1200

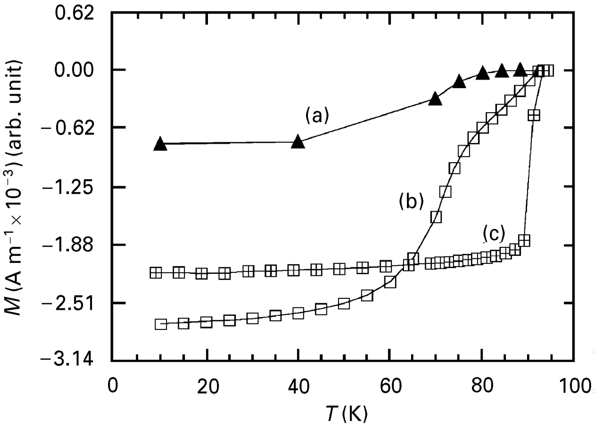

Figure 2 The temperature dependence of magnetization for sample Sr5 sintered at 950 °C (curve a), sample SSC sintered at 950 °C (curve b), and sample Sr5 sintered at 920 °C (curve c). The measurements are performed in ZFC mode under a magnetic field of 10 gauss.

factors than oxygen content. The carbon content analysis shows, indeed, a rather high degree of carbon retention in the sintered Sr5 sample (2600 p.p.m.), contrary to the SSC sintered sample (560 p.p.m.). This suggests that carbon retention is due to densification of the ceramics. Shaw *et al.* [3] have indeed reported that in highly densified YBCO ceramics, nominal carbon retained by the powder is trapped in the ceramics matrix as a result of porosity closing. This is the case of the 950 °C sintered Sr5 sample that has nearly reached theoretical density, so that the open porosity has been eliminated. On the contrary, the sintered SSC sample has lower densification: less than 90% of the theoretical density, so that open porosity still exists. The Microstructural examination of Sr5 and SSC after sintering at 950 °C for 24 h in flowing oxygen is shown in Fig. 3a and b, respectively, using polarized optical microscopy. One observes that the Sr5 sintered sample has a large grain size with closed porosity, while SSC has almost the same grain size but with interconnected pores. Note that, comparing the initial carbon contents in the precursors, decarbonation of the Sr5 950 °C sintered sample is less than 15%, whereas that of the SSC 950 °C sintered sample reaches 50%.

The above results lead us to suggest that, for a high carbon content containing precursor, densification during sintering should not be too high in order to avoid the trapping of carbon. Following this consideration, it is straightforward to think that a lower sintering temperature, allowing a lower densification, should be beneficial for the Sr5 powder in terms of decarbonation. Thus precursor sintering of the Sr5 powder was performed at 920 °C for 24 h. Its superconducting transition curve is strongly modified (Fig. 2, curve c). We see that $T_{c,\mathrm{onset}}$ is restored to 92 K and the diamagnetic signal is enhanced strongly, but the large transition width observed implies the existence of some inhomogeneous regions that have lower values of T_c. Actually, the carbon content in this sample decreased to 1200 p.p.m., corresponding to a 60% decarbonation; which is significantly lower than its 950 °C sintered counterpart.

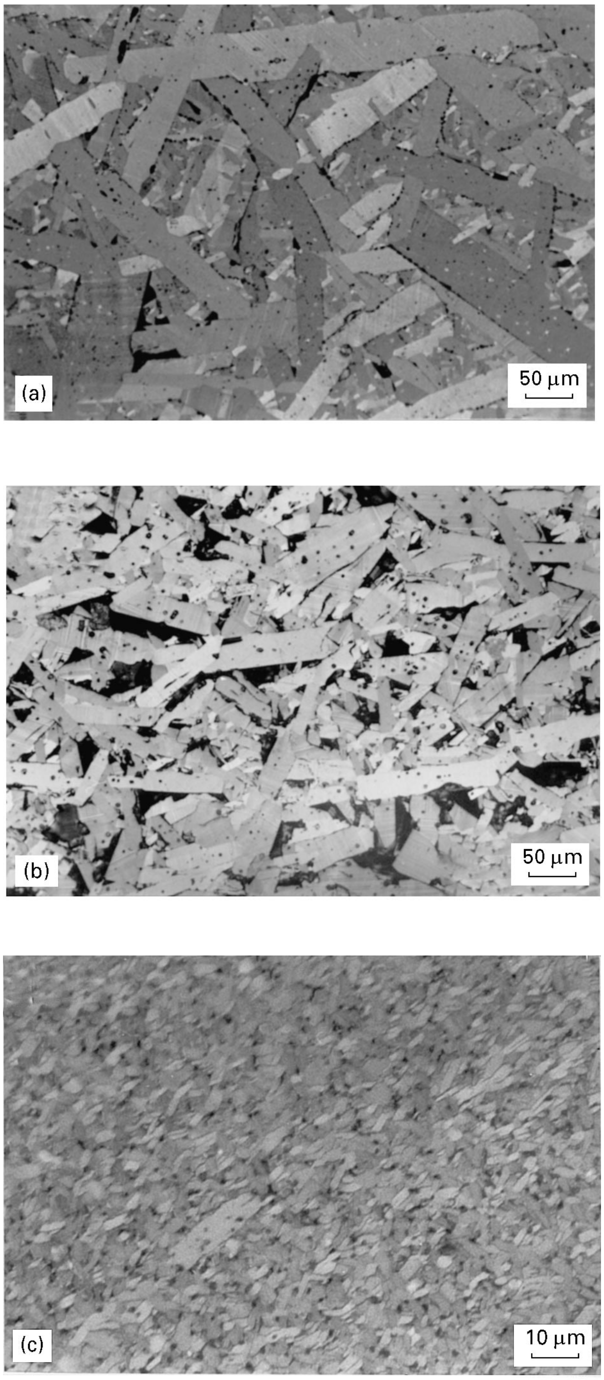

Figure 3 Polarized optical microstructure for (a) Sr5 950 °C sintered sample, (b) SSC 950 °C sintered sample, and (c) 920 °C Sr5 sintered sample.

In order to check the idea that lower carbon trapping is a result of less stronger densification, we further examined the densification behaviour and the microstructure (Fig. 3c) of the 920 °C sintered Sr5 sample. Fig. 1b shows the dilatometric curve of the Sr5 sample with a heating schedule of 920 °C for 2 h. Surprisingly, one observes that at the end of 2 h soaking, the shrinkage reaches 17%, which is very close to that of the 950 °C sintered Sr5 sample. The final density corresponds to 92% of the theoretical density.

At this level of densification, the open porosity should be almost eliminated. The microstructure of the Sr5 sample sintered at 920 °C for 24 h is shown in Fig. 3c. We see that although the grain size remains

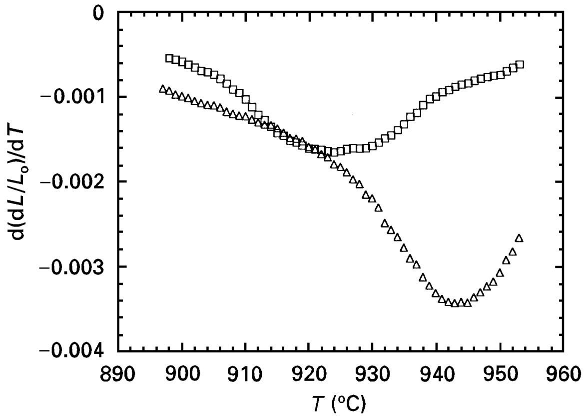

Figure 4 The temperature dependence of densification rate (derived shrinkage) for Sr5 (△) and SSC (□).

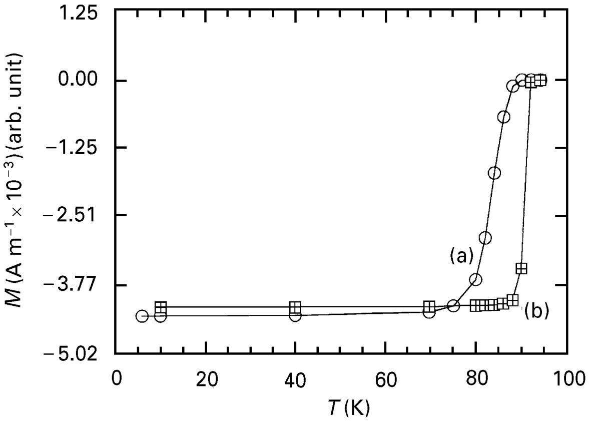

Figure 5 The temperature dependence of magnetization for the melt-textured sample using the 950 °C sintered Sr5 sample (curve a) and the 950 °C sintered SSC sample (curve b) as the starting precursors. The measurements were performed in ZFC mode under a magnetic field of 10 gauss.

smaller as compared with its 950 °C sintered homologue, the observed porosity is almost closed without interconnection between the pores. Such results indicate that the hypothesis we made concerning carbon trapping and porosity closing is not sufficient, because a distinct decarbonation behaviour is observed in the Sr5 sample sintered at 920 °C having a high degree of densification. This led us to investigate further the different densification behaviours of the Sr5 powder for sintering at 950 and 920 °C. Fig. 4 shows the densification kinetics, i.e. the shrinkage rate, $d(dL/L_o)/dT$, where L = the sample length and L_0 = initial length of sample, as a function of temperature for samples Sr5 and SSC. For the Sr5 sample, one observes a change of the slope of the shrinkage rate at around 920 °C, above which the shrinkage accelerates and reaches a maximum rate at 945 °C. So for sintering at 950 °C, the densification rate of Sr5 is twice as rapid as at 920 °C. This gives the evidence that porosity closing is one possible mechanism of carbon trapping, whereas densification kinetics may also play an important role in carbon trapping. Note also that the Sr5 precursor always has a higher densification rate than the SSC sample.

The above results indicate that carbon retention in the sintering process is much more complicated than simply considering the final density of the ceramics. It is obvious that in the presence of open porosity, carbon can be more easily burned out, as shown for the SSC sample. It is also important to realize that by controlling the kinetics of densification, we can also control the carbon content without being detrimental to the final sintered density.

Finally it should be noted that retention of carbon in the initial powders corresponds probably to surface absorption, while in the densely sintered ceramics, the carbon is incorporated in the YBCO structure as CO_3 groups [6], so that it results in a decrease of the copper valency and thus T_c. Evidence for carbon substitution into the YBCO structure has been reported elsewhere [6].

3.3. The melt-textured samples

To investigate the influence of carbon retention on the properties of melt-textured samples further, melt-texturing was performed using the above presintered monoliths as precursors, and their resulting superconducting properties were examined in terms of superconducting transition characteristics.

The temperature dependencies of susceptibility for the so obtained melt-textured samples derived from Sr5 and SSC precursors, both presintered at 950 °C for 24 h, are shown in Fig. 5, curves a and b, respectively. Compared with the presintered ceramics, we see that $T_{c,\mathrm{onset}}$ of Sr5, 950 °C-sintering precursor derived melt-textured sample, is modified to 88 K and the transition is less broad. The carbon content in this sample is reduced to 820 p.p.m. For the SSC, 950 °C-sintering precursor derived melt-textured sample, the carbon content is 400 p.p.m., the $T_{c,\mathrm{onset}}$ is 92 K and the susceptibility curve exhibits a rather sharp transition. For the Sr5–920 °C sintering derived melt-textured sample, the superconducting transition curve is quite similar to that of SSC and the residual carbon content is also close to 400 p.p.m. These results indicate that the melt process is effective for decarbonation because the carbon content decreases with respect to its precursor. This is in good agreement with the results of Maciejewski *et al.* [4] who reported that heating above the peritectic temperature is effective for decreasing carbon content. However, our results also show that an excessive amount of carbon may still be retained during the MTG process in the case of the Sr5 starting powder, so that the superconducting properties still deteriorate. The above results emphasize the absolute necessity of controlling the carbon content of the precursor materials prior to melt-texturing.

3.4. The relation between superconducting transition characteristics and carbon content

Table II summarizes the carbon content analysis, superconducting transition temperature, $T_{c,\mathrm{onset}}$ and transition width ΔT_c, for the samples studied above. In addition, two other samples are also included in

TABLE II The carbon content and superconducting characteristics (T_c, ΔT_c) of different bulk Y-123 samples investigated in this work

	Sample label	C content (p.p.m.)	$T_{c,\mathrm{onset}}$(K)	ΔT_c (K)
Sintered samples	Sr5, 950 °C	2600	80	26
	SSC, 950 °C	600	92	4
	Sr5 + 20% 211 + PtO_2, 950 °C	1400	80	
Melt-textured samples	Sr5, 950 °C presintering	820	88	13
	Sr5, 920 °C presintering	420	91	5
	SSC, 950 °C presintering	400	92	4
	123(Sr5) + 211 + PtO_2, 950 °C presintering	200	92	2
	123(Sr5) + 211, 950 °C presintering	870	88	10

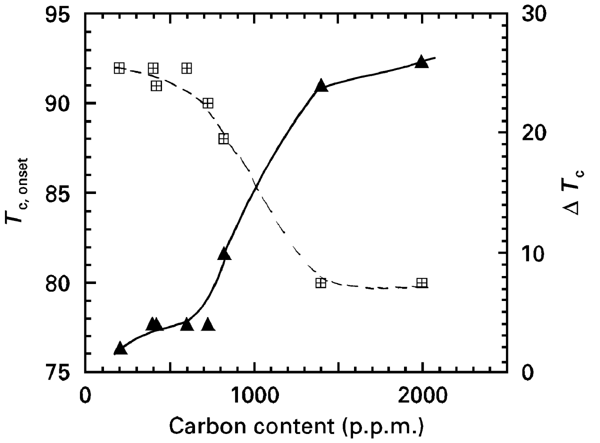

Figure 6 Correlation between the carbon content and the superconducting transition characteristics [(■) T_c, (▲) ΔT_c] established from the investigated samples in the present work (Table II). Lines are drawn only as a guide for the eye.

this table. One is a melt-process YBCO sample with Y-211 addition, the other is a platinum doped melt-processed sample. The last sample shows the lowest carbon content and the sharpest transition curve.

From this table, a straightforward correlation can be established between the carbon content and $T_{c,\mathrm{onset}}$ and ΔT_c from the samples investigated in this work, as shown in Fig. 6. It can be seen that in order to obtain an optimum T_c and a small transition width, the limit of the carbon content should be controlled at less than 500 p.p.m.

4. Conclusions

Starting with a carbon containing precursor, the sintering conditions must be carefully controlled for the elimination of carbon: clearly not only the final density but also the kinetics of densification are important in affecting the carbon trapping.

The carbon content in the precursor prior to melt-texturing has a great influence on the quality of the textured sample and the carbon content in such a precursor should be carefully controlled.

A straightforward correlation between carbon content and superconducting transition characteristics of YBCO materials can be made, which shows that the carbon contamination level should be lower than 500 p.p.m. in order to obtain optimized superconducting transition properties.

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