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THE INFLUENCE OF Ag AND Ag(In) ALLOY ON Y–Ba–Cu–O EQUILIBRIUM DIAGRAM AROUND THE Y-123 SUPERCONDUCTING PHASE

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Abstract

We studied the chemical compatibility of Ag, Ag(In) alloy, Y_2BaCuO_5 (the so-called Y-211 green phase) and $YBa_2Cu_3O_{7-\delta}$ (Y-123) phase in order to check if better grain growth and alignment with minimum contamination were possible during the Y-123 melt texturing. We demonstrate that the addition of silver to Y-123 always led to an enhanced texture. The typical microstructure of the composite Y-123 plus Y-211 (that is believed essential for high critical currents in these High Tc superconductors) was not disturbed by addition of silver up to 7.5 wt%, while higher concentrations of metal led to a degradation of the texture. DTA–TG analysis was used to investigate the influence of Ag and Ag(In) alloy on the Y–Ba–Cu–O equilibria around the Y-123 phase. We found a very unexpected thermal behaviour, similar to an eutectic equilibrium, when the silver concentration was increased to 35 wt%. We believe that this effect was essentially due to the increasingly higher concentration of silver that could react with the secondary phases present in the melt.

Keywords: alloy, superconductor, Y–Ba–Cu–O equilibrium diagram

Introduction

Since the discovery of the high-T_c $YBa_2Cu_3O_{7-\delta}$ (Y-123) superconductor, considerable efforts have been made to improve the superconducting properties of these materials, in particular the critical density value (J_c) at 77 K.

Monocrystals are ideal samples for getting a good J_c, but up to date, unfortunately, their growth does not exceed a centimetre in length and their morphology is plate like; for this a great attention is directed towards the investigation of alternative fabrication methods. Unfortunately, the sintered superconductors form weak links due to the presence of high-angle grain boundaries, microcracks, off-stoichiometry, impurity phases at grain boundaries and poor connectivity between grains [1]. So the J_c values of these materials are usually several hundred A cm^{-2}, and so far below the required level for industrial and commercial uses that is almost a five-order higher.

The Melt-Texture-Growth (MTG) techniques based on the controlled solidification of the melt allow the grains to grow unidirectionally [2] overcoming these problems. To this purpose, it was essential to study the phase diagram Y_2O_3/CuO/BaO,

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and specially the equilibria between Y-123 and the neighboring phases, varying the partial PO_2 [2]. At present, many triangular fields of stability in the pseudoternary phase diagram of Y–Ba–Cu oxides are known [3], but a systematic knowledge of this system is far to be made, as some phases are stabilised by CO_2 content. The results concerning the Y-123/Y_2O_3, Y-123/CuO and Y-211/CuO binary systems are reported elsewhere [*e.g.* 4–6].

Higher J_c request also the introduction of effective flux pinning centres as secondary phase addictions (Pt, Ca, Fe, Al, Ni, Zn, Te, CaO_2, SiC, ZrO_2, $BaZrO_3$ and $BaSnO_3$) [7–12]. As already observed by I. Monot *et al.*[13], the results depend on the processing conditions and on the reactivity of the doping element, especially on its action on the size and shape of the Y_2BaCuO_5 (Y-211) particles included in the crystals. The phase diagrams with the various additives are not known, but simply the reactivity was reported.

To date, some authors seem to agree that the Y-123 MTG superconductors' microstructure formed under the influence of Ag mixtures, and they observed the growth of enlarged and well aligned grains in the superconducting phase [14–16]. Silver was also found useful in improving mechanical properties and promotes densification specially in large dimension samples [17, 18]. On the contrary, the effects of silver addition on J_c are not clear since some contradictory results have been reported: most of the authors found an enhancement of the critical current density [16, 19–22]; however, other studies have indicated that the Ag addictions have detrimental effects on it [24–26].

In the present work we have attempted to obtained more information about the stability of Y-123 plus silver and Y-123 plus Y-211 plus silver. We started from a high quality single phase Y-123 and we searched for the optimum silver content addiction for the best grain alignment and growth, to check the literature reports on microstructure. Then, we tested the chemical compatibility of silver with the Y-211 phase, and finally we checked the texturing of Y-123 samples in presence of an excess of Y-211 phase (up to 30 wt%), as suggested by various authors [27, 28], and silver.

The silver was believed to be a non-reacting component, producing heterogeneous mixtures with Y-123. Although the results of Aswal *et al.* [14] on the very low solubility of silver in Y-123 and its decomposition products (less than 0.1 at%) can be confirmed, the converse is not true. In fact, we observed a relevant contamination of Y-123 and its secondary phases on silver. So, to avoid the solution of these products in silver, we introduced indium, yielding a non-reacting silver alloy. We studied the thermal properties of the mixtures obtained, extending the knowledge of the Y–Ba–Cu–O–Ag phase diagram, which Wiesner *et al.* [29] have recently investigated around the $YBa_2Cu_3O_{7-\delta}$ – Ag phase only for the terminal composition.

Experimental

Samples of different compositions around the $YBa_2Cu_3O_{7-\delta}$ (Y-123) superconducting phase were prepared increasing the silver content, starting from powders of

$YBa_2Cu_3O_{7-\delta}$ and Ag_2O. The Y-123 samples (orthorhombic, a=3.817(1), b=3.883(1), c=11.666(2) Å) were prepared by the solid state reaction starting from pure oxides with a preparation method well standardised in our laboratory [4], followed by the MTG process.

The sintered pellets so obtained were ground and when necessary mixed with the suitable content of Ag_2O or Y-211. The silver oxide (Fluka, 4N) was used because it is finely subdivided and can be uniformly dispersed in the Y-123 powder. Moreover, it easily decomposes at 415°C to metallic silver during the texturing experiments, that reach very elevated temperatures (around 1100°C).

The Y_2BaCuO_5 (orthorhombic, a=7.119(4), b=12.157(6), c=5.649(2) Å) , when used as an addictive, was also obtained by the solid state reaction mixing Y_2O_3, CuO and BaO_2 in stoichiometric amounts and sintering in flowing oxygen at 1000°C for 48 h. The Ag(In) alloy at 90/10 wt% composition was obtained in pellets from the metals by arc-melting and reduced in powder by mechanical filing.

The mixed powders were subsequently pressed into bars, with dimensions of $40\times5\times3$ mm^3, rapidly heated at 900, then held at 1080°C for 1/2 h in a horizontal furnace (MTG technique) in flowing oxygen and finally cooled to room temperature at 60°C h^{-1}, to avoid the formation of microcracks, which may arise from the tetragonal/orthorhombic structural transition.

The MTG samples were annealed and subsequently investigated by SEM-EDAX, optical microscopy and X-rays. The X-ray data were obtained on a Philips PW 1729 powder diffractometer with filtered CuK_α radiation, using 0.02° steps and 0.58 count times. Smoothing, background corrections and refinements were made by the computer software package ASPO [30].

The DTA–TG thermal analysis of the different samples were carried out on a Netzsch STA 409 apparatus at a fixed temperature rate (10°C min^{-1}). The reference (Al_2O_3) and the sample cells were open, so that the product was in contact with the surrounding gas atmosphere. The reactivity of each sample was tested in $P(O_2)=0.2$, 0.6, 1 atm at $P_{tot}=1$ atm.

Results and discussion

The silver fluid bed

In the first series of experiments we have investigated the behaviour of some Y-123/Ag samples increasing the silver content (1, 5, 7.5, 15, 30 and, finally, 35 wt%). We take into consideration both the microstructural aspect and the thermal behaviour of the samples, while its transport characteristics are discussed elsewhere [31].

The SEM analysis performed on Ag 1 wt% charged Y-123 made it possible to observe silver flakes at grain boundaries, confirming that the solubility of Ag in Y-123 is low, in agreement with literature data [14].

We observed positive effects on the grains' alignment. In Fig. 1(a) we report a highly disordered Y-123 sample without silver, where small grains are observed. Increasing the silver content to an optimum value (7.5 wt%), grains become larger and more aligned, although grown in the same thermal conditions of temperature and gradient (Fig. 1(b)). It can be observed that at higher silver concentrations (15–30 wt%) Ag was found to collect in drops starting from the voids of the sample. The drops grow more and more at expense of the surrounding silver, leading to catastrophic disorder as confirmed by metallographic examinations. The effect of microstructure on transport properties will be to discuss elsewhere [32]. We only note here that the resistivity *vs.* concentration behaviour in our samples depends on the morphology of grains.

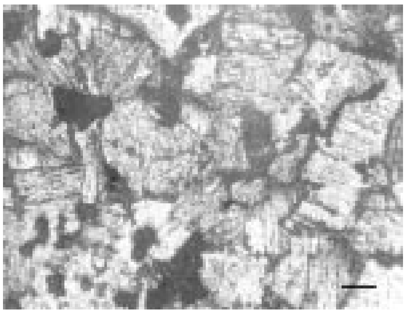

Fig. 1a Micrographic aspect of Y-123 sample melt processed at 1090°C without spurious phases addition. The marker represents 100 μ

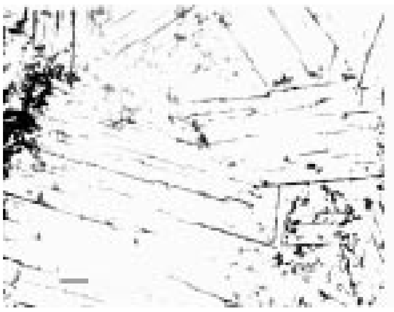

Fig. 1b Micrographic aspect of Y-123 sample with Ag 7.5 wt% melt processed at 1090°C. The marker represents 100 μ

At this level, we tried to explain the interaction between silver and the Y-123 superconducting phase using the concept of 'fluid bed'. Our system is composed by the silver and the Y-123 superconducting phase, with densities slightly different (the silver density is about 11 g cm^{-3}, while the Y-123 one is in the order of 6 g cm^{-3}). In a simplified frame, the two phases can be considered mutually inert. In general, these kind of fluids tend to segregate and become stratified. In fact, testing the Y-123 decomposition on a silver layer contained in an alumina boat, we observed that the Y-123 decomposition products can migrate on the silver. When the experiment was repeated introducing the silver directly into the Y-123 bars, the metal was able to form a continuous web on which Y-123 can freely float and then decompose (T_p= 1040°C). These facts can be explained considering that the melting point of silver is 960°C [28]. After the decomposition of the Y-123 phase some melt remains liquid at about 920°C, in pure oxygen as in our experiment, or at lower temperature in inert atmosphere or in vacuum, as reported by Nakamura *et al.* [33]. In the course of the cooling, the Y-123 grains are free to float, move and rotate on the melted silver layer. We had experimental evidence of this fact by observing the Y-123 domains' stratification due to the gravity effect. But all the grains grow, so are partially blocked each other, and finally join together. Consequently, the silver is ejected out of the Y-123 phase grains, but fill the voids remaining in the sample and the grain boundaries. The optimum would be to gradually but completely remove Ag from the sample when the grain growth and alignment is better, without disturbing the ordered microstructure. So we mean for 'fluid bed' an inert phase that may allow the addensation of the primary phases that float freely on it. In our case, of course, the fluid bed is the silver layer and the primary phases are Y-123 and its decomposition products.

The chemical reactivity of the melts

The results of DTA–TG analysis (summarised in Fig. 2) concern the heating thermal effects due to Ag melting and Y-123 decomposition at $P(O_2)$=1 atm and show unexpected behaviour. In fact, although silver was previously believed to be a non-reacting element with Y-123, by the reported data there are clearly strong interactions between the two phases. The peritectic decomposition of Y-123 is strongly affected by a high content of Ag, around the 35 wt%, showing a decrease from 1040 till to 931°C. A slightly similar effect around the same composition, occurs by melting temperature of Ag, that decreases from 960 to 944°C. The Tables 1 and 2 give a summary of the experimental results obtained from the examination in $P(O_2)$= 0.2, 0.6 and 1 atm for both samples of pure Y-123 and with the addition of 35 wt% Ag. The thermal effects could be the evidence of a very complex eutectic equilibrium, that involves silver and the Y-123 phase, or its decomposition products, or both of them. Work is in progress to investigate the concerned species.

Table 1 Thermal behaviour of pure Y-123 varying the oxygen partial pressure

Y-123 peritectic decomposition temperature T_p/°C	Oxygen partial pressures $P(O_2)$/atm
1034	0.2
1036	0.6
1041	1.0

Table 2 Thermal behaviour of the Y-123+35 wt% sample varying the oxygen partial pressure

Y-123 peritectic decomposition temperature T_p/°C	Silver melting point T_m/°C	Oxygen partial pressures $P(O_2)$/atm
1022	947	0.2
1012	945	0.6
931	944	1.0

These results induced us to consider whether also another phases was really non reacting with silver as believed. For example, Murakami *et al.* observed in some works [2, 13, 28] that the presence of Y-211 phase (green phase) in Y-123 matrix is highly positive for the transport properties in this ceramic superconductor. Then we performed DTA–TG thermal analysis to study the chemical compatibility between silver and the Y-211 phase, without finding any relevant interaction.

The compound $YBa_2Cu_3O_{7-\delta}$ melts incongruently at about 1030°C (in oxygen) to Y_2BaCuO_5 plus liquid. This thermal instability of the Y-123 phase is a serious limitation in the high temperature processing of the superconductor: as a sample is cooled from higher temperature, at 1040°C the peritectic reaction takes place, but the formation of the Y-123 compound cannot be complete. In fact it is difficult to realise the perfect reversibility of the phenomenon: by reaction with the liquid the Y-211 inclusions are coated by Y-123 and so they are partially removed from the reaction system, as the liquid is unable to penetrate the Y-123 coating to react with the Y-211 core. Hence, the remaining liquid becomes poor in yttria and solidifies at some lower temperature, segregating at the grain boundaries. This liquid is constituted of non-superconducting phase, as $BaCuO_2$ and CuO. A stoichiometric excess of the Y-211 phase makes it possible a peritectic reaction with the liquid that segregates at the grain boundaries: the liquid is withdrawn in the excess Y-211 phase and can react, yielding Y-123.

In this way, we also obtain grains larger, well connected and characterized by clean grain boundaries, in agreement with some results of Salama *et al.* [1, 34]. We have also verified that in Y-123+30 wt% Y-211 samples the addition of Ag allows good texture and large grain size to be obtained without observing any change in the microstructure of the Y-123 superconductor [31]. This is shown by comparison in Figs 3(a) and 3(b), where a high degree of grain alignment is reached and the typical Y-211 inclusions are observed.

In part this can be explained by higher temperature of the thermal process necessary for grain alignment (1170 instead of 1090°C) as it can be observed in Fig. 3(a). But again the addition of silver greatly improves the alignment and grain growth

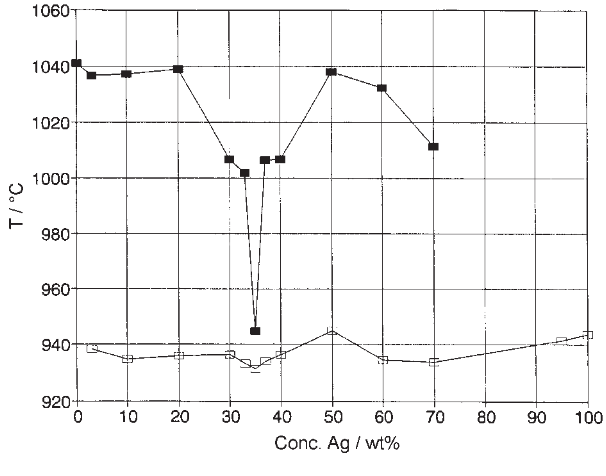

Fig. 2 Thermal effects in Y-123/Ag samples at $P(O_2)$=1 atm: Y-123 peritectic decomposition temperature (■) and silver melting temperature ( )

(Fig. 3(b)). The aim of these tests is not the improvement of J_c, that it is known to degrade progressively at higher silver content [14], but to observe the effect of a fluid bed on the alignment of the superconducting grains and the stability of the compounds.

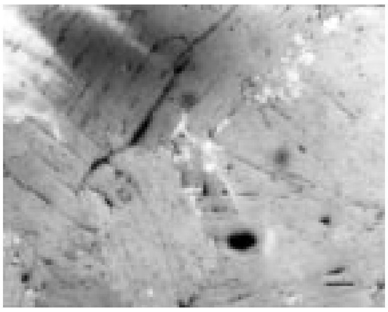

Fig. 3a Micrographic aspect of Y-123 sample with Y-211 30 wt% melt processed at 1170°C. The marker represents 100 μ

It is known that the texturing process is very long and very low cooling rates (less than 0.5°C h^{-1}) are believed necessary to grow large crystals: the higher the cooling rates, the larger the aspect ratio (length to thickness) of the crystals in the material. At high cooling rate (60°C h^{-1}), that is profitable for industrial production, aspect ratio of 10^3 is obtained [35], so very thin crystals are expected. However, in the presence of the silver fluid bed and the Y-211 phase we easily obtained a ratio of 1:2 although we used the same high cooling rate. Our results on synthesis of highly textured samples are summarised in Fig. 4 by introducing the parameters *G* and *A*%. Figure 4(a) shows evidence of an optimum silver concentration for the grain size. *G* is expressed in mm, and is calculated as the square root of the mean grain surface as detected by direct microscopy in an area up to 5 mm^2. In Fig. 4(b) the same technique is used to detect the alignment of grain in respect to temperature gradient: here we report the percentage *A*% of aligned grains in an angle of 15 degrees.

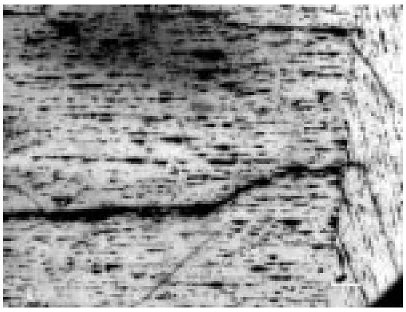

Fig. 3b Micrographic aspect of Y-123 sample with Ag 7.5 wt% and Y-211 30 wt% melt processed at 1170°C. The marker represents 100 μ

A non-reacting fluid bed

The previously reported (Fig. 2) thermal data results clearly showed that a relevant contamination of silver by Y-123 and its secondary phases was present. In this framework, the pure silver is not a completely satisfactory fluid bed, because of the dissolution of these products in silver. It is known that is possible in some cases to limit the solid solutions previously dissolving a non-reacting material in the primary metal. To avoid this problem, we introduced indium, yielding a more stable silver alloy. In this case, we may say that another fluid bed was used, with a melting temperature lower than the silver one (930°C for 90/10 wt% alloy) and that is also more fluid than the pure silver. In general, a very important fluid bed parameter is the fluidity of the liquid on which the solid primary phase floats. We found evidence that the silver increases its own fluidity in the presence of indium, so that it was completely ejected

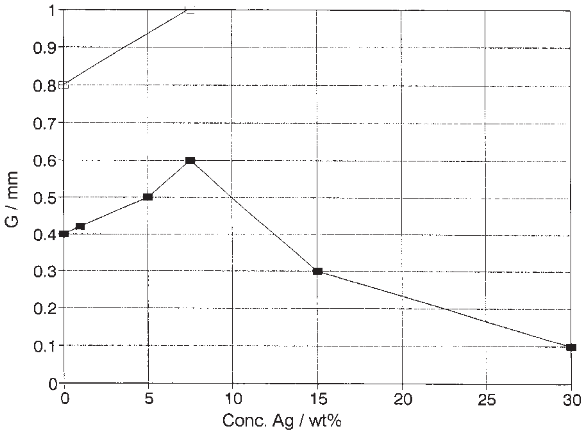

Fig. 4a Grain growth in Y-123/Ag samples (■) and Y-123/Ag/Y-211 30 wt% samples ( ) varying silver concentration

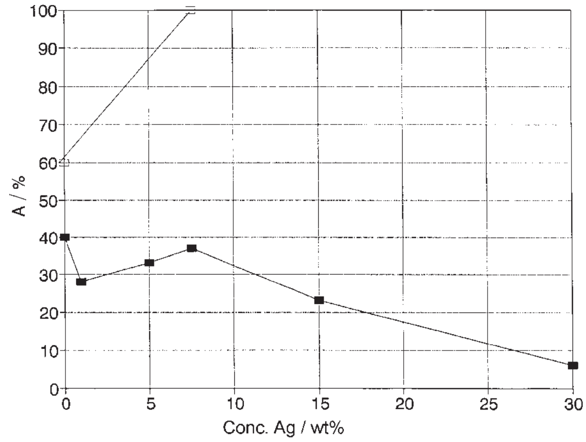

Fig. 4b Grain alignment in Y-123/Ag samplesa (■) and Y-123/Ag/Y-211 30 wt% samples ( ) varying silver concentration

out of the sample, and wetted the alumina boat, while leaving only the indium inside, as observed by SEM-EDAX analysis. In this way, the fluid can exercise its ordering effect on the grain arrangement, and afterwards leave the sample without any apparent reaction with Y-123 phase.

This is confirmed by the DTA–TG analysis data of the Y-123/Ag(In) samples that do not show any significant thermal effect (Fig. 5).

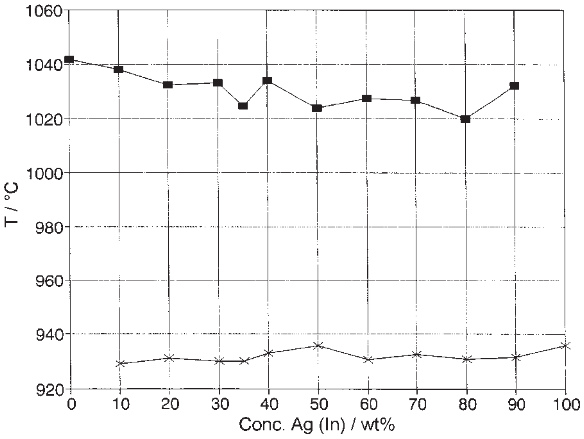

Fig. 5 Thermal effects in Y-123/Ag(In) samples at $P(O_2)$=1 atm: Y-123 peritectic decomposition temperatureand (■) and silver melting temperature (×)

Very good MTG samples were also obtained adding to Y-123 and the silver alloy at 7.5 wt% and the Y-211 phase at 30 wt%. The grain growth and alignment is reported in the micrograpic picture of Fig. 6.

All these reasons suggest that the Ag(In) alloy seems to act as a better fluid bed for the Y-123 superconducting phase.

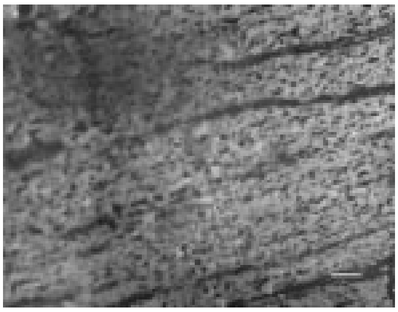

Fig. 6 Micrographic aspect of Y-123 sample with Ag(In) 7.5 wt% and Y-211 30 wt% melt processed at 1170°C. The marker represents 100 μ

Conclusions

Silver is an important additive in $YBa_2Cu_3O_{7-\delta}$ (Y-123) powders for melt processing and growth of oriented polycrystals.

Contrary to what believed in the past, the silver does in effect react with Y-123 melt in the composition around the 35 wt%, showing unexpected behaviour. In fact, to date the addition of Ag to the superconducting phase was believed to have no effect on the structure. Nevertheless, both Ag melting temperature and, mostly, Y-123 peritectic decomposition are deeply lowered for these compositions, producing a similar thermal behaviour to that of an eutectic equilibrium. This reactivity can be greatly limited by the addition of a foreign metal like indium. The Ag(In) alloy (90/10 wt%) does not react with Y-123 in a very high range of compositions, and may therefore act as a better fluid bed for the superconducting phase growth.

At lower concentration (less than 7.5 wt%) Ag allows the orientation of the crystals of the Y-123 phase that nucleates during the cooling process. Unfortunately, the solidification of silver proceeds at higher temperatures when some liquid is still present, if the Y_2BaCuO_5 (Y-211) phase could not completely react with it to form Y-123. In the metallurgical process the presence of this liquid must be avoided. Furthermore, it should be very important to study the possibility of withdrawing the silver just before it solidifies to further improve the connection of the grains.

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