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THERMAL AND MICROSTRUCTURAL ANALYSIS OF THE Y–Ba–Cu–O/Ag EQUILIBRIUM AROUND THE CRITICAL COMPOSITION $YBa_2Cu_3O_x$/Ag 35 MASS%

G. A. Costa and P. Mele

INFM and Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, I-16146 Genova, Italy

Abstract

We studied the Y–Ba–Cu–O/Ag equilibrium diagram in oxygen atmosphere around the composition $YBa_2Cu_3O_x$/Ag 35 mass%. We found a high thermal effect: the peritectic decomposition temperature of Y-123 phase is lowered from 1040 to 940°C. We demonstrate here that the nature of the phenomenon is not chemical. We explained it as the result of a mechanical segregation of Y-123 decomposition products from Y-123 phase, performed by silver.

Keywords: mechanical segregation, silver, superconductor, Y–Ba–Cu–O equilibrium diagram

Introduction

This work is included in a larger research project focused on studying the properties of composites formed by $YBa_2Cu_3O_x$ (Y-123) and silver.

Many works have been realized on Y-123/Ag sintered specimens, concerning both electrical [1, 2] and mechanical properties and also the microstructure development of composites [3, 4]. The silver charges are not enough to solve the weak-link problems of sintered materials, even if silver is useful to provide an electric shunt in the case of superconducting quench. The transport properties of pure Y-123 oxides were enhanced introducing the melt-processing, based on the controlled solidification of the melt [5, 6].

We found that silver additions combined with melt-processing further improve the performances of Y-123 material.

Earlier studies on Y-123 formation and decomposition were performed by standard DTA measurements [7–9]. The investigation of phase distribution [10], thermal properties and phase equilibria [11, 12] are quite important to check possible applications also in Y-123/Ag system. Wiesner *et al.* [13] limited the investigation to the terminal compositions, while in our previous works [11, 12] we checked the whole range of compositions. Even if some authors [14] reported that silver is an inert component for Y-123, we found a strong interaction around 35 mass% of silver [11, 12]: the peritectic decomposition temperature of Y-123 phase is lowered from 1040 to 950°C.

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The aim of this work is to investigate the nature of this interaction in the framework of Y-123/Ag phase diagram.

The study of phase equilibria were performed by DTA/TG measurements. All results were checked by X-ray diffractometry, optical microscopy, SEM and EDAX microanalysis.

Experimental

$YBa_2Cu_3O_{7-\delta}$/silver samples were prepared starting from powders of $YBa_2Cu_3O_{7-\delta}$ (Y-123) and Ag_2O.

Y-123 powders were prepared (by a method well standardised in our laboratory [15]) by the solid state reaction of pure oxides, Y_2O_3 (Johnson Matthey, 2N) and CuO (Merck, 99%). The barium source was BaO_2 instead of the most common $BaCO_3$ in order to avoid carbon contamination.

The sintered pellets obtained so were ground and mixed with the suitable content of Ag_2O (Aldrich, 99%). The silver added to the samples covered a wide range of compositions (starting from 1 to 70 mass%). The silver oxide was used because it is finely subdivided and can be uniformly dispersed in Y-123 powder. Moreover, it easily decomposes at 415°C to metallic silver during the texturing experiments, which reaches much higher temperatures.

The products were subsequently pressed into bars, with dimensions of 40×5×3 mm, to rapidly heated 900, then held at 1080°C for 0.5 h in a horizontal furnace (MTG technique [6]) in flowing oxygen and finally cooled to room temperature at 60°C h^{-1} to avoid the formation of microcracks.

MTG samples were cut into small pieces and polished for micrographic analysis, performed using a Reichert optical microscope equipped with Carl Zeiss lens. A systematic study of the microstructures was also performed in an Oxford scanning electron microscope (SEM) equipped with electron dispersive spectroscopy (EDS). Surface and cross-section images were taken to observe the final microstructures formed after the melt-texturing process.

The thermal analysis of the different samples were carried out on a Netzsch STA 409 apparatus: 100 mg of the material, ground and sieved, were transferred into an alumina crucible, and then DTA/TG runs were carried out at a fixed heating rate (10°C min^{-1}). The reference (Al_2O_3) and the sample cells were open to surrounding gas atmosphere (P_{O_2}=1 atm). According to ICTAC recommendation, the extrapolated onset temperature is used in this paper as the reaction temperature.

Results and discussion

It is well known that the oxygen partial pressure plays an important role in all oxide decompositions. In particular, Y-123 phase decomposition temperature was measured at 1030°C in pure O_2, 1000°C in air and 940°C in high vacuum [16].

We chose Y-123/Ag composites at P_{O_2} =1 atm, because Y-123 textures are usually performed in flowing oxygen. As described in the experimental section, in our system, Y-123 was prepared starting from BaO_2 and other oxides. The absence of carbon impurities explains why we observed for the pure phase a decomposition temperature higher than in other cases, where Y-123 was formed by the citrate reaction [13].

The results of DTA/TG analysis are summarised in Fig. 1. It is clear that strong interactions between the two phases occur, at least in the region around 35 mass% Ag, although it is reported [14] that the addition of Ag to the superconducting phase has no effects on the structure and properties. In fact, peritectic decomposition of Y-123 is strongly affected by a high content of Ag , around the 35 mass%, showing a decrease from 1040 to 945°C. A slightly similar effect, around the same composition, is shown by the melting temperature of Ag, that decreases from about 940 to 930°C.

We did not observe any thermal effects around Ag 5 mass% composition, as elsewhere reported. [13, 17, 18]. On the contrary, the silver fusion temperature seems to be poorly affected by Y-123. In fact, when we textured Y-123 samples in the presence of a silver content around 7.5 mass%, we did not find silver in the ceramic grains, but only at the grain boundaries [11, 12]. Moreover, we did not find silver contaminations from Y-123 or from its decomposition products.

The micrographic optical analysis of the silver distribution in the samples revealed that the samples with silver content under 5 mass% appeared almost without visible silver aggregates, except flakes at the grain boundaries [19]. Increasing the silver content, the metal collects into well separated small islands embedded in Y-123 matrix. The size of the islands is roughly proportional to the silver content [11]. We also found that around 35 mass% of silver, the aggregates appear as spheres connected to each other to form a complex network. The morphology of the silver drops was widely described elsewhere [10].

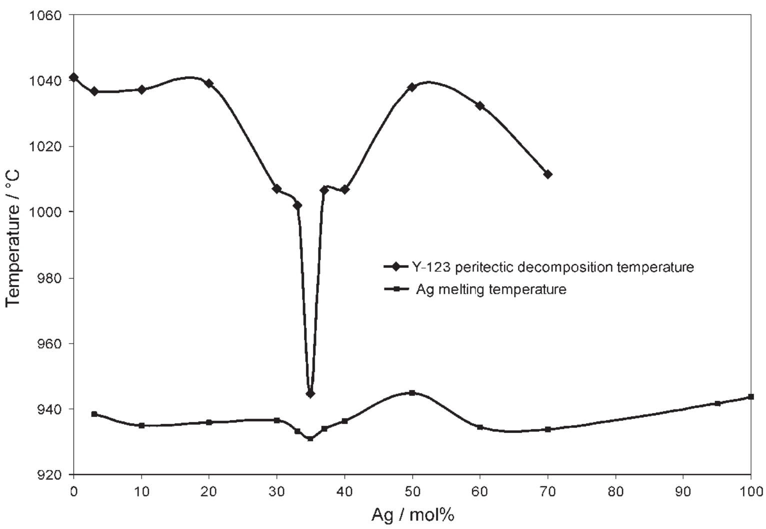

Fig. 1 Y-123 decomposition temperature and Ag melting temperature measured at increasing silver contents

The micrographic SEM investigations revealed that at the critical composition (Y-123/Ag 35 mass%), and for this only, a black phase is situated as round aggregates inside the silver particles. This phenomenon happens in all silver particles of this composition. Each silver particle contains one or more black smaller particles (Fig. 2).

Fig. 2 SEM picture of a silver island in Y-123/Ag 35 mass% sample

At higher magnification, we found that those black inclusions in turn contain further silver inclusions. The line analysis (Fig. 3) clearly reveals that the black phase in the silver islands contains a big amount of Cu, less Ba and only traces of Y. This means that the black phase is not Y-123, but Y-123 decomposition products, such as $BaCuO_2$. This is

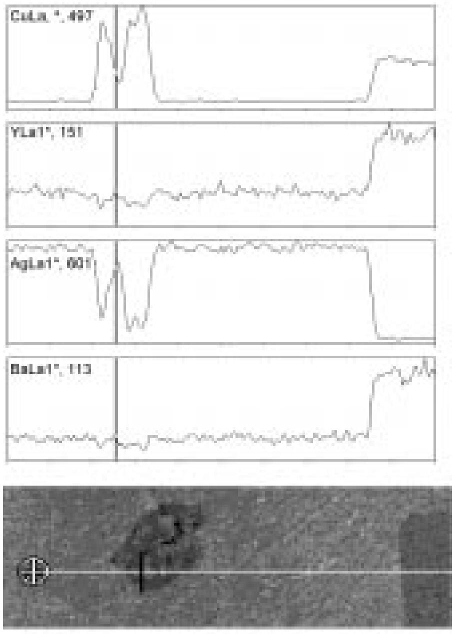

Fig. 3 Profile analysis of Cu, Y, Ag and Ba along the white line. The black inclusion is the same reported in Fig. 2

easily clarified remembering that, after the thermal MTG program, the involved phases are changed. Before the reaction, we had well mixed Y-123 and Ag_2O powders. At the typical temperatures reached in the melt-textured process (1180°C), silver remains fluid for a certain amount of time, while the peritectic decomposition of Y-123 gives Y-211 green phase, which remains in the solid state, and two (Ba, Cu) rich phases, which, on the contrary, are liquids. The black phase outside the silver islands are constituted of Y-123 phase, as clearly appeared from the EDAX spectra.

The point that has to be explained is the correlation between the (Ba, Cu) rich inclusions in the silver islands and the strong fall in the peritectic decomposition temperature.

From the thermal analysis of pure Ag_2O we observed that the decomposition occurs at around 420°C, when the stoichiometric mass loss is 6.64%. The oxygen adsorption is easier in melted silver than in the solid one. In fact, we also observed that at 943°C the system adsorbs oxygen, because its mass increases by 0.24% (Fig. 4). This value is in agreement with some literature data [20] where the silver content of the system is reported to be 0.25% at 943°C in the silver/oxygen phase diagram.

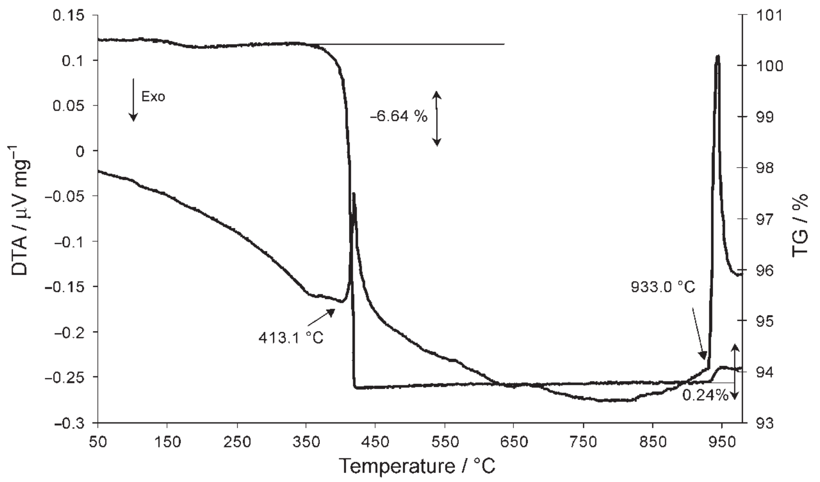

Fig. 4 DTA/TG analysis of pure Ag_2O

Considering those observations, we made a comparison between the thermal analysis performed on the critical composition and the thermal analysis of two nearby compositions, with silver contents of 33 and 37 mass% (Fig. 5).

In both side compositions we observe two thermal effects. The first one can be ascribed to the oxygen adsorption by melted silver, that we recognised in Ag_2O curve at around 933°C. The second one is the peritectic decomposition peak of Y-123 phase. The two effects are separated by 80°C.

At the central composition, the two effects happen almost without separation, in the temperature range of 10°C only: this means that silver adsorbs oxygen, but tends to rapidly release it in the presence of the decomposition products. At the side compositions, silver releases oxygen later, because at higher peritectic temperature the amount of decomposition products is higher.

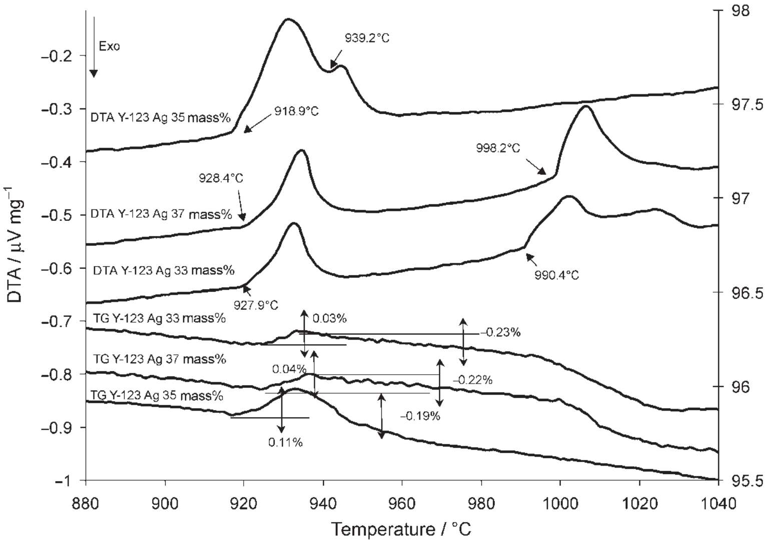

Fig. 5 DTA/TG curves for three Y-123/Ag mixtures with 33, 35 and 37 mass% Ag

The strong fall in temperature that happens at 35 mass% silver content could be correlated to a eutectic interaction between Y-123 (or another phase of the Y–Ba–Cu–O system, such as its decomposition products) and silver. On the other hand, the presence of the silver drops, that we found at this critical composition in

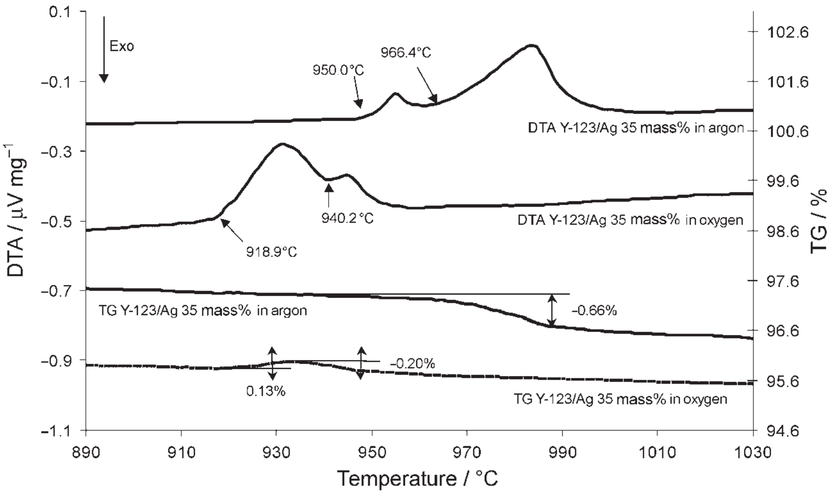

Fig 6 DTA/TG curves given in the range 900–1020°C for Y-123/Ag in oxygen and in argon

Y-123 matrix, could be connected to a globular-morphology. It is one of the characteristic eutectic microstructure, that is widely reported in all metallographic handbooks [21, 22].

It is useful to compare two DTA/TG analyses of the critical composition in oxygen and in argon atmosphere (Fig. 6): in the second case there is no oxygen absorption from silver, but only mass loss due to Y-123 decomposition. On the other hand, when we repeated the thermal analysis on powders of the critical composition and ball-milled for 1 and 2 h, we found the thermal effect in both cases (Fig. 7). This demonstrated that the fall in temperature was not due to a non uniform mixing of the starting phases.

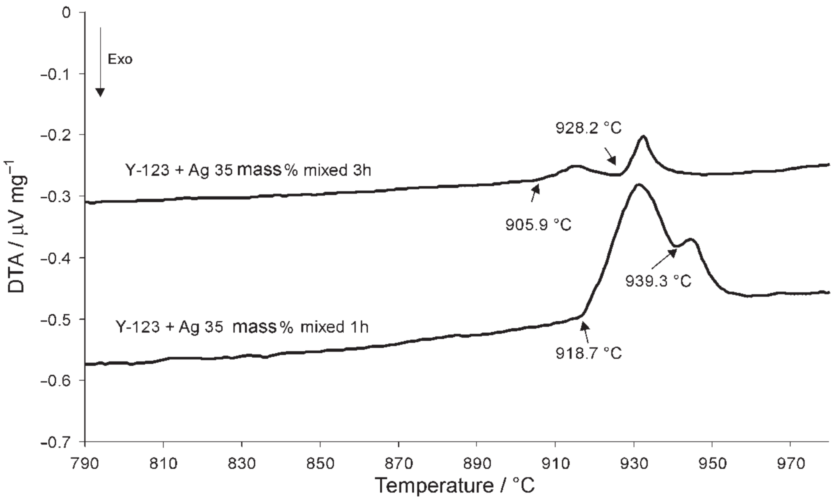

Fig. 7 DTA profiles performed on Y-123/Ag 35 mass% powders differently mixed

The curves reported in Figs 6 and 7 allow us to discard the hypothesis that the thermal effect could be explained invoking any chemical interactions between the involved phases.

Here is useful to remember that, after the thermal MTG program, the involved phases are completely different from the initial ones. At the beginning, we had well mixed Y-123 and Ag_2O powders. The typical temperatures reached in the melt-textured process (1180°C) allow that silver remains fluid for a certain amount of time, while Y-123 peritectic decomposition follows the complex equilibrium

$$\text{Y-123(S)=Y-211(S)+L1+L2}$$

where L1 and L2 are two (Ba, Cu) rich phases [23].

Because of different densities (10.5 g cm^{-2} for Ag and 6.38 g cm^{-2} for Y-123), those phases should completely stratificate. We demonstrated elsewhere [12] that the silver presence highly favors the orientation of the crystals of Y-123 phase that nucleates during the cooling process. In this case, Y-123 decomposition products tend to segregate at the grain boundaries. This situation can be considered true only for silver contents lower than the critical one (35 mass%). The metal and the decomposition products of Y-123 and Y-123 are reported as mutually inert phases by some authors (Aswal *et al.* [14]). They correctly discarded any chemical interaction between silver and Y-123. But there is a special kind of interaction, related to the gravitational force and to different densities of the involved species. The metal, that has high superficial tension, tends to collect into drops, and the situation is freezed out when the samples are cooled. This starts to happen at a silver content <35 mass%, but only at this specific content silver is able to separate the liquid decomposition products from Y-211 solid phase. This segregation results in the formation of the black globular inclusions and allows Y-123 to decompose at the lowest peritectic temperature.

When the silver content is higher than 35 mass%, the drops start to connect to each other, giving huge aggregates. Using the Laplace equation [24], and neglecting the influence of other fluids present in the system, we estimated for the silver drops an internal pressure around 10 atm (for drops with 20 μm diameter). So, a possible way of avoiding this effect is to carry out the texturing process of Y-123/Ag composites under high pressures.

Conclusions

We definitively conclude that notwithstanding the high thermal effect, no chemical reaction takes place in Y-123/silver system. But hydrostatic forces are able to remove some liquid decomposition products promoting further decomposition of Y-123 phase. This is a special system where density and gravitational forces are assumed of enormous importance. It could be the subject to study the phase segregation in space in microgravity conditions.

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