Development of Granular Structure in $Cu_{90}Co_{10}$ Ribbons Through Furnace and Current Annealing

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***Abstract*—On-line measurements of resistance and temperature in melt-spun $Cu_{90}Co_{10}$ ribbons are made using two different annealing techniques: conventional furnace annealing, and linearly varying current Joule heating. The aim of this paper is to consider the electrical current, flowing through the sample during the annealing, as a possible parameter to control thermal treatment parameters and thus the microstructure of these systems. Although an exact way to obtain the temperature from the annealing current remains a difficult task, the on-line changes in resistance with current allows one to identify structural changes in the sample during annealing. Also, because the temperature is found to increase continuously with electrical current, it is possible to calibrate the Joule heating system to precisely determine the annealing temperature.**

***Index Terms*—Joule heating, binary alloys, nanocrystalline materials.**

I. Introduction

JOULE heating techniques, based on thermal effects of an electrical current flowing through a metallic ribbon or wire, are conceptually simple and experimentally versatile [1]. These unconventional thermal treatments are very useful to produce a great quantity of samples in order to make a systematic investigation on the development of the materials microstructure. Typcally, a pulse of electrical current is applied through the sample where a great fraction of the heat released by the Joule power increases sample's temperature. Depending on the current amplitude and its time duration, the sample can undergo structural transformations [1]. When current is varied rather slowly, it allows one to control, for example, these transformations through on-line monitoring of the resistance of the materials while current is increasing [2]. Also, it has been shown that Joule heating techniques are especially useful to develop off-equilibrium nanocrystalline structures with improved magnetic and mechanical properties [3], [4]. Furthermore, CuCo granular samples treated with this technique have systematically shown higher magnetoresistance ratios, when compared to samples annealed by conventional furnaces [5].

Despite the extreme experimental simplicity of Joule heating, and the excellent physical properties obtained by using appropriate currents and times of treatment, some hindrance to its widespread use has been caused by the intrinsic difficulty to determine the temperature achieved by the samples. This is important to control the transformation kinetics and to carry out similar thermal treatments in different samples. A theory of dc Joule heating in amorphous ribbons was proposed recently [1], [6], [7], allowing one to estimate the temperature achieved by the ribbon through the variations in its electrical resistance. Although the theory included a detailed analysis of the effects of crystallization (in the case of amorphous ribbons), it is extremely difficult to theoretically predict (or calculate from experimental curves) the changes in temperature during thermal treatment. In order to gain some insight on the relationship between the applied current intensity and the attained temperature during the treatment, additional measurements must be performed, which, however, are difficult to perform or they bring about modifications in the experimental conditions [4]. In this paper we compare the results of electrical resistance measurements obtained from conventional furnace annealing and Joule heating on melt-spun $Cu_{90}Co_{10}$ ribbons. In this way, one extracts hints about the effective heating rates, the structural transformations and therefore the treatment temperatures. The main result is that temperature always increases with the applied current. This result allows one to control the annealing temperature by monitoring the electrical current flowing through the sample.

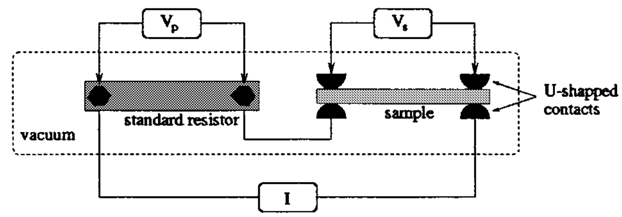

Fig. 1. Linear varying current Joule heating setup.

II. Experimental Setup

Melt-spun $Cu_{90}Co_{10}$ ribbons (10 cm long, 5 mm wide and $\approx 25\ \mu$m thick), kindly supplied by P. Tiberto and F. Vinai, were produced at the Istituto Elettrotecnico Nazionale Galileo Ferraris, Torino, Italy. We applied the technique of on-line monitoring the sample's resistance while increasing the electrical current step-by-step ($\delta I = 0.1$ A, $\delta t = 10$ s). We used the four probe technique (Fig. 1) with minimized U-shaped contacts. The annealing current is controlled through the voltage drop V_p across a standard resistance of 1 mΩ and the sample's resistance is straightforwardly obtained by measuring the voltage

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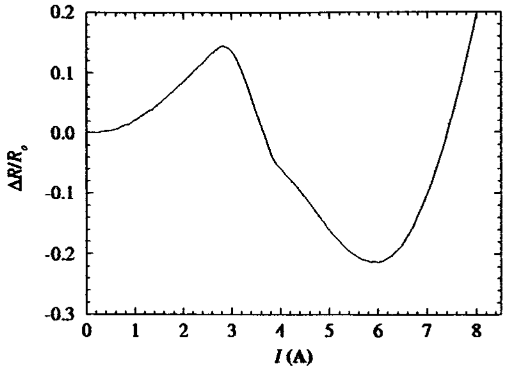

Fig. 2. Typical variation of the resistance relative to its room temperature value $\Delta R/R_o$ versus the applied current I during Joule heating of as quenched $Cu_{90}Co_{10}$ ribbon.

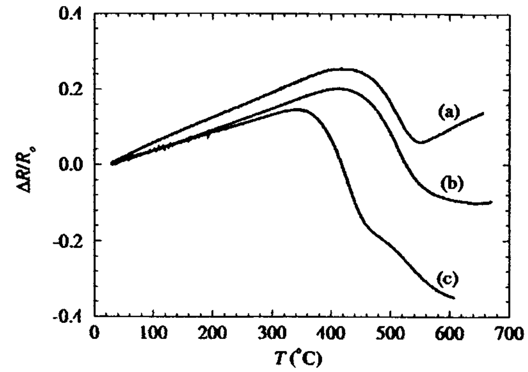

Fig. 3. Variation of the resistance relative to its room temperature value $\Delta R/R_o$ versus temperature T curves during furnace annealing of three different as quenched $Cu_{90}Co_{10}$ samples. The three samples were submitted to diferent heating rates: 77°C/min (a), 50°C/min (b), and 2.5°C/min (c).

drop in the sample (V_s). The experimental setup is fully controlled by a computer, which allows one to choose the current steps and their duration, and the final electrical current. Also, it is possible to interrupt the treatment at any desired point, and one can choose between an abrupt interruption (quenching), or a slow decrease of the applied current. The samples were kept in vacuum to avoid oxidation and all except radiative thermal losses. This technique was recently introduced and denominated linearly varying current Joule heating (LVC-JH), which is extremely sensitive to follow and control the grain coalescence in granular systems [2], [8]. Measurements of the sample's resistance were also performed as a function of the temperature during isochronal lamp furnace heating in Ar atmosphere with different heating rates, to compare with the LVC-JH results. The results are generally expressed as relative changes of the electrical resistance in comparison with the room temperature value ($\Delta R/R_o$).

III. Results and Discussions

The as-cast sample is in a metastable solid solution configuration due to the quenching above melting temperatures [8]. This metastable state changes to a more ordered state during thermal treatments at high enough temperatures. The corresponding behaviors of $\Delta R/R_o$ as a function of the applied current I (Fig. 2) and as a function of the temperature T (Fig. 3) are very useful to characterize these structural changes: Co precipitation starts after an initial heating stage in which the resistance displays a parabolic dependence on the current and a linear dependence on the temperature, which is a typical metallic behavior. The temperature coefficient of resistivity ($\alpha = (\Delta R/R_o)/(T - T_o)$), that is, the slope of the $\Delta R/R_o$ versus T curve, continuously increases with rising heating rate. The values extracted from Fig. 3 are $\alpha = 4.8 \times 10^{-4\circ}\mathrm{C}^{-1}$ (a), $\alpha = 5.6 \times 10^{-4\circ}\mathrm{C}^{-1}$ (b), and $\alpha = 6.7 \times 10^{-4\circ}\mathrm{C}^{-1}$ (c). For the Joule heated sample, $\alpha = 2.1 \times 10^{-3\circ}\mathrm{C}^{-1}$, as obtained by fitting a parabola to the initial segment of the R vs I curve of Fig. 2.

The LVC-JH technique produces heating rates comparable to the ones attained by the lamp furnace under uniform heating conditions. For slow increase of current as in the present case ($\delta I/\delta t = 0.01$ A/s), the average heating rate is ≈35°C/min. However care must be taken when considering this average value in certain special points such as in the begining of the treatment (≈20°C/min) and during the begining of precipitation (≈70°C/min).

Note that the Co precipitation using the furnace setup starts at lower temperatures for smaller heating rates simply because the heating times are longer enough for the structure to relax to a more ordered state. Therefore, as the heating rate increases, the inflexion of the $\Delta R/R_o$ versus T curve is gradually converted into a minimum similar to the minimum of the $\Delta R/R_o$ versus I curve.

In order to properly characterize the changes of the alloy's granular structure, we made a series of LVC-JH treatments quenching the samples at different annealing stages and then measuring their hysteresis loops and the magnetoresistance ratios at room temperature [2], [8]. We observed that the same processes that occur during the treatment from the maximum to the minimum of the $\Delta R/R_o$ versus I curve occur from the maximum to the inflexion point of the $\Delta R/R_o$ versus T curve. Precipitation of small, superparamagnetic Co rich granules starts near the first maximum and continues until the vicinity of the minimum or inflexion point. At this stage, practically all Co atoms contribute to the saturation magnetization and the density of granules and the magnetoresistance ratios have their maximum values [2], [9]. Beyond the minimum or inflexion point a coarsening occurs rapidly, the precipitates become much larger, and the density of granules and the magnetoresistance ratio drops abruptly [8]–[10]. It has been shown that the rapid increase of the resistance observed for high electrical currents (or high temperatures) is owing to the redifusion of Co atoms back to the Cu matrix [8]. Furthermore, it is possible to "freeze" the high temperature nanostructure by switching off the applied current, which produces a kind of quenching of the off-equilibrium state [8]. In this way, it is possible to appropriately control the final nanostructure by properly choosing the final annealing current and the cooling rate of the system down to room temperature.

Three small thermocouples were attached on the surface of a probe Joule heated sample to test the uniformity of the thermal treatments and to measure the temperatures achieved for each applied current. These thermocouples were placed one at the middle of the sample, and the other two symmetrically placed

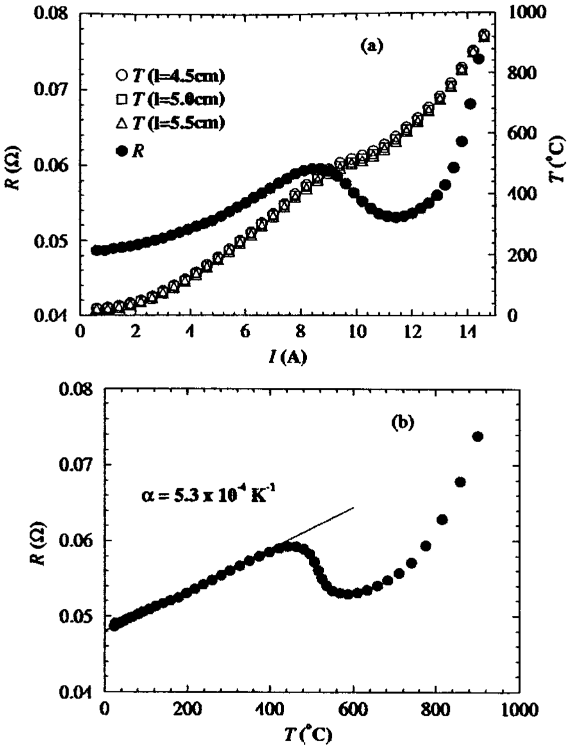

Fig. 4. Resistance and temperature measurements during linearly varying current Joule heating: R versus I and T versus I curves (a). Crossing the data one obtains the relationship between R and T (b), which is the final calibration curve of the system.

at 0.5 cm from the middle of the sample. Fig. 4 shows the direct relationship between the applied current and the temperature of the sample, giving a complete idea about the LVC-JH. This figure can therefore be used as a reference to unequivocally associate a given electrical current with a definite temperature: the higher the applied current, the higher the reached temperature. Notice that the initial portion of the resistance curve [Fig. 4(a)]shows the expected metallic behavior, with a clear parabola up to 7.5 A. Crossing the resistance and temperature data, one observes a linear relationship in this range [Fig. 4(b)] For higher currents (between 7.5 and 10.5 A) the temperature continues to increase, but with a reduced pace. In this region the precipitation and growth of the Co clusters occurs, reducing the resistivity of the sample, and therefore the released Joule power. Notice, however, that the increase of the applied current surpasses the effect of the reduction in the total resistance, and the temperature increases continuously as a function of the electrical current. For higher currents, the derivative of the T versus I curve increases again, reflecting the effect of the redissolution of Co atoms back in the Cu matrix.

There are many interesting features that are worth noticing. Joule heating is an extremely versatile technique to perform fast thermal treatments in metallic materials, allowing one to tailor different microstructures for specific purposes. Besides the characteristics depicted above, it is important to stress that annealing times of the order of less than one minute are usually enough to produce the desired result. Also, the thermal inertia found in many conventional furnaces here does not appear, and a rather rapid quenching from a very high temperature can be performed, without moving the sample from its position and following the resistance variations on-line. As expected from theoretical considerations and experimental data on other systems, Joule heating promotes very homogeneous thermal treatments, as seen in Fig. 4 for thermocouples placed in different positions of the sample. We tried to place the thermocouples in many other points, in order to verify the extension of the homogeneity region. Near the extremes (where the electrical contacts are done), the temperatures achieve much lower values due to the high thermal conductivity of Cu. However, we concluded that the temperature is almost the same in about 60% of the central portion of the sample. Also, we have exhaustively repeated the thermal treatments (indeed, more than 100 Joule heating runs were performed), and the repeatability of the resistance curves is astonishing [8]. They can be used as reference curves, to determine the stage of precipitation of one sample, or, if the sample was calibrated in a similar way as done in Fig. 4(b), to determine the temperature of one particular sample.

IV. Conclusion

In conclusion, although Joule heating is not an isothermal treatment, and it also depends on the structural changes that occur during the annealing, it is possible to follow the changes of temperature during the treatment, when it is performed rather slowly. The electrical resistance measured during the annealing procedure gives important information about the evolution of the granular structure. In particular, for $Cu_{90}Co_{10}$ samples we have observed that LVC-JH gives practically the same information as those obtained by conventional furnace annealing. We have also measured the temperature changes during the Joule heating procedure, and an accurate calibration of the system could be performed. We have also found that the temperature profile of these samples is homogeneous in about 60% of the central region of the samples and that the heating rates and final temperatures are substantially higher than those obtained by conventional furnaces.

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