

# Kinetic effects in the mixed $\beta$ to $\beta'_3 + \gamma'_3$ martensitic transformation in a Cu–Al–Ni shape memory alloy

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## Abstract

A single crystal with a selected composition of a Cu–Al–Ni shape memory alloy, undergoing two martensitic phase transformations when cooling from the common parent phase,  $\beta_3 \rightarrow \beta'_3 + \gamma'_3$ , has been studied by adiabatic calorimetry. As the coexistence of two different martensites has a strong influence on the transformation kinetics, both the forward and the reverse phase martensitic transformation have been carefully studied by means of very low thermal rate dynamic thermograms. Temperature memory effects have been observed in the  $\beta'_3$  transformation but not in the  $\gamma'_3$  one. Finally, radiation-cooling procedures were used to study the forward transformation and showed the interaction between the two types of martensite variants on the nucleation processes. This last technique was found useful to evaluate the latent heat released at each individual nucleation event, throughout the transformation progress. The consequent sample self-heating alters this process, which dramatically affects the  $\beta'_3/\gamma'_3$  ratio and the final martensitic state.

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## 1. Introduction

Among the wide variety of shape memory alloys (SMAs), the Cu-based ternary alloys such as Cu–Al–Ni and Cu–Zn–Al have been the subject of many experimental and theoretical studies mainly focused on the thermoelastic martensitic transformation (MT) (see Refs. [1–3] for reviews). As is well known [4–10], Cu–Al–Ni alloys exhibit a first-order diffusionless transformation, either by cooling or stress-induced, from the austenitic parent high-temperature cubic phase  $\beta_3$  (L2<sub>1</sub>, space group:  $Fm\bar{3}m$  [11] to the monoclinic  $\beta'_3$  (space group:  $C2/m$ ) [12] or orthorhombic  $\gamma'_3$  (space group:  $Pmmm$ ) [13,14] low-temperature martensitic phases. The presence of  $\beta'_3$  or  $\gamma'_3$  and even the simultaneous coexistence of both phases mainly depends on the alloy composition. Previous studies have established a reliable phase diagram, which identifies the expected martensitic

phases and the transformation temperatures for a fixed alloy composition under specific thermal treatments [15–18]. The simultaneous nucleation of  $\beta'_3$  and  $\gamma'_3$  phases and their mutual interaction have also been widely studied [5,8,19]. These phases are the result of a similar shear lattice distortion of the cubic parent phase but some differences in the  $\beta_3 \rightarrow \beta'_3$  and  $\beta_3 \rightarrow \gamma'_3$  intrinsic transformation enthalpies have been reported [20]. Other authors [6,21] also found this quantity to be different between the forward and the reverse MT. Nevertheless the successive thermal cycling also alters the relative amounts of  $\beta'_3$  and  $\gamma'_3$  phases when both are present [4]. Moreover a phenomenological model, which accounts for the elastic energy stored in the martensite variants, has been proposed [7].

In addition to the shape memory, superelastic and pseudoelastic effects, these alloys also present a temperature memory effect (TME), which appears after an incomplete reverse MT. This effect is characterized by a neat delay of the thermally induced transformation to higher temperatures where an additional calorimetric peak

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appears [22–24]. As a consequence, partial cycling also modifies the transformation kinetics. Finally, the forward and reverse stress-induced MT also shows the so-called thermal effect, which is associated with the latent heat [25,26]. This explains the dependence of the stress–strain curves on the strain rate in superelastic tests [27,28], but this effect has no relation to the TME. As regards the forward MT, the thermal effect is due to the heat dissipation, which increases the sample temperature when a high enough strain rate is applied. In these conditions the transformation can be considered as quasi-adiabatic. The same effect can be observed in the thermally activated forward MT during cooling experiments, where noticeable alterations of the fixed cooling rates can be expected.

The aim of this work is to provide a satisfactory procedure to account for the mixed  $\beta_3 \leftrightarrow \beta'_3 + \gamma'_3$  MT anomalous kinetics, by using an adiabatic calorimeter in various operating modes. The standard mode is used to study the kinetics of the reverse MT associated with the TME and the interactive double nucleation in the forward MT. On the other hand, the thermal effects associated with the abrupt latent heat dissipation of the  $\gamma'_3$  plate nucleation can be also studied, by using a non-standard mode. For these purposes a Cu–Al–Ni sample, in which both  $\beta'_3$  and  $\gamma'_3$  variants coexist, has been selected.

## 2. Experimental

A single crystal of chemical composition 82.0% Cu–14.0% Al–4% Ni (wt.%) (hereafter CAN2) has been selected. The crystals were grown using the Stephanov method and show a chemical composition accuracy and sample homogeneity better than 0.1% for the three metals. The sample was annealed at 1173 K for 30 min and then quenched into ice–water. Finally, it was aged at 353 K for 24 h in order to stabilize the atomic order [29], avoiding further evolution of the transformation temperatures [30].

The specific heat at constant pressure of CAN2 was measured by adiabatic calorimetry from 80 to 340 K. A large calorimeter vessel was used to accommodate a few single-crystal bars obtained from the same crystal growth process. The total sample mass was  $m = 77.316$  g. In these conditions the signal/noise ratio is high enough to allow detailed observation of the nucleation kinetics in the forward MT. The experimental setup has been described in Refs. [31,32] and permits various experimental procedures to be used. In the following we proceed to briefly describe these techniques because a precise understanding of the experimental results and data treatment is required to give a correct interpretation of the thermal behaviour around the MT when non-conventional procedures are performed. The most common way to measure the specific heat is the discontinuous heating method, or the pulse technique: the amount of heat  $\Delta Q$  required to attain a final equilibrium state at  $T_f$  from a previous one at  $T_i < T_f$ , is carefully measured and then the mean specific heat at  $T_m = \frac{T_i+T_f}{2}$  is determined by:  $C_p^*(T_m) = \frac{\Delta Q}{T_f-T_i}$ , where  $C_p^*$  is the sample plus

calorimeter vessel total heat capacity. This technique is appropriate to define the calorimetric curve for the whole temperature range, and provides the most accurate sample specific heat values ( $C_p$ ), which in our experimental setup attains 0.1% from 50 to 330 K. However, this procedure has two shortcomings: (i) to maintain the  $C_p$  accuracy,  $T_f - T_i$  should be higher than 1 K but this limits the curve resolution and (ii) it cannot be used on cooling. Nevertheless, the  $C_p$  resolution can be improved around the phase transformation regions by means of dynamic thermograms. It should be noted that these measurements are not performed between equilibrium states and, in some cases, they do not provide reliable  $C_p$  values. However, careful control of the electrical heater permits heating rates as low as  $0.1 \text{ K h}^{-1}$ , which approaches thermal equilibrium conditions. By using this method, the sample specific heat  $C_p$  is determined from:

$$Pdt = C_p^*dT = (C_{cal} + mC_p)dT \quad (1)$$

where  $P$  is the supplied heating power,  $C_{cal}$  the calorimeter heat capacity, and  $m$  the sample mass. Routine temperature data acquisition establishes the temperature vs. time function. The  $dT/dt$  drift values can be obtained by means of various smoothing procedures depending on the experimental conditions and the required resolution.

The power can also be supplied by heat transfer between the sample vessel and the adiabatic shield by means of a controlled thermal imbalance  $\Delta T$  (usually a few K). This can be achieved by a fixed EMF offset ( $\Delta\varepsilon$ ) in the main thermocouple circuit. In this case, the continuous and dynamic techniques also give the possibility to perform cooling measurements. The use of the adiabatic controllers guarantees  $\Delta T$  ( $\sim \Delta\varepsilon$ ) to be constant within very narrow margins (a few mK). The power exchange can be described by the conduction ( $\propto \Delta T$ ) and radiation ( $\propto T^4$ ) terms:

$$\begin{aligned} P &= A'\Delta T + B'[(T + \Delta T)^4 - T^4] \\ &= A'\Delta T + B'[(T^4 + 2T^3\Delta T + 3T^2\Delta T^2 + 2T\Delta T^3 - T^4)] \\ &\cong A + BT^3 = C_p^*(T) \frac{dT}{dt} \end{aligned} \quad (2)$$

where the approach is valid for  $\Delta T \ll T$ . If the specific heat values and the temperature drifts at temperatures  $T_1$  and  $T_2$ , (usually below and above the phase transformation temperature) are known, we obtain values for the constants  $A$  and  $B$  from the expressions:

$$B = \frac{C_p^*(T_1) \cdot \left(\frac{dT}{dt}\right)_1 - C_p^*(T_2) \cdot \left(\frac{dT}{dt}\right)_2}{T_1^3 - T_2^3} \quad (3)$$

$$A = C_p^*(T_2) \cdot \left(\frac{dT}{dt}\right)_2 - BT_2^3 \quad (4)$$

and, at any interpolated temperature  $T_i < T_i < T_2$ :

$$C_p^*(T_i) = \frac{(A + BT_i^3)}{\left(\frac{dT}{dt}\right)_i} \quad (5)$$

from which  $C_p(T_i)$  can finally be calculated.

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