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Low temperature isothermal ageing in shape memory CuAlNi single crystals

Rosana Gastien[a,*], Cristina E. Corbellani[a], Patricia B. Bozzano[b], Marcos L. Sade[c,d], Francisco C. Lovey[c]

[a] Dto. Ciencia y Técnica de Materiales, Instituto de Investigaciones Científicas y Técnicas para la Defensa (CITEFA), J.B. de La Salle 4397, (1603) Villa Martelli, Buenos Aires, Argentina
[b] Lab. de Microscopía Electrónica, Centro Atómico Constituyentes-Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, (B1650KNA) San Martín, Buenos Aires, Argentina
[c] Grupo Física de Metales, Centro Atómico Bariloche-Comisión Nacional de Energía Atómica e I.Balseiro (U.N. de Cuyo), (8400) S.C. de Bariloche, Río Negro, Argentina
[d] Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina

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ABSTRACT

Some CuAlNi alloys can undergo martensitic transformations by cooling or by applying stress from a metastable β body-centred cubic (bcc) phase. These martensitic transformations are responsible for the shape memory and pseudoelastic effects that these alloys present. Low temperature isothermal ageing of this metastable β phase can favor the culmination of an ordering process and the decomposition into stable phases. These two processes can generate changes in both thermally and stress-induced martensitic transformations, modifying the characteristic martensitic transformation temperatures, the type of induced martensitic phases, the critical stress and the hysteresis width of the martensitic transformations.

1. Introduction

In some CuAlNi alloys, a metastable β body-centred cubic (bcc) ordered phase can be obtained at room temperature from the high temperature disordered β phase after an appropriate quenching treatment. The ordered β phase (sometimes called β_1) can undergo martensitic transformations by cooling (thermally induced martensitic transformations) or by applying stress (stress-induced martensitic transformations) [1–4]. These martensitic transformations are responsible for the shape memory and pseudoelastic effects that these alloys present.

The type of thermally induced martensite depends mainly on the chemical composition of the alloy [5]. When the martensitic transformation is stress induced, the type of martensite obtained depends on factors such as chemical composition, crystal orientation, type of applied stress and test temperature [6–8].

Low temperature isothermal ageing of this metastable β phase can cause the decomposition into the stable phases α (fcc) or γ (bcc), depending on the chemical composition of the alloy. The kinetics of precipitation also depends on temperature and duration of the ageing treatment [9–11]. The presence of precipitates in the β matrix generates changes in thermally induced martensitic transformations, modifying the characteristic martensitic transformation temperatures, the type of induced martensitic phases and the hysteresis width [12–15]. Another contribution, specially for an increase of the transformation temperatures for shorter time treatments, can be attributed to an ordering process that would take place during ageing, assuming that some kind of disordering is present after quenching from the high temperature β phase. The aim of this work is to present experimental results concerning the effect of low temperature ageing on the martensitic transitions in CuAlNi single crystals.

2. Experimental procedure

The Cu–14.3Al–4.1Ni (wt.%) alloy was prepared from 99.99% Cu and 99.99% Ni by melting in an arc furnace under argon atmosphere, adding 99.99% Al to the primary alloy by melting in a resistance furnace. The resulting Cu–Al–Ni ingots were cut and the single crystals grown by the Bridgman method in sealed vycor tubes. The single crystals were solution treated at 1173 K for 1 h and then quenched into water at 273 K, to obtain a metastable β phase at RT.

Thermal treatments on samples extracted from these crystals were performed on a resistance furnace, at 423 and 473 K for different periods: 1, 10 and 100 h. After that, the samples were air cooled.

To control the characteristic martensitic temperatures upon thermal treatments, electrical resistance was measured as a function of temperature by the four-wire method on plate-shaped samples, in order to analyze the change of the transformation temperatures and the morphology of the hysteresis involved. These characteristic temperatures are M_s, M_f, A_s and A_f (M_s and M_f indicate the start and ending of the martensitic transformation. A_s and A_f indicate the start and ending of the reverse transformation to the β phase). The hysteresis width is calculated as $(M_s - A_f)$.

Mechanical tests were performed to follow the evolution of the stress-induced martensitic transformations. Tensile tests were carried out in a MTS Sintech 2/DL Machine, under well-controlled temperature conditions in a MTS 651 Environmental Chamber on plate-like samples. The specimens were mechanically (SiC, 600 and

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* Corresponding author.
E-mail addresses: rgastien@citefa.gov.ar (R. Gastien), corbellani@citefa.gov.ar (C.E. Corbellani), pbozzano@cnea.gov.ar (P.B. Bozzano), sade@cab.cnea.gov.ar (M.L. Sade), lovey@cab.cnea.gov.ar (F.C. Lovey).

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1000 grit) and electrolytically polished (in 15% nitric acid in methanol at 293 K, 10 V) before mechanical tests.

The microstructure of the samples was analyzed by transmission electron microscopy using a Philips CM200 Transmission Electron Microscope (TEM), operating at 100 and 200 kV.

3. Results and discussion

The spontaneous martensitic transformation for the chemical composition Cu–14.3Al–4.1Ni (wt.%) is the $\beta \leftrightarrow \gamma'$ transition, with a typical hysteresis width of around 30 K. Thermal treatments of 1, 10 and 100 h at 423 K were done on samples belonging to the same single crystal, and the variation of the martensite start temperature (M_s) with the duration of the thermal treatments is shown in Fig. 1. It can be noticed that M_s increases with time ageing at 423 K.

Thermal treatments at 473 K of 1, 10 and 100 h were performed on samples of the same chemical composition. The spontaneous martensitic transformation showed not only an increase of the martensite start temperature but a change in the morphology of the curves, and according to previous results [3] it can be inferred that the $\beta \leftrightarrow \gamma'$ transition (before ageing) changes to $\beta \leftrightarrow \beta'$ for the thermal treatment of 100 h at 473 K, as can be seen in Fig. 2(a)–(d).

On the other hand, to study the effect of low temperature ageing treatments on the stress-induced martensitic transformations, tensile pseudoelastic cycles were performed at different temperatures, to construct the so-called σ–T diagrams [4]. For the purpose of this paper, only the $\beta \leftrightarrow \beta'$ transitions were studied, as this transformation shows well defined stress–strain curves, with an hysteresis width around 4 MPa. Pseudoelastic cycles before and after thermal treatments can be seen in Fig. 3. A σ–T diagram for a particular chemical composition and orientation of the tensile axis can

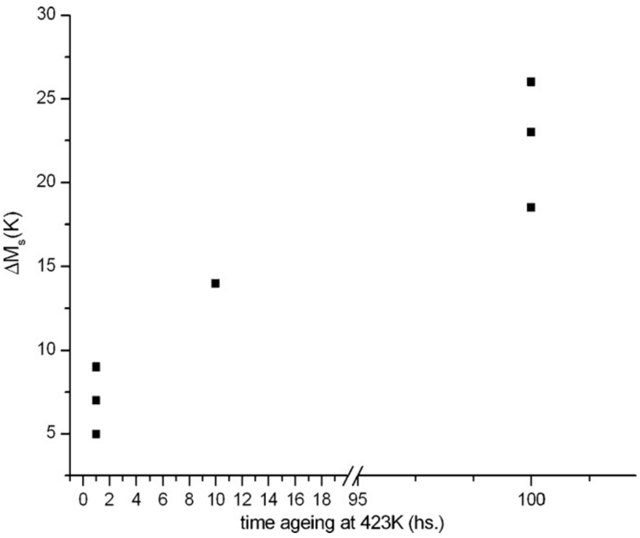

Fig. 1. Change of the martensite start temperature (M_s) with time ageing at 423 K, for different samples of Cu–14.3Al–4.1Ni (wt.%).

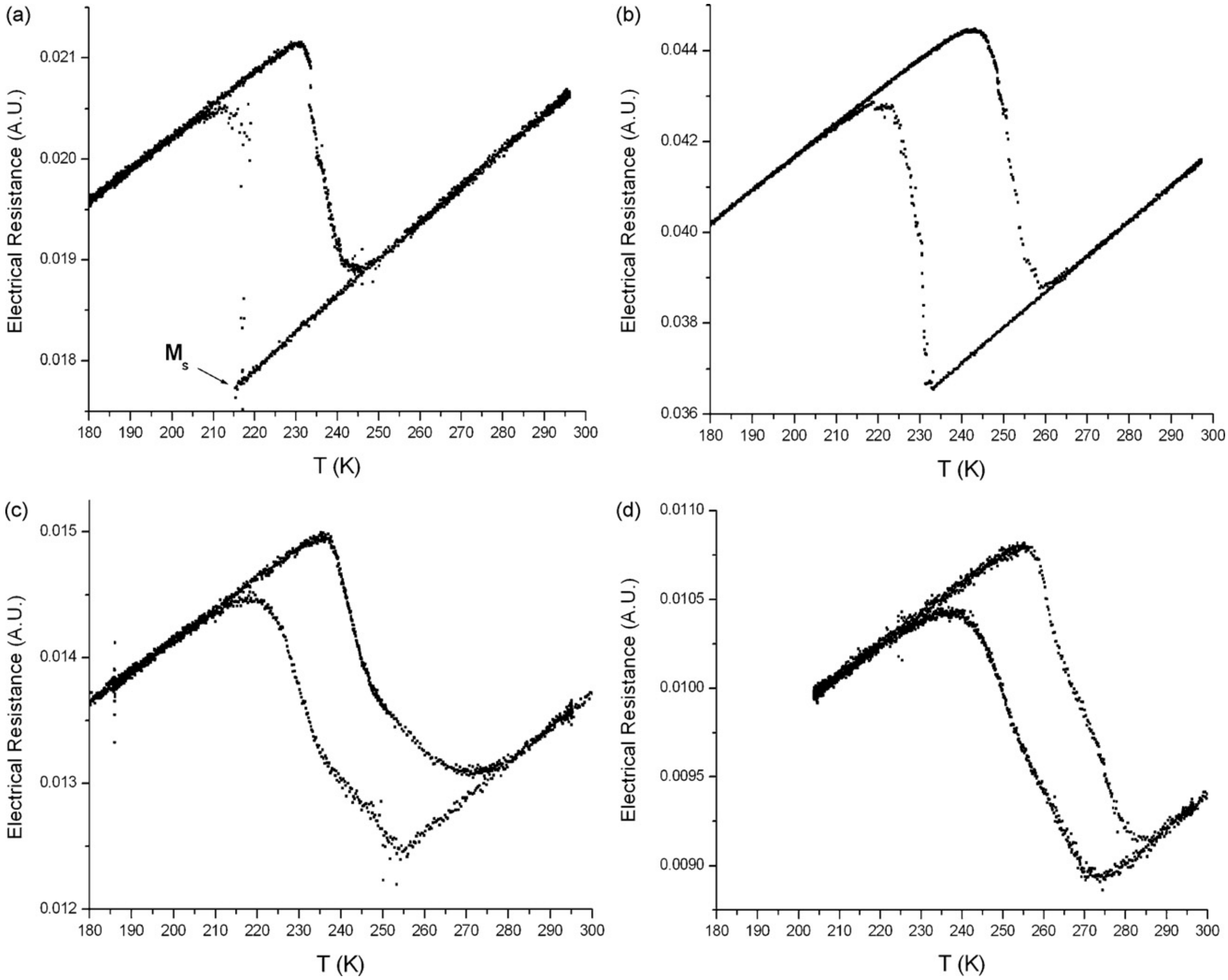

Fig. 2. Electrical vs. temperature measurements (a) before ageing treatment, (b) after 1 h at 473 K, (c) after 10 h at 473 K, and (d) after 100 h at 473 K.

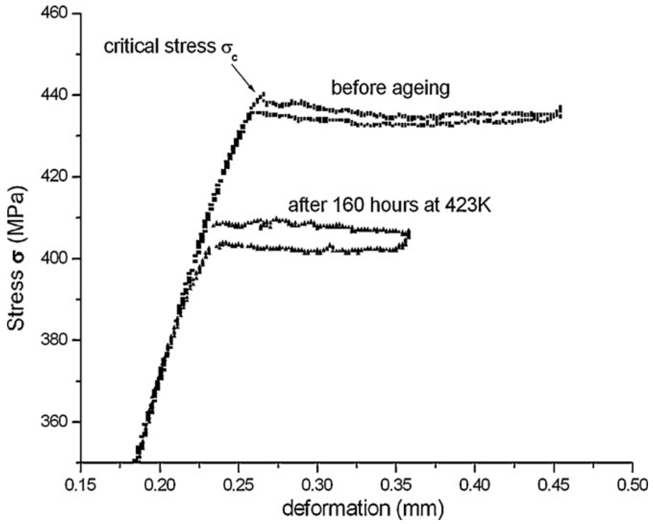

Fig. 3. Pseudoelastic cycles (β ↔ β′ transition) before and after 160 h at 423 K, performed at 323 K.

be drawn, determining the critical stress (the stress at which the martensitic transformation starts) for each temperature. Following this procedure, β ↔ β′ lines before and after the thermal treatments were drawn for each sample. An example is shown in Fig. 4 for a sample aged 10 h at 423 K. It can be observed that the transformation line moves to the right when the sample is subjected to a thermal treatment, i.e. for the same test temperature, the sample transforms to martensite at a lower stress. It can be observed that the slopes of both curves are the same, indicating that the entropy change between β and β′ remains constant after the thermal treatments.

The effect of pseudoelastic cycling was studied as follows: samples subjected to 10 and 70 h at 423 K were cycled through the β ↔ β′ transition up to 350 cycles at 330 K. Neither changes in the critical stress nor in the hysteresis width were observed during cycling. This indicates that once the critical stress to transform has decreased due to the thermal treatment, the main parameters which characterize the stress-induced transition do not change up to 350 cycles.

An additional experiment was designed to study the effect of low temperature treatments on the stress-induced martensitic transformations. Instead of performing cycles at different temperatures, one cycle was made at a particular temperature, called T_1 (temperature high enough to induce β′ martensite). Then the sample is subjected at various thermal treatments, performing only a few pseudoelastic cycles to control the critical stress and hysteresis width of the β ↔ β′ cycle between each treatment. The experimental steps were as follows:

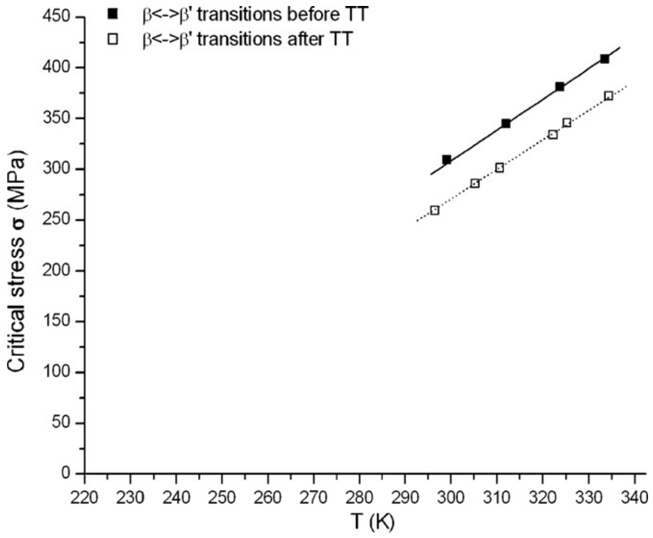

Fig. 4. Critical stress vs. temperature for β ↔ β′ transitions before and after 10 h at 423 K.

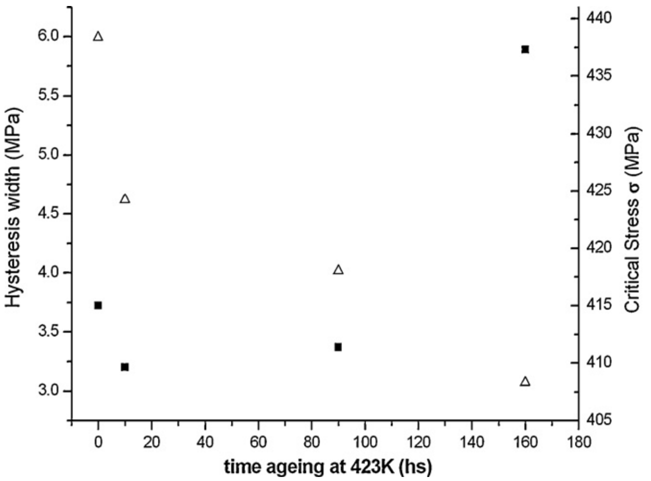

Fig. 5. Hysteresis width (full square) and critical stress (open triangle) vs. time ageing at 423 K for pseudoelastic β ↔ β′ transitions.

1. One pseudoelastic cycle at T_1.
2. TT1: 10 h at 423 K.
3. Pseudoelastic cycles at T_1.
4. TT2: 90 h at 423 K.
5. Pseudoelastic cycles at T_1.
6. TT3: 60 h at 423 K.
7. Pseudoelastic cycles at T_1.

The variation of the hysteresis width and the critical stress of the cycles at T_1 are shown in Fig. 5. It can be noted that the critical stress decreases with the quantity of hours the sample is subjected to the thermal treatment. On the other hand, the hysteresis remains constant until at least 100 h of ageing at 423 K, when ordering prevails in structural modification, but for 160 h of thermal treatment, the hysteresis width increases abruptly.

The microstructure of the specimens was studied by transmission electron microscopy observations. Fig. 6 corresponds to a sample subjected to 100 h at 423 K. Small precipitates of approximately 30 nm can be observed.

The presence of small precipitates in the β matrix can be the responsible of the increase in the martensitic transformation temperatures. If these precipitates correspond to γ phase, as many authors suggested [13,14], the β phase around the precipitates would have lower aluminum content, increasing the transformation temperatures [5]. This reduction of aluminum content can be the reason of the change in the induced martensite observed in Fig. 2, as the chemical composition of the β matrix changed. Phase diagrams reported in [5] indicate that the β matrix for this chemical composition has to transform to β′.

Recently, Suresh and Ramamurty [15] suggested that a possible cause for the precipitation is the coalescence of the quenched-in vacancies that result in compositional gradients due to a local decrease in the Al concentration. This favors the formation of precipitates of high aluminum content, in whose vicinity nucleation of martensite occurs at a higher M_s temperature. This reasoning can also be used to understand the decrease of the critical stress after thermal treatment, as the martensitic transformation lines in the

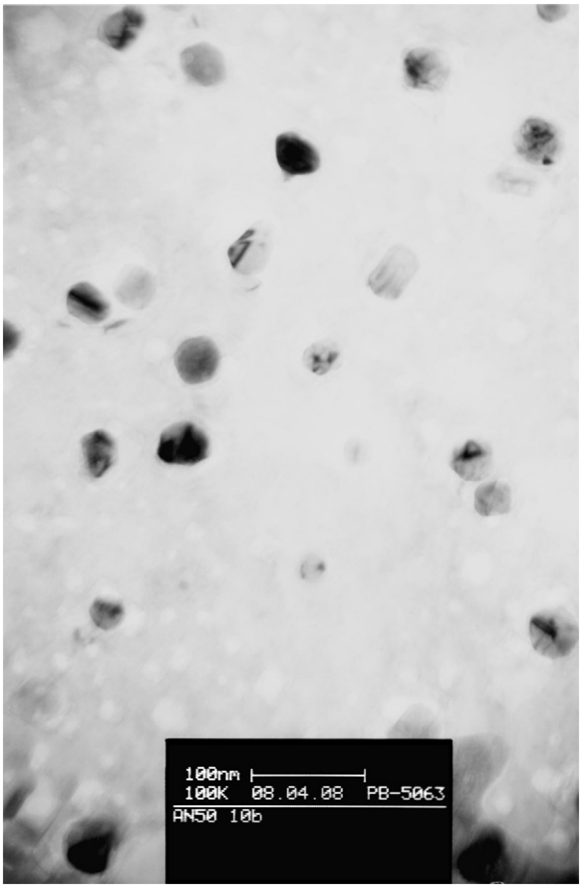

Fig. 6. Transmission electron microscopy micrograph of an specimen subjected to 100 h at 423 K. The white line indicates 100 nm.

σ–T diagrams would have to move towards the high temperature zone and consequently, decreasing the critical stress to transform.

The presence of small precipitates after 100 h at 423 K (Fig. 6) can be the reason for the important increase of the hysteresis width observed in samples after 160 h at this temperature (Fig. 5), indicating that the precipitates observed after 100 h of ageing probably increased their size and density.

The increase of the martensitic transformations temperatures in samples subjected to ageing treatments shorter than 100 h at 423 K can be attributed to an ordering process that would take place during ageing, assuming that some kind of disordering is present after quenching [16,17].

4. Conclusions

Low temperature ageing in CuAlNi single crystals generates changes in the martensitic phase transitions induced from the metastable β phase. These changes are evidenced in the thermally induced transformations as an increase in the martensite start temperature and a change in the type of martensite induced. On the other hand, for the stress-induced transformations, a decrease of the critical stress in addition with an increase of the hysteresis width of the pseudoelastic cycles were observed. For thermal treatments of the order of 100 h at 423 K, these changes are probably due to the presence of small precipitates of stable phases into the β matrix. For shorter ageing times the increase of the martensitic transformation temperatures can be attributed to an ordering process that would take place during ageing, assuming that some kind of disordering is present after quenching.

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