A TWO-STAGE TRANSFORMATION IN Cu-Zn-Al SMA WIRES

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Abstract: *Actually, some compositions of Cu-Zn-Al alloys are commercially available with the potential to present shape memory properties after a suitable thermomechanical treatment. For applications as sensor and/or actuator, the smallest product of Cu-based shape memory alloys (SMA) are wires with 0.5mm in diameter. In this work, Cu-25.3Zn-4.0Al (wt%) wires with 0.5mm in diameter were supplied by Societé Tréfimetaux (France) without martensitic transformation due to the fabrication process. After betatization of the wires, physical characterization was carried out by means of optical micrograph, DSC and X-ray diffraction while the thermomechanical behavior of the samples was verified by thermal cycling under constant load. The obtained results have demonstrated the apparition of a two-stage transformation rarely observed in these shape memory alloys.*

Keywords: *Shape memory alloys, Cu-Zn-Al alloys, Thermomechanical behavior.*

1. Introduction

Shape memory phenomena presented by a variety of metallic alloys, named shape memory alloys (SMA), are associated to a thermoelastic reversible martensitic transformation (Otsuka & Wayman, 1998). The shape memory effect (SME), superelasticity (SE) and rubber-like behavior (RLB) properties, directly associated to this special phase transformation, are the main macroscopic characteristics of interest for development of industrial and medical applications (Otsuka & Wayman, 1998). It is known that this transformation can occurs in two-steps, both in Cu-based and Ti-Ni-based SMA. Recently, Otsuka & Ren (2005) reviewing the physical metallurgy of Ti–Ni-based alloys has explained two-stage transformations occurring in these binary and ternary alloys. Ti-Ni and Ti-Ni-Cu SMA can transform from austenite to martensite in two-stages following the sequence B2 (cubic) – R (rhombohedral) – B19' (monoclinic) and B2 – B19 (orthorhombic) – B19', respectively. Two-stage transformations affect physical and thermomechanical properties. In Ti-Ni-based SMA's, for example, the B2 – R – B19' and B2 – B19 – B19' are responsible by the appearance of a second peak during DSC calorimetric measurements and discontinuities in the electrical resistivity behavior as a function of temperature (Otsuka & Ren, 2005). These microscopic effects are directly associated with macroscopic changes in the stress-strain (σ - ε) and strain-temperature (ε - T) behaviors during the two-stage transformations. Similar behaviors can be observed in Cu-based SMA. However, successive martensitic transformations in these alloys are mainly linked to stress induced martensites during pseudoelasticity, as verified in Cu-Al-Ni alloys (Otsuka *et al*, 1979). In these alloys, the austenitic β phase first transforms under mechanical load in a $\gamma_1{}'$ (hexagonal) martensite, which, by increasing applied stress changes for a new different martensitic structure named $\alpha_1{}'$ (FCC). A similar behavior can be observed in Cu-Al-Be SMA, where austenitic β phase first transforms under mechanical load in a $\beta_1{}'$ (orthorhombic) and further in the $\alpha_1{}'$ martensite (Gonzalez, 2002). Recently, Gastien *et al* (2005) has demonstrated a clear competition between β' and γ' martensitic phases in thermal and pseudoelastic $\beta \leftrightarrow \beta' + \gamma'$ cyclings for Cu–14.1Al–4.2Ni (wt%) single crystals. Mechanical loading directly in martensite structure also can originate a two-stage transformation, as demonstrated recently by Gonzalez (2002) in Cu-Zn-Al single crystals. However, successive transformations in Cu-Zn-Al SMA are rarely observed during both, single thermal cycling and thermal cycling under constant load.

In this work, a two-stage martensitic transformation in Cu-Zn-Al SMA wires was initially detected during DSC tests as a first small peak during cooling followed by a second more energetic peak. To confirm this successive transformation, thermal cycles under constant load were performed for applied stresses between 10 and 110 MPa. The ε - T curves have demonstrated that the presence of this two-step transformation is favored by the applied load during cooling and heating.

2. Experimental procedure

The material used in this study had been obtained as commercial Cu-25.9Zn-4.0Al (%wt) alloy wires with 0.5 mm diameter from Societé Tréfimetaux in France. Wire samples were solution treated in β-phase condition at 900°C for 10 min (betatization) and quenched in air. Microstructures were observed using a Nikkon optical microscope. The crystalline structure was characterized by X-rays diffraction (XRD) using a Siemens D-5000 diffractometer with Cu-Kα radiation (λ= 0.15418 nm). Phase transformation and thermal stability were verified by means of a Mettler TA-3000 DSC instrument at heating – cooling rate of 10 °C/min. The shape memory effect under constant load was measured with a thermomechanical apparatus specially designed by the first author for this task (De Araújo, 1999). In this apparatus, thermal cycles are performed by a thermo-controlled silicone oil bath while sample is loaded by a dead weight. The deformation of the wire sample is continuously measured by a LVDT displacement sensor. All sample lengths for these tests were of the order of 27 mm.

3. Results and discussions

Figure 1 shows optical micrographs revealing large grains distributed longitudinally along the as-quenched wire. Figure 1(a) clearly demonstrates that grain sizes can be as large as the wire diameter. The Fig. 1(b) shown that microstructures into grains consist of plate-like and V- shaped martensites. Figure 1(b) also shows that some of these martensite plates are internally twinned.

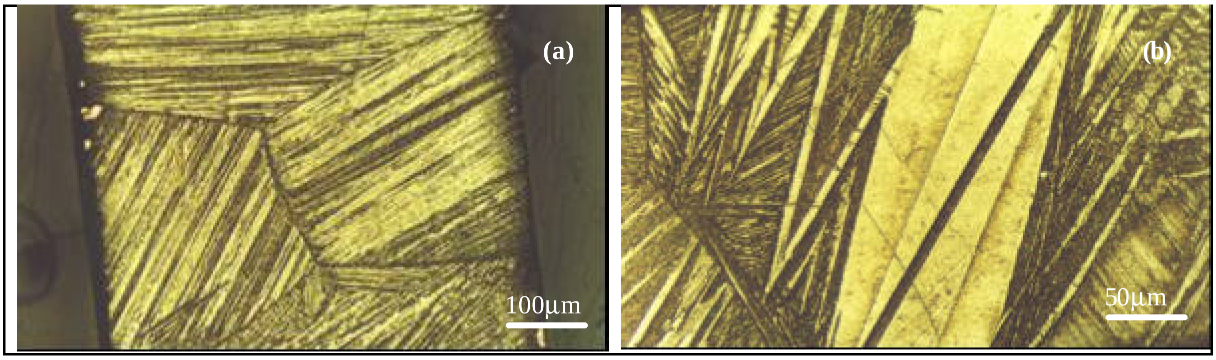

Figure 1 - Optical microscope images showing the microstructures of as-quenched wire. (a) Plate-like martensites. (b) Plate-like and V-shaped martensites.

The X-ray diffraction pattern showed in Fig. 2 confirms that the structure of the wires is fully martensitic, without traces of β and α phases. This XRD pattern is typical of an orthorhombic martensitic structure β_1' (Jolley & Hull, 1964; Lee & Kim, 1990), which was indexed as indicated in Fig. 2.

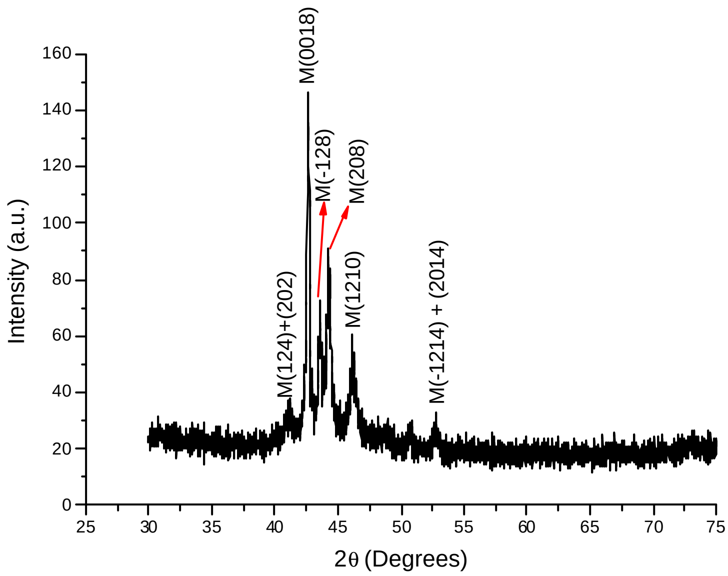

Figure 2 – XRD pattern of as-quenched wires.

Some days after betatization and air quench, the martensitic phase transformation was studied by DSC. Figure 3 show the first and second thermal cycle for the as-quenched wires, with transformation temperatures determined using the tangent method. By comparison of Figs. 3(a) and 3(b), it is verified a larger energetic peak occurring at about A_p = 74.7^{o}C during heating for the first thermal cycle. This peak can be attributed to the reversion of stabilized martensites, which starts at A_s = 57.2^{o}C and finishes at A_f = 91.5^{o}C. Stabilization of the martensitic phase is a phenomenon that can appear in Cu-based SMA after quench due to the presence of vacancies (Gonzalez, 2002). After reversion of stabilized martensite variants, transformation occurs normally in the temperatures indicated in figure 3(b) for the second thermal cycle. However, Figs. 3(a) and 3(b) also show that martensitic transformation in the wires occurs in two steps during cooling and heating, both presenting a reduced thermal hysteresis (~2^{o}C). The first transformation is detected as a small peak starting at M_s' temperature during cooling and the second corresponds to a high sharp peak starting at M_s. The reversion of the first direct transformation appears clearly during heating, finishing at A_f'.

Figure 4 reveal the effect of a few number of thermal cycles on the phase transformation. As indicated in Fig. 4(a), the two-stage transformation detected in the second DSC thermogram (Fig. 3b) is practically unaffected by cycling. Transformation temperatures as a function of the number of thermal cycles are summarized in Fig. 4(b). In this figure, several drops in the reverse transformation temperatures (A_s e A_f) after the first thermal cycle is due to elimination of stabilized martensites, as confirmed by the larger peak detected during this cycle (Fig. 3a).

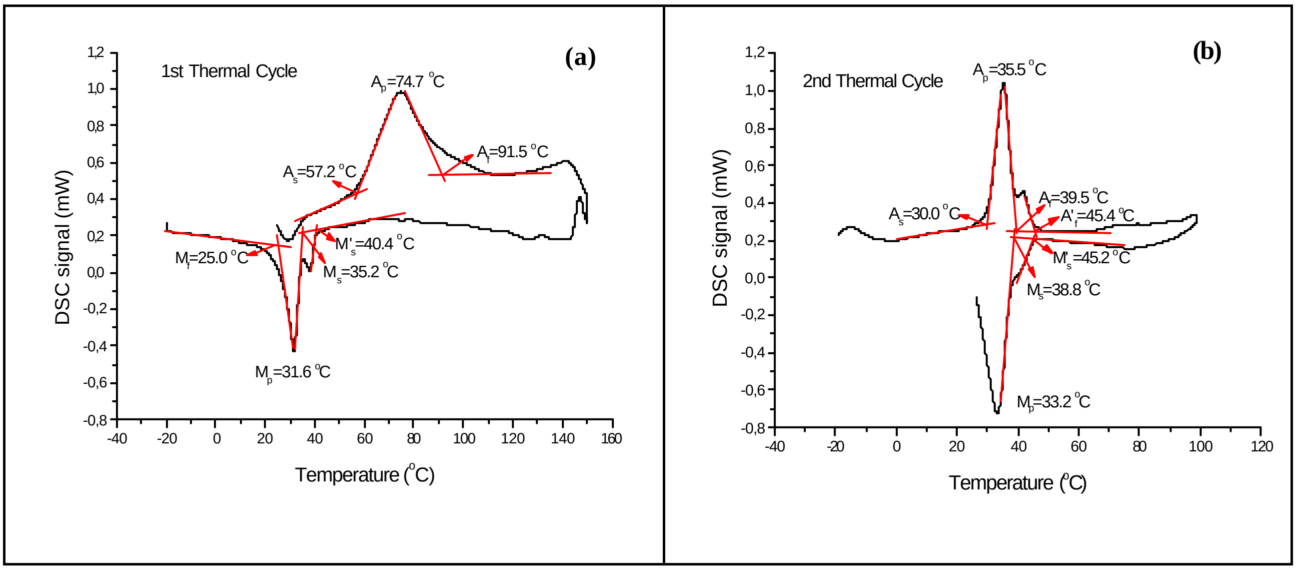

Figure 3 – DSC thermograms for the as-quenched wires. (a) First thermal cycle. (b) Second thermal cycle.

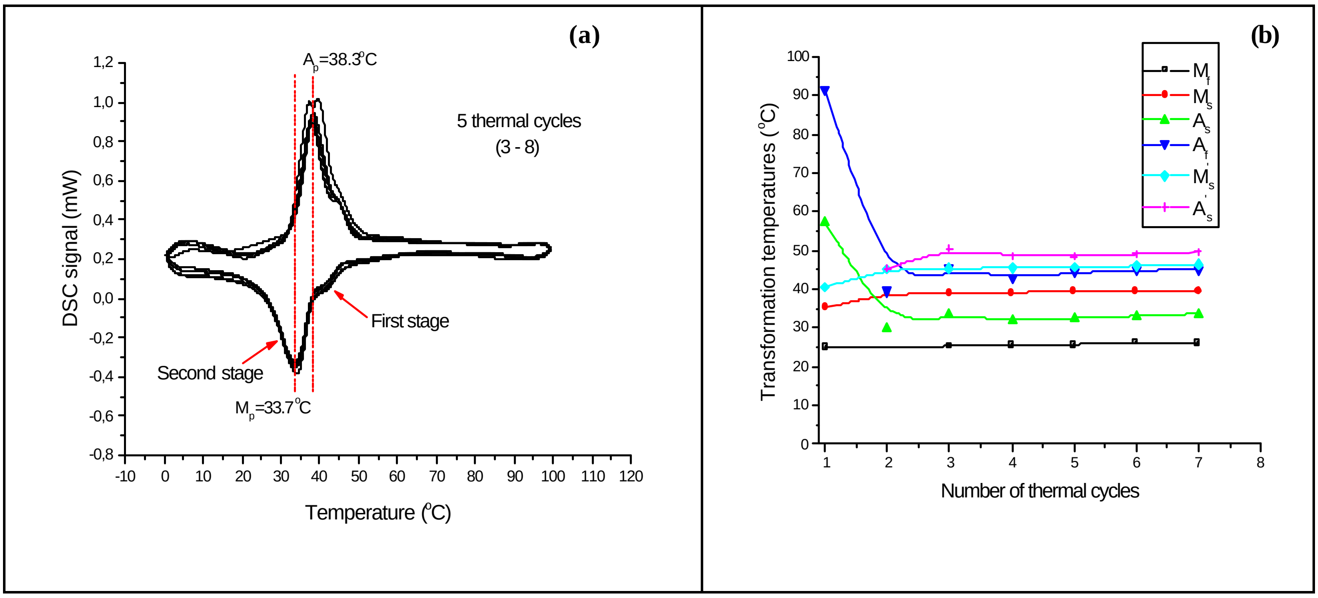

Figure 4 – Effect of thermal cycling on the transformation of as-quenched wires. (a) Superposition of five thermal cycles. (b) Transformation temperatures for the transformation in two stages.

To verify the influence of the mechanical loading on the two-stage transformation detected initially by DSC, thermal cycles under constant load (dead weight) were performed. Figure 5 show the displacement (ε) versus temperature (T) behavior for some applied stress (σ). The sequence of Figs. 5 (a, b, c, d) reveals clearly the increase of transformation temperatures, improvement of the shape memory effect (SME) under load and the presence of the two-stage transformation. It can be verified more clearly from Fig. 5(c) that the first stage transformation under cooling is characterized by a deviation in ε - T curve starting at M_s' = 74.0°C. The second stage start at M_s = 64.3°C and finishes at M_f = 33.7°C. Reversion of this two-stage transformation during heating is defined on the ε - T loop by the critical temperatures A_s = 44.9°C, A_f = 75.8°C and A_f' = 87.0°C. These figures also confirms that reversion of this two-stage transformation originates a first contraction region defined by the ($SME-SME_1$) displacement followed by a second one defined by SME_1. For all applied stresses, residual strain (ε_{plast}) after heating was very limited, except for σ = 101.8 MPa as shown in figure 5(d).

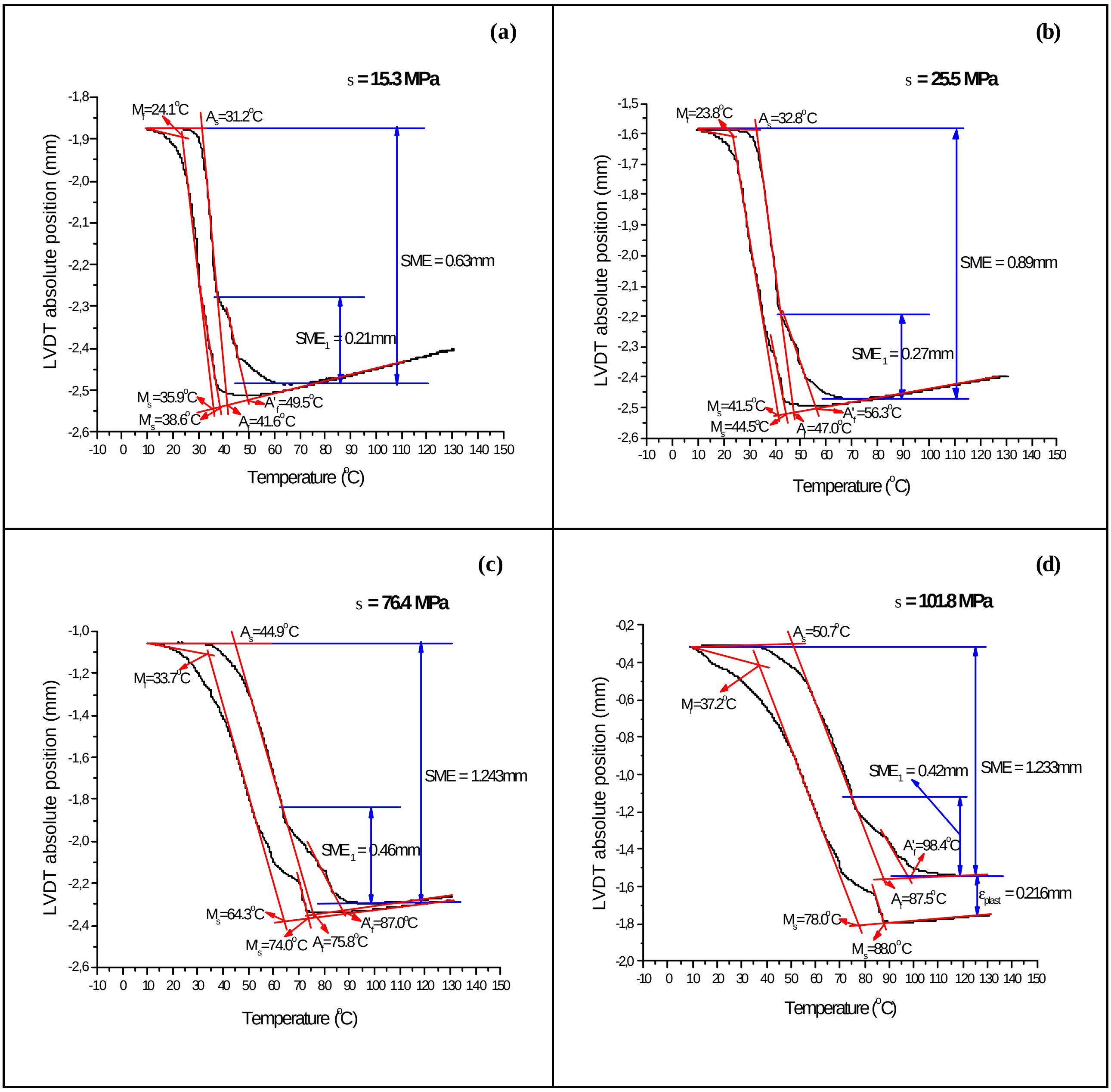

Figure 5 – Displacement versus temperature loops for some applied stresses. (a) σ = 15.3 MPa. (b) σ = 25.5 MPa. (c) σ = 76.4 MPa. (d) σ = 101.8 MPa.

In general, the coexistence of two martensites like β' and γ' in Cu-based SMA is characterized by different hysteresis, i.e., about 5–10 and 30–40 °C for the β - β' and for the β - γ' transition, respectively (Gastien *et al*, 2005). Therefore, the transformation associated to the ε - T loops shown in Fig. 5 is related to a unique β - β' transition. A possible explanation for the two step transformation observed in Figs. 3 and 5 is probably related to the order configuration changes phenomenon observed in copper-based alloys (Gonzalez, 2002). In fact, the first DSC of Fig. 3(a) confirms martensite stabilization. After the first cycle, martensite is total or partially destabilized. One hypothesis for the apparition of two peaks in Figs. 3 and 4(a) is due to the presence of the β' martensite with two different orders that during heating transforms to β-phase with two different orders (lattice correspondence martensite – austenite) (Gonzalez *et al*, 2003; Gonzalez *et al*, 2004). This ordering difference probably originates the two-step transformation during cooling and heating in the studied Cu-Zn-Al SMA wires.

Important shape memory parameters like SME, transformation temperatures and thermal hysteresis can be extracted from Fig. 5. The behavior of SME as a function of applied stress is presented in Fig. 6. It is observed an increase of the total SME from 2.2 % to 4.5% between 15.3 MPa and 101.8 MPa. The shape memory displacement corresponding to the reversion of the first stage (SME_1) saturates with applied stress at the same time that total SME. This behavior is attributed to an optimization of orientation of martensite variants by increasing applied stress.

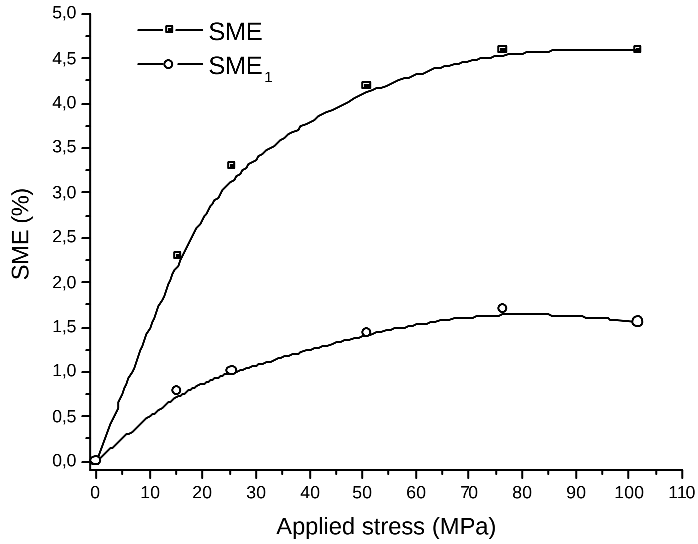

Figure 6 – Shape memory effect as a function of applied stresses.

The ε - T curves showed in Fig. 5 indicate that thermal hysteresis can be defined as the temperature difference A_s - M_f. Figure 7 shows the behavior of thermal hysteresis and transformation temperatures as a function of the applied stress.

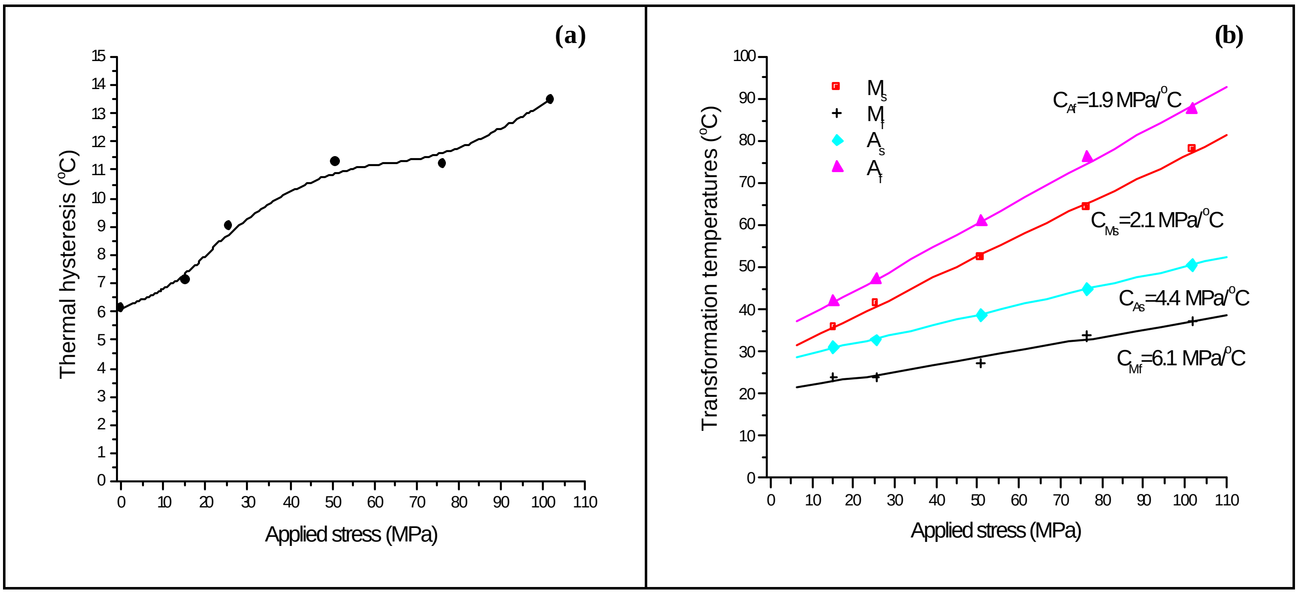

Figure 7 – Thermal properties extracted from ε - T curves. (a) Thermal hysteresis. (b) Transformation temperatures.

The clear augmentation of thermal hysteresis noticed in Fig. 5 was plotted in Fig. 7(a). This figure shows that hysteresis increases from 6^oC to about 14^oC for the stress range between 0 and 101.8 MPa. These thermal hysteresis values are relatively small compared with the ones observed in the literature for Cu-Zn-Al polycristals. For example, Benchiheub *et al* (2000) studying ribbons obtained by cold rolling from a similar Cu-25.9Zn-4.0Al (%wt) wire with 0,8mm, has measured thermal hysteresis between 15^oC and 25^oC for a stress range between 0 and 90 MPa. On the other hand, reduced thermal hysteresis (between 3 and 6^oC) in the stress free state has been measured by electrical resistivity in Cu-Zn-Al single crystals (Gonzalez, 2002). The linear augmentation of transformation temperatures as a function of applied stresses is characterized by four slopes C_{Mf}, C_{Ms}, C_{As} e C_{Af} as indicated in Fig. 7(b). Slopes between 2 and 20 $MPa/^oC$ are normally found in the literature (Otsuka & Wayman, 1998).

A few numbers of thermal cycles under constant load was performed to verify stability of the two-stage SME. Figure 8 shows the collection of results for the same stresses plotted in Fig. 5.

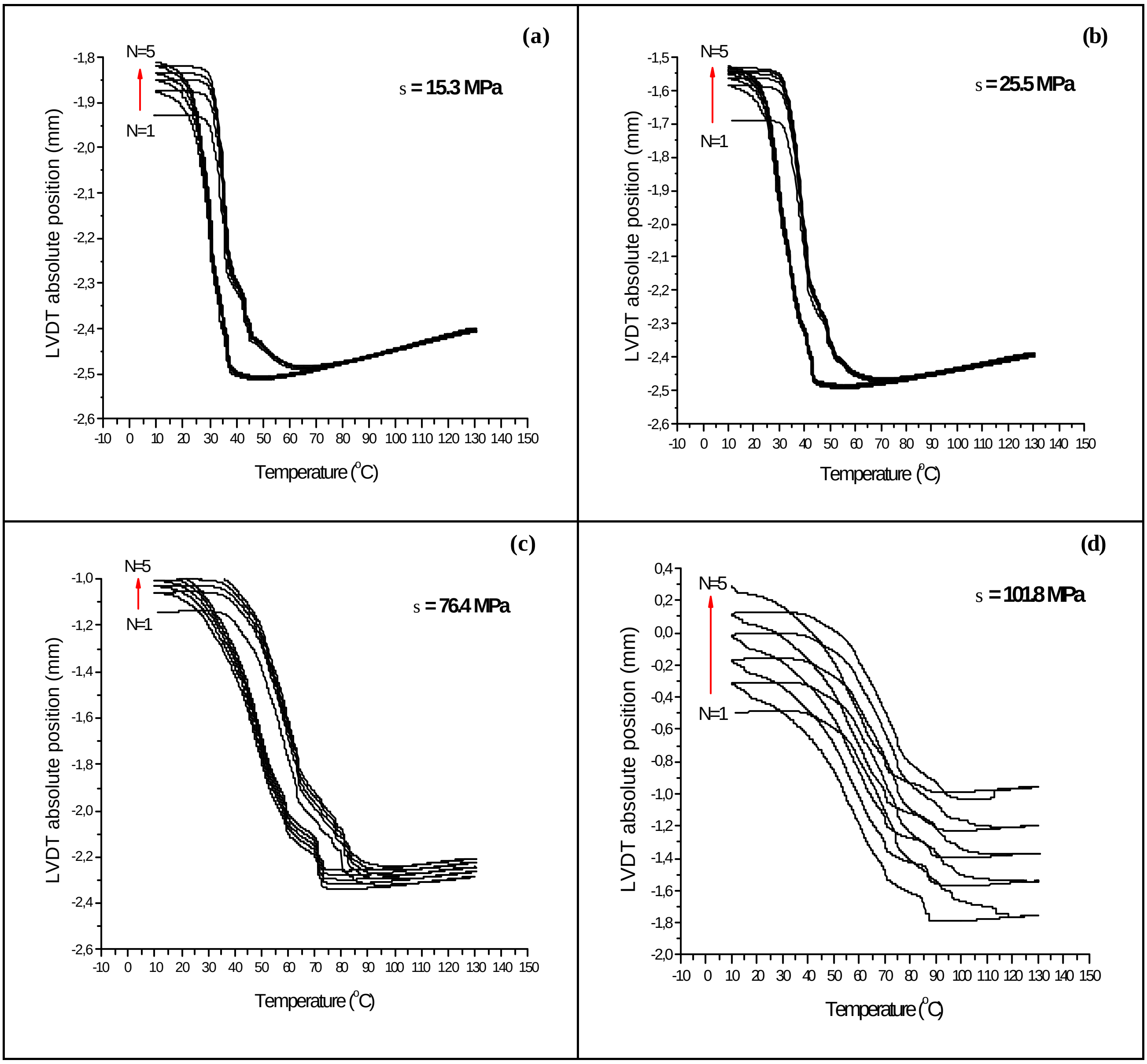

Figure 8 - Five ε - T loops for some applied stresses. (a) σ = 15.3 MPa. (b) σ = 25.5 MPa. (c) σ = 76.4 MPa. (d) σ = 101.8 MPa.

Figure 8 shows that the anomalies corresponding to the two-stage transformation observed on ε - T curves are practically unaffected during five thermal cycles. In addition, for applied stresses between 15 MPa and 75 MPa, as shown in Figs. 8(a-c), it was verified an improvement of the SME and a limited accumulation of plastic strain under load (ε_{plast}, as defined in Fig. 5d). As indicated in Fig. 8(d), for stresses as higher as 100 MPa a relative stability of SME was observed, but accompanied of an important accumulation of plastic strain under load. These behaviors are similar to the ones observed in Cu-25,9Zn-4,0Al (%wt) ribbons by Benchiheub *et al* (2000) and in Ti-Ni based thin wires (De Araújo, 1999; Lopez-Cuellar, 2002).

4. Conclusions

In this work, a two-stage transformation was detected by DSC and thermal cycling under constant load in Cu-Zn-Al SMA commercial wires. The reduced and similar thermal hysteresis (5 – 15 ^{o}C) for both stages of the transformation allows concluding that the coexistence of two different martensites (β' and γ') is not at the origin of this phenomenon. The more plausible hypothesis is that the two-step transformation appears probably due to the presence of a unique β' martensite with two different orders which during heating transforms to a β austenite phase also with two different orders. It was observed that this two-stage transformation is practically unaffected by a few number of thermal cycles under load between 10 and 110 MPa.

5. Acknowledgments

The authors thanks the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) brazilian agency for the award of research (CT-Energ grant 400724/2003-0 and CT-Petro grant 504365/2004-5) during the course of these investigations.

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