Stress-induced phase transformations studied by in-situ transmission electron microscopy

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Abstract. In this work, we carry out a detailed study, by in-situ Transmission Electron Microscopy (in-situ TEM), focused on two single-crystals of Cu-Al-Ni shape memory alloys with different transformation temperatures. The first single crystal is in beta phase at Room Temperature (RT) and has been cycled under stress, by super-elastic effect, inside the TEM. Two different mechanisms for the nucleation of $\beta'$ and $\gamma'$ martensite phases were observed: a) Martensite can nucleate on dislocations during super-elastic tests and when withdrawing the stress, the reverse transformation takes place by the disappearance of the martensite plate on the dislocation. b) During mechanical cycling martensite plates nucleate in other plates. The second single crystal is in martensite phase at RT, and when the stress is applied different mechanisms are observed: a) Reorientation and interface motion of the plates under the external applied stress, b) nucleation of mobile dislocations inside the martensite. A quantitative analysis of the experimental results, having into account the images and the diffraction patterns, has been realized and different mechanisms have been proposed to explain the experimental results.

1. Introduction

It is well known that TEM is a very powerful technique to study the microstructure of materials because it can give information on the real and reciprocal space from the same sample region. In particular in-situ TEM under cooling and heating is commonly used to study phase transformations in small volumes. With a similar idea, the study of structural phase transformations able of being induced under stress by loading and unloading cycles inside the microscope could be very useful. In particular the in-situ TEM study of the super-elastic and pseudo-elastic effects exhibited by Shape Memory Alloys (SMA) must give information about the sites for martensite nucleation (volume, dislocations etc.), the kind of martensites, the plates favored by the stress, the interface planes, austenite-martensite and martensite-martensite, as well as the microstructure evolution taking place during cycling.

Up today very few studies, concerning the super-elastic and pseudo-elastic effects of SMA [1], have been realized by in-situ TEM [2-7]. However, in-situ TEM experiments could give a unique information at nano-scale, which at present is becoming of paramount importance to understand and master the super-elastic and pseudo-elastic behavior observed in micro and nano devices, where even size effects have been recently observed [8, 9]. So, the objective of this work is to obtain microscopic information at nano-scale about the mechanisms taking place during super-elastic and pseudo-elastic effects on Cu-Al-Ni SMA, by using different in-situ TEM experiments.
2. Experimental

Two single crystals with compositions Cu-27.96%Al-3.62%Ni (at%) (sample I) and Cu-27.14%Al-4.54%Ni (at%) (sample II) were grown by the Stephanov method. From these single crystals, tensile samples 5mm x 1mm in cross-section and 25 mm in gauge length between the two gripping heads, were spark-machined with [001]L21 and (0-10) L21 as tensile axis and plane of the sample respectively (Samples IA and IIA). Other samples 50mmx5mmx1mm with the same orientation than the tensile samples were also cut (samples IB and IIB) for TEM observations. All the samples were annealed at 1173K for 1800s in argon atmosphere and quenched in iced water in order to prevent precipitation and to obtain the β1 metastable L21 (Fm-3m, a=5.82nm) ordered phase [10]. Furthermore samples I and II were aged during 4h and 24h respectively at 453K to increase the transformation temperatures [11]. Moreover the surfaces were mechanically polished to remove the damaged surface and the oxide layer produced during thermal treatments.

Thin foil samples for TEM were obtained from samples IB and IIB by mechanical polishing, until a thickness between 100μm and 200μm and punching in 3mm diameter discs. Then, they were electro-polished in a Struers Tenupol-5, using a mixture of 33% HNO 3 in methanol at about 258K. The TEM analysis of annealed samples was performed in a Philips CM200 with Gatan double-tilt and double-tilt heating holders.

The transformation temperatures were measured at 5% and 95% of the transformed volume fraction, calculated from the integral of the normalized entropy change associated to the martensitic transformation [12], measured by Differential Scanning Calorimetry (DSC) at a temperature rate of 10K/min in a Perkin Elmer DSC7. The transformation temperatures $\beta_1$ <-> $\gamma_1$ remain below RT for sample I, ($M_s = 233K$, $M_f = 231K$, $A_s = 271K$, $A_f = 276K$), while for sample II the transformation temperatures $\beta_3$ <-> $\beta'_3$+ $\gamma'_3$ are above RT ($M_s = 329K$, $M_f = 317K$, $A_s = 325K$, $A_f = 363K$). Consequently super-elastic and pseudo-elastic effect tests can be carried out at room temperature for samples I and II respectively.

The super-elastic and pseudo-elastic effects have been studied, on samples IA and IIA respectively, at RT with a 4467 Universal Instron test machine at a strain rate of $6.67\times10^{-4}$s$^{-1}$, and using an extensometer to measure the strain.

Rectangular 3 x 1mm$^2$ samples with the same orientation as IA tensile samples (tensile axis [001]L21, foil normal [0-10] L21) were also cut by spark cutting from sample IB to perform the super-elastic cycling inside the TEM. In addition, samples with the same shape and orientation were cut from sample IA after 54 previous cycles in the testing machine in order to continue the in situ super-elastic cycling at RT in the microscope.

Finally samples with the same rectangular shape were cut from sample IIB in order to observe pseudo-elastic behavior when the stress is applied in-situ at the TEM.

All the in situ TEM samples were mechanically polished to 40μm thickness and final electro-polished to electron transparency. Samples IA and IB were mounted in a single tilt Gatan tensile holder with [001]L21 in the tensile direction (in coincidence with the goniometer tilt axis) and [0-10] L21 perpendicular to the foil. The holder was introduced in a JEOL JEM2010 TEM and a digital video recorder was used to register the in-situ observations. The observed areas have been chosen having into account the simulation realized by Coujou et al. [13] in order to have the tensile stress in the same direction that the external applied stress $\sigma$=[001].

3. Super-elastic effect: Results and discussion

A preliminary study of the microstructure before thermo-mechanical tests was carried out on sample I. Antiphase boundaries (APB), corresponding to B2 and L2, order, have been observed by TEM, as for the quenched samples [14]. The microstructure of dislocations (Figure1a) is constituted by: a) prismatic loops in the foil plane (0-10) L21 with $b = (1/2) [0-10] L21$, b) straight edge dislocations with $b = (1/2) [100] L21$, c) mixed dislocations with vector line <111> L21, d) other mixed dislocations. A detailed analysis of this microstructure has been
carried out by LACBED [15]. Figure 1b shows the stress-strain curves for sample IA, after 34 and 54 cycles for a maximum strain about 5.5%. It can be observed that there is no remaining deformation after the completely repetitive super-elastic cycles. However when the stress is applied on sample IIA in the $\beta'_3 + \gamma'_3$ martensitic phase the pseudo-elastic behaviour takes place by the interfaces motion during loading-unloading and a 7.5% remaining deformation is observed, which will be recovered when the sample is heated at a temperature higher than $A_f$.

Figure 1a. Microstructure of sample IB just before applying the stress. TEM 200KV Bright field. Figure 1b. Curves IA: Super-elastic effect of sample IA. Cycles 34 and 54 are represented. Curve IIA: Pseudo-elastic effect for sample IIA in martensite phase.

3.1. Martensite nucleation on dislocations

When the stress is applied on sample IB it can be observed, during the loading cycles 3 to 13, the nucleation and growing of different martensite plates on dislocations. These events correspond to the direct transformation $\beta_3 \rightarrow$martensite. When the stress is withdrawn, the reverse transformation martensite-$\beta_3$ takes place and the martensite plate disappears on the dislocation. Figure 2 shows the last 34 seconds of the reverse transformation martensite-$\beta_3$ during unloading of the eighth cycle $\sigma$-$\epsilon$.

As shown in Figure 2e, the martensite plate disappears just in the dislocation. The line vector $u = [1-1-2]_{\text{L}21}$ of the dislocation was determined by trace analysis method for different tilts, but the Burgers vector cannot be univocally determined by the extinction method due to the high anisotropy of the Cu-Al-Ni alloys ($A_e$=13 [16]). It cannot either be determined by weak beam or large convergent beam techniques with the holder and microscopes employed. The extinction method gives three possible Burgers vectors: $b = (1/4)[1-1-1]_{\text{L}21}$, $b = (1/4)[1-11]_{\text{L}21}$ and $b = (1/2)[001]_{\text{L}21}$ but in any case the dislocation glide plane is (-1-10)$_{\text{L}21}$.

Figure 3 shows, under a different diffraction condition, the nucleation and growth of the martensite plate on the same dislocation, during the loading of the tenth cycle $\sigma$-$\epsilon$. The Select Area Diffraction Pattern (SADP) realized on the plate at the end of the tenth cycle (Figure 3e), shows that it is $\gamma'_3$ martensite (Pmmn, $a=0.53424$nm, $b=0.42244$nm, $c=0.43896$ [17, 5]). Its basal plane $(020)_{\gamma'_3}$ comes from the $(202)_{\beta_3}$ plane of the $\beta_3$ phase. The shear direction $[001]_{\gamma'_3}$, near the [-101]$_{\text{L}21}$, and the normal plane takes about 45º with the stress direction [001]$_{\beta_3}$. If the equivalence with dislocations is made, the Schmidt factor is near 0.5 and this plate is preferentially favored by the stress.

The previous results show that $\gamma'_3$ martensite can be nucleated on mixed dislocations, in a similar way than $\beta'_3$ martensite, which was shown to be able of nucleating in dislocations [5]. Along $\sigma$-$\epsilon$ cycling, the dislocation is not modified during martensite nucleation, what means that the dislocation is compatible with both phases $\beta_3$ and $\gamma'_3$. Among the three possible Burgers vectors for the dislocation, $b = (1/4)[1-1-1]_{\text{L}21}$ is the only one belonging to the basal plane of the $\gamma'_3$ martensite and we can assume that this is the Burgers vector of the dislocation. Consequently the dislocation has almost a screw character, which will be promoted by the applied stress in the [001]$_{\text{L}21}$ direction. In this situation the
atomic shearing along [10-1]_{L21} introduced by the dislocation is 0.133a√2 (Figure 4a and 4b) when the dissociation of the <111>_{L21} screw dislocations in B2 ordered alloys is considered [18,19]. Figure 4c shows γ′₃ martensite with their basal plane (020)₃ parallel to the (202)₃ (Figure 4a) as was experimentally observed. In this situation the shearing produced between the β₃ and γ′₃ structures is 0.137a√2. Consequently, in the core of dislocation pre-exists the atomic shearing that γ′₃ martensite requires to be nucleated, and when the applied stress has a high Schmidt factor, for a specific shear direction and basal plane, the martensite plate is nucleated in the dislocation core.

Figure 2. Eighth mechanical cycle on the sample, when the external stress is withdrawn. a-d) γ′₃-β₃ reverse transformation. The size of the martensitic plate decreases versus time (indicated in pictures. e) The martensite plate disappears on dislocation u. TEM 200KV Bright field. B=[0-10]_{L21}

Figure 3. Tenth mechanical cycle on the sample. The external stress is applied. a-d) β₃-γ′₃ direct transformation. Nucleation and growth of the plate versus time, which is indicated on the pictures. B=[1-20]_{L21} e) SADP of the martensite plate. B=[100]_{γ′₃} TEM 200KV Bright field.
3.2. Martensite nucleation on other martensite

Figure 5a shows a martensite plate (A1) nucleated when the stress is applied on sample IA, after the 54 previous σ-ε cycles from Figure 1b. The SADPs in Figures 5b and 5c were taken on martensite plate A1 and β3 phase respectively. The martensite plate A1 can be indexed as β’3 (C2/m, a=1.38017nm, b=0.52856nm, c=0.43987, β=113.60º [4]) and it can be observed that the basal plane (600)β’3 comes from the (202) L21 plane. Considering the nomenclature used by Saburi and Wayman [20] this plate will be named as variant 4 (β’3-4). The streaks along [600]β’3 direction in the reciprocal space are perpendicular to the defects observed on the basal planes in the Bright field (BF) image (Figure 5a). Having into account the twinining planes for β3 martensite and the SADP of Figure 5b, these streaks can only be interpreted as stacking faults in the basal plane. The transformation β3->β’3-4 continues growing, under the stress effect, along the [701] L21 direction, and other plate (A’1) is nucleated in the interface between the β3 phase and the β’3-4 martensite plate A1 (Figure 5a and 5d).

The SADP corresponding to the A’1 plate (Figure 5e) show that this plate is also β3 martensite with stacking faults in its basal plane (600)β3 coming from the (-202) L21 plane. It corresponds to variant 3 from Sabury and Wayman nomenclature [20] and will be named as β’3-3. The analysis of the SADP taken on the interface β’3-4 β’3-3 [21] shows that the interface plane is the twinning plane (201) L21 (-20-1) β’3-3. In Figure 5f the stereographic projection for β3 phase, β’3-3 and β’3-4 martensites, as well as the applied stress direction, have been represented. For β’3-4 martensite it can be observed an angle near to 45º between the shear direction [00-1] β’3-4 and the stress direction [001] L21. Also an angle of about 45º exists between the normal plane (600)β’3-4 and the stress direction. Equivalent results for β’3-4 martensite are observed in Figure 5f. Consequently we can assume that the nucleation of martensite is favored by the stress, similarly to the mobility of dislocations, when the shear direction is considered as the Burgers vector and the basal plane as the gliding plane of dislocations [21]. Directions [7 0 1] L21 and [70-2] L21 correspond to the intersection between the β’3-4 and β’3-3 martensite habit plane and the normal to the sample plane respectively, showing that both martensites take part of the self-accommodating groups I or II from Saburi et al. [22]. Variants 5 and 6 of the same self-accommodating groups are not favored by the stress and they are not observed. The explanation is given by the fact that the normal to the basal planes and their shear directions are at 90º with respect the applied stress direction and consequently these basal planes are not favored by the stress. Finally when unloading the sample, the reverse transformation from β’3-4 and β’3-3 martensites to β3 phase was experimentally observed, in agreement with the macroscopic super-elastic tests (Figure 1b).

When a stress is applied on sample IB, new B martensite plates were nucleated and propagated on the sample. They are β3 martensite plates and parallels between them [4]. When deformation increases new plates are nucleated at the interface β’ γ’  β3, and these new martensite plates can be γ’3 type [21]. Figure 6a shows a martensite plate A nucleated on one of the two B plates, growing until it reaches the other plate B, and the interfaces A-B are indicated by arrows. The SADPs in Figure 6b and 6c...
correspond to A plate (β', martensite) and B plates (γ', martensite) respectively. A detailed analysis of the interface plane has been realized in [21] for an equivalent interface β'γ'.

Figure 5. TEM 200KV. Martensite variants A1 and A’1 nucleated under the stress σ. a) BF B=[0-10]_L21. b) A1 martensite plate SADP. c) β3 phase SADP. d) BF B=[0-10]_L21. e) A’1 martensite plate SADP. f) Stereographic projection: Black-a β'_{3,3} martensite, black-b β’_{3,4} martensite, grey β3 phase.

The stereographic projection for both martensites and the β3 phase is represented in Figure 6d. The interface plane A-B is the basal plane (600)_β' || (020)_γ'. Both plates are favored by the stress because the shear direction [00-1]_{β'} || [00-1]_{γ'} for both plates takes 45º with the stress direction [001]_L21 and an angle of 45º exist between the normal planes (600)_{β'} || (020)_{γ'} and the stress direction. Directions [11 0-2]_{L21} and [1 0-3]_{L21} correspond to the intersection between the β'3 and γ'3 martensite habit planes and
the $\approx (0-10)_{L21}$ plane respectively, showing that both martensites belong to different self-accommodating groups having into account the Saburi et al. [22] nomenclature. A and B plates belong to groups I (or II) and V (or VI) respectively. Once again, when the sample is unloaded the reverse transformation $\beta^*_3 + \gamma^*_3$ to $\beta_3$ takes place.

We can summarize that for sample I and [001]$_{L21}$ stress direction, two $\beta^*_3$ plates of martensite with a twin relationship can be nucleated. Moreover $\beta^*_3$ and $\gamma^*_3$ plates can also be nucleated when the interface plane is the basal plane. In both cases the shear direction and the normal basal planes must be favored by the stress ($\approx 45^\circ$ between shear direction and normal basal planes with the stress direction).

4. Pseudo-elastic effect: Results and discussion

Sample II is in martensite phase at RT and so different mechanisms are observed when the stress is applied. Figure 7 shows the nucleation of dislocations on the surroundings of an interface between two martensite plates, then they move through a $\gamma^*_3$ plate. This kind of phenomena, although it has been scarcely observed, indicates that $\gamma^*_3$ martensite can be plastically deformed by creation and motion of dislocations when their Schmidt factor is high enough. Due to the ability of the $\gamma^*_3$ martensite for easily twinning it can be suggested that the dislocation mechanisms must be produced when twinning is not favored by the stress.

Figure 7. TEM 200KV. Nucleation and mobility dislocations on a $\gamma^*_3$ martensite plate. The arrows show the positions where a dislocation is moving.

On other hand, during loading it can also be observed how the different $\gamma^*_3$ and $\beta^*_3$ martensite plates are reoriented by the effect of the stress. In Figure 8 it is show how $\beta^*_3$ martensite plate is the more favored by the stress and then the interface between both plates moves by steps due to the presence of the stacking faults in the basal planes of both martensites. The interface position and shape change versus time and can be observed by comparing the figures 8a, 8b and 8c.

Figure 8. TEM 200KV $\gamma^*_3$-$\beta^*_3$ interface. The arrow shows the mean motion direction of the interface versus time. The interface is not flat and moves by steps.

5. Conclusions

The experimental results discussed on the previous sections show us that in-situ TEM is a good choice to analyze the microscopic mechanisms taking place during super-elastic and pseudo-elastic effects.
In particular during super-elastic effect on Cu-Al-Ni SMA, it has been observed that both \( \gamma' \) and \( \beta' \) martensite plates can be nucleated on dislocations as well as in the interfaces between other plates and the beta phase. In all cases the nucleation of plates must be preferentially favored by the stress and for that, the shear direction and the normal to the basal plane must be at about 45º from the stress direction in order to have a high Schmidt factor. In these conditions, the core of dislocations near to the screw character and with the adequate orientation versus the stress can be favorable nucleation points for both kind of martensite variants \( \gamma' \) and \( \beta' \). When \( \sigma \) is applied in the [001] \( L_21 \) direction only two kinds of interfaces are favored by the stress: a) The twin plane (201) \( \beta' \) for variants 3 and 4 from the self-accommodating groups I or II, b) The basal plane (600) \( \beta' \) as interface plane, but in this last case \( \beta' \) and \( \gamma' \) martensites are variants from different self-accommodating groups, I (or II) for \( \beta' \) and V (or VI) for \( \gamma' \).

During pseudo-elastic effect the plastic deformation of the \( \gamma' \) phase has been observed by nucleation and mobility of dislocations inside the martensite plates. In addition we have also observed the stepped mobility of the \( \gamma' \) interfaces due to the presence of numerous stacking faults in both structures.

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