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Effect of grain size on stress induced martensitic transformations in a Cu–Al–Be polycrystalline shape-memory alloy. Pseudoelastic cycling effects and microstructural modifications



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ABSTRACT

Grain size has a strong effect on the pseudoelastic properties of shape-memory alloys. Different grain sizes and several related phenomena are studied. This involves the dependence of the transformation and retransformation stresses on grain size and on the amount of transformed material. A pronounced drop of transformation stresses on cycling is observed, until an asymptotic behavior is reached. This is related to the creation of defects (dislocations and dislocation arrays) and microplates of martensite, which are the defects necessary to allow the grains to accommodate due to the shape change imposed by the martensitic transformation. The asymptotic hysteresis is related to the internal work for the grains to accommodate each other once the necessary defects were created. The asymptotic hysteresis increases linearly as the grain size decreases. A simple model shows that the slope is related to the (d/e) ratio, where *d* is the average grain size and *e* is the width of the specimen. This effect arises from the presence of the free surfaces that release the plastic work for grain accommodation.

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1. Introduction

One of the targets of research concerning shape-memory alloys is the development of devices to dissipate energy coming from different events, such as earthquakes [1–6]. The most relevant property to be used here is pseudoelasticity, which is found in some systems that exhibit martensitic transformations [7,8]. These solid–solid phase transitions take place between a metastable structure usually called "austenite", regardless of the type of system considered, and another metastable structure usually named "martensite", which has a lower symmetry than the austenitic structure. Even though the martensitic structure can be thermally or mechanically induced, the critical transformation temperatures usually given to characterize the material, i.e., $M_{\rm s}$, $M_{\rm f}$, $A_{\rm s}$ and $A_{\rm f}$, refer to thermally induced transformations [9,10]. The first two temperatures indicate the start and the end of the transformation, and the

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last two indicate the start and the end of the retransformation from martensite to austenite. If the martensitic transition is mechanically induced, a critical applied stress to start the transition at a given temperature can usually be determined, although several possibilities arise depending on the system and its microstructure [11]. Two different situations should be considered: (a) martensite is mechanically induced after loading the material but retransformation does not take place after unloading and (b) austenite is recovered if the material is unloaded. In the second case, hysteresis is usually exhibited in the force-elongation diagram and this is the origin of a strong research effort aiming to use the dissipation of energy associated to the mentioned mechanical hysteresis [4]. The formation of martensite under applied stress followed by the retransformation to austenite at a lower applied stress is called pseudoelastic effect or pseudoelasticity [12].

Among the systems with pseudoelasticity, Cu-base alloys have been extensively analyzed, especially CuZnAl [10,13–16] and CuAlNi [17–20], and, to a lesser extent, CuAlBe [21–26].

There is a strong relationship between the microstructure of a shape-memory alloy and its pseudoelastic properties [27]. Thermomechanical processing determines the final microstructure of the alloy (grain size and morphology, texture, precipitates, etc.) and has, therefore, a direct impact on its pseudoelastic properties [28]. Grain size is one of the most important microstructural

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parameters which play a role in the mechanical properties of shapememory alloys, and it is directly related to the spatial distribution of grain boundaries [29]. Grain size has a critical influence on the morphology of stress-strain curves, the amount of pseudoelastic hysteresis and whether a constant stress transformation plateau will exist or not [30]. Single crystals can be thought of as an extreme case where grain boundaries are absent. In polycrystals, the limit cases are very large and very small (nanostructured) grain sizes. Compared with materials with nanostructured grains, samples with very large grain sizes are expected to have mechanical properties more closely related to their single crystal counterparts. In case austenite-martensite transitions are analyzed, the hysteresis of a given phase transformation is usually smaller in single crystals than in polycrystalline samples. However, martensite to martensite transitions with wide hysteresis are clearly observed in Cu based single crystals, depending on the composition and orientation of the tensile axis [8,10,31]. This has been recently shown for CuZnAl single crystals, where the introduction of nanoprecipitates improves the mechanical properties of the 6R martensite [32]. Consequently, the mechanical behavior of the 18R-6R martensite to martensite transition becomes competitive due to its wide hysteresis and good stability during at least 1000 cycles at high frequency [33]. However, if the austenite to martensite transformation is considered, the polycrystalline material usually presents wider hysteresis than the single crystal, which is more attractive if dissipative devices are considered.

To obtain optimum pseudoelastic properties in NiTi alloys, for instance, grain size must be kept very small, and new processing routes to refine grain size are being studied [34,35]. Texture may also be an important variable and, in some Fe-base alloys, good pseudoelasticity only occurs for specific textures, such as in the alloy invented by Tanaka et al. [36]. Precipitates may also be used to optimize mechanical properties, changing transformation stresses and improving shape recovery [32,37–39].

In the last few years, some studies have been carried out to improve the comprehension of the mechanical behavior of CuAlBe alloys [22]. Several martensitic transformations have been studied in single crystals [25,40–43] and, recently, a phase transformation diagram has been proposed [21]. In polycrystals, the relationship between grain size and pseudoelastic properties has been presented [29,44–47]. However, no results on the evolution of the microstructure with cycling have been published. The purpose of this work is to determine the irreversible mechanisms taking place during mechanical pseudoelastic cycling, for a deformation level high enough to obtain noticeable dissipation in each cycle but, at the same time, low enough to avoid early fracture or large irreversible deformation. Different grain sizes are considered and a comparative analysis is performed to evaluate the role grain boundaries play in the mechanical evolution. Results after tensile cycling, at constant temperature and at frequencies still far below the ones present in natural events (like earthquakes) are shown. The effect of grain size can be well shown. Additionally, thermally induced transformations are determined and critical transformation temperatures are obtained for different grain sizes, in order to evaluate the contribution of mechanical interactions with grain boundaries after pseudoelastic cycling. Finally, a model is presented to enable the comprehension of the asymptotic behavior after cycling.

2. Experimental methods

The nominal composition of the alloys used is Cu–23.35 at% Al–2.96 at% Be, (Cu–11.8 wt% Al, 0.5 wt% Be). The nominal transformation temperatures are M_s =255 K, M_f =226 K, A_s =253 K and A_f =275 K. The alloys were furnished by Trefimetaux, France, and

delivered as wires of different diameters. Most of the samples used in the present work were obtained from 3.4-mm diameter wires. The transformation temperatures of the material as received, determined by electrical resistivity measurements, are: M_s =237 K, M_f =211 K, A_s =235 K and A_f =252 K, with a grain size of 89 µm, determined by the method detailed below. Samples were machined to a gauge length of 30 mm and a diameter close to 2.5 mm in the central part.

Several grain sizes were obtained by the following thermal treatment: a time interval t in a tubular resistive furnace set at 1123 K followed by a quench in water at 298 K. For *t* periods shorter than 2 min, the temperature of the samples did not reach 1123 K. However, after 1.1 min, temperature had already reached 1073 K and the treatment mentioned above was suitable to control grain size. After this, all samples were kept at 323 K for one week, unless otherwise specified, and quenched in water at 298 K. All samples were mechanically polished with sandpaper and then electropolished in a solution of 15% Nitric Acid in Methanol under a voltage of 9 V. Grain size was determined by optical microscopy with the linear intercept method, as described in ASTM E112-12, and mechanical tests were performed in an Instron 5567 electromechanical machine inside a temperature chamber. An MTS 632.13F-20 extensometer with 10-mm gage length, attached to the central portion of the specimen, was used to measure deformation. A thermocouple was fixed to one of the grips, close to the sample head, to check the stability of the test temperature. When specifically stated, a thermocouple was spot welded on the tensile sample.

In order to determine the test parameters for this work, sample B (Table 1) was submitted to several tensile cycles. The maximum deformation was increased at each cycle. The main point which we detected here is how the permanent deformation increases after each cycle, up to 3% for a maximum applied deformation equal to 7%. Taking this result into consideration, a maximum deformation close to 4% was selected for the cycling tests so as to have sufficiently high mechanical reversibility in each cycle, as explained below. The samples were pseudoelastically cycled under a tensile load at a selected temperature (303 K, unless specifically stated), between a fixed minimum load in the austenitic range and a strain limit of 4.3% deformation, corresponding to a partial martensitic transformation. This deformation will be named ε_{max} . All cycles were performed at a crosshead speed equal to 0.1 mm/ min, slow enough so we can disregard thermal effects due to the change of enthalpy of the transformation. The samples used are listed in Table 1.

In order to distinguish those changes of the martensitic transition temperatures which can be observed in thermally induced transitions from those which are clearly originated by mechanical interactions, several samples were submitted to the same thermal treatments as the mechanical samples; then, the martensitic transformation temperatures were determined by electrical resistivity

Table 1Samples used to study the pseudoelastic behavior.

Sample	t (s)	d (µm)	d/e	$\sigma_{\rm s}^{N=1}$ (MPa)
А	10	93	0.039	210.7
В	240	313	0.110	152.8
G	3060	703	0.253	118.4
F	960	347	0.124	128.0
D	480	313	0.110	129.5
E	240	291	0.103	143.9
J	120	178	0.07	175.7
Н	10	93	0.038	210.0

Sample B was deformed up to increasing deformation values. Samples A and G to H were cycled up to e_{max} =4.3%. Interval *t* indicates time at 1023 K, *d*=grain size and e indicates the width of the sample.

measurements. Samples used for this purpose are included in Table 2. Two letters are used to name the samples, being R the second one. Samples GR, FR, and HR are used to measure the martensitic transformation temperatures for different grain sizes. Samples IR and KR are used to determine variations in martensitic transformation temperatures after a small number of thermally induced cycles.

Finally, some samples were chosen for observation by transmission electron microscopy to analyze the presence of dislocations and/or retained martensite after cycling. A Philips CM200 Ultratwin transmission electron microscope, operating at 200 kV, was used.

3. Experimental results

The mechanical evolution at T=303 K for sample G (the largest grain size used in the present manuscript) is presented in Fig. 1. Fig. 1a shows the σ - ε curves obtained for cycles 1 and 74. The main features which characterize the pseudoelastic cycle are shown in this figure, i.e., the critical stress to induce the β -18R transformation, the slope during the pseudoelastic transition, the hysteresis and, finally, the retained deformation after unloading. The effect of cycling is also noticeable after a rather low number of cycles. Two main features are observed here: hysteresis clearly decreases during cycling; the final stress, which is also the maximum stress of each cycle, remains nearly constant if the maximum deformation is kept at a fixed value and permanent deformation is retained in the sample, even though a closed loop with complete mechanical reversibility is obtained after several

Table 2

Samples measured by the electrical resistivity method.

Sample	<i>t</i> (s)	<i>d</i> (µm)
GR	3060	703
FR	960	347
HR	10	93
IR	60	124
KR	60	124

Samples GR, FR, and HR are used to measure the martensitic transformation temperatures for different grain sizes. Samples IR and KR are used to determine variations in martensitic transformation temperatures after a small number of thermally induced cycles.

cycles. This permanent deformation is either the result of plastic deformation, incomplete retransformation of martensite - as some martensite might remain retained even after the load has been completely removed – or a combination of both phenomena. It is, thus, necessary to use a powerful materials characterization tool, such as TEM, to accurately determine which mechanisms are responsible for the permanent deformation observed. During cycling, a decrease in the critical stress to start the martensitic transformation (σ_s) is observed, leading to an increase in the pseudoelastic slope which is observed while the maximum stress remains constant. Two direct consequences arise from the observed evolution during pseudoelastic cycling: a "softening" in the mechanical behavior and a pronounced decrease in hysteresis. Several points should be addressed here before we present and analyze further experimental results. On the one hand, the critical stress to transform to martensite depends on the transformation strain, increasing from the start of the martensitic transformation and reaching its maximum value at the maximum transformation strain. Additionally, the critical stress to start the transformation for cycle number 1 ($\sigma_s^{N=1}$) can be determined quite precisely, whereas the start of the transition becomes less defined as the number of cycles increases. We should also notice that the stress to transform decreases during cycling, leading to an absence of pseudoelasticity for part of the sample. This is well observed in Fig. 1a, which shows cycle 74 starting at ε equal to approximately 0.6%. This is a consequence of the permanent deformation which remains at the end of each cycle and accumulates during several cycles. In order to distinguish the permanent deformation retained in one cycle from the accumulated retained deformation, the former term will be named $\varepsilon_{\rm rpc}$ (retained deformation per cycle) and the latter term ε_{ard} (accumulated retained deformation).

It is necessary to measure several parameters during the whole stage of cycling in order to follow the mechanical evolution of the material. A well-defined, conventional deformation amount ε_d is then selected, which results from:

$$\varepsilon_{\rm d} = (\varepsilon_{\rm max} - 1.5\%).$$

where $\varepsilon_{\rm d}$ and $\varepsilon_{\rm max}$ are measured in %.

For this arbitrarily selected deformation, it is possible to obtain the critical stresses to transform and retransform during the whole stage of cycling (see Fig. 1a). The critical stresses obtained for this deformation will be named $\sigma^{tr}(\varepsilon_d)$ and $\sigma^{ret}(\varepsilon_d)$. Considering as a first approach that the sequence of transformation does not change during cycling, $\sigma^{tr}(\varepsilon_d)$ and $\sigma^{ret}(\varepsilon_d)$ can be assigned to the same volume of material in the sample during the whole cycling



Fig. 1. Mechanical evolution for sample G (the largest grain size used in the present work). Tensile tests were performed at T=303 K, crosshead speed=0.1 mm/min and an extensioneter with Lo=10 mm was used to obtain deformation. (a) Cycles 1(dot line) and 74 (solid line) are plotted. The selected deformation e_d at which transformation stresses are obtained is also marked with a straight dash line; (b) transformation stresses $\sigma^{tr}(e_d)$ and $\sigma^{ret}(e_d)$ obtained at e_d are shown for several cycles. The hysteresis $\Delta\sigma(e_d)$ obtained at the same deformation is also plotted. The total decrease in $\sigma^{tr}(e_d)$ and $\sigma^{ret}(e_d)$ is indicated.

test, and this is the main advantage of selecting ε_{d} . It is reasonable to consider that the transformation sequence does not change during cycling, as the mechanical evolution of the samples during tensile cycles results in decreased transformation stresses, leading to a progressive "softening" of the material with each transformation. In this way, the first part of the sample which transforms in cycle N should also transform first in cycle N+1, unless it is retained as martensite, i.e., it does not retransform to austenite. This hypothesis might be slightly affected by the presence of retained deformation in each cycle. However the total amount of retained deformation is rather small for the selected maximum amount of deformation. Additionally, the selection of ε_d to evaluate critical stresses to transform allows us to follow their evolution during cycling up to the asymptotic state, because this deformation corresponds to approximately half the transformation strain of the closed asymptotic loop. An interesting point concerning the evolution during cycling is observed in Fig. 1b, which shows the critical stresses to transform and to retransform as well as the hysteresis obtained at ε_{d} for several cycles. From this result, it is clear that the critical stresses to transform and retransform do decrease with the number of cycles, and this decrease is more pronounced for the transformation than the retransformation critical stresses. This asymmetric behavior between transformation and retransformation leads to a decrease in hysteresis with the number of cycles (*N*). The hysteresis $\Delta \sigma$ is evaluated at ε_{d} and is defined as:

 $\Delta \sigma(\varepsilon_d) = \sigma^{tr}(\varepsilon_d) - \sigma^{ret}(\varepsilon_d)$

 $\Delta \sigma(\varepsilon_{\rm d})$ is also plotted for sample G in Fig. 1b.

Experiments similar to the ones mentioned above were performed to assess the mechanical behavior during the pseudoelastic transformation and pseudoelastic cycling for samples with different grain sizes. The maximum deformation and test temperature were kept constant. An example of the effect of grain size can be observed in Fig. 2 when compared with Fig. 1. Fig. 2 shows σ - ε curves corresponding to selected cycles for sample H, (the smallest grain size used in this work).

Cycles 1 and 74 are plotted in Fig. 2a. Additionally, the evolution of the critical stresses obtained at ε_d and corresponding hysteresis are plotted in Fig. 2b. Interesting points can be mentioned here if the results shown in Fig. 2 are compared with those of Fig. 1. On one hand, several significant changes are observed for both the largest and smallest grain sizes, such as a decrease in critical stresses and hysteresis during cycling. On the other hand, some differences are also noticeable, such as an important

modification in the morphology of the curves in the beginning of cycling, the amount of the decrease in critical stresses and also the amount of accumulated retained deformation.

Although a difference in morphology between stress strain curves for different grain sizes can be observed if Figs. 1a and 2a are analyzed, Fig. 3 shows the first cycle for several samples with different grain sizes, highlighting the effect of grain size on the mechanical behavior. A rather systematic decrease in critical stresses for the whole range of transformation, as well as in the slope of the σ - ε curves during transformation and in the hysteresis is well stated as grain size increases.

The change in pseudoelastic properties during cycling makes it necessary to measure the effect of cycling on the retained deformation per cycle (ε_{rdc}) and on the accumulated retained deformation (ε_{ard}). The first one shows the mechanical irreversibility or lack of pseudoelasticity in each cycle, while the second parameter gives information on the total amount of deformation which does not revert after cycling. Fig. 4 shows the evolution of both parameters for samples G and H (the largest and smallest grain sizes in the present work).

From Fig. 4, we can notice that the behavior concerning irreversible deformation is qualitatively similar for different grain



Fig. 3. Effect of grain size on the stress–strain curves for cycle number 1. Results for samples G (703 μ m), E (291 μ m) and H (93 μ m) are shown. Parameters of the samples are shown in Table 1 and grain size is also indicated in the figure for each curve. Crosshead speed=0.1 mm/min in all cases and test temperature=303 K.



Fig. 2. Mechanical evolution for sample H (the smallest grain size used in the present work). Tensile tests were performed at T=303 K, crosshead speed=0.1 mm/min and an extensioneter with Lo=10 mm was used. (a) cycles 1 and 74 are plotted. The selected deformation ε_d at which transformation stresses are obtained is also marked with a straight line; a horizontal line at $\sigma = 16$ MPa emphasizes the retained deformation in the first cycle (b) transformation stresses $\sigma^{tr}(\varepsilon_d)$ and $\sigma^{ret}(\varepsilon_d)$ obtained at ε_d are shown for several cycles. The hysteresis $\Delta\sigma(\varepsilon_d)$ obtained at the same deformation is also plotted.

sizes. About 25% of the initial transformation strain does not revert after approximately 100 cycles and an asymptotic behavior is clearly obtained, where the retained deformation per cycle decreases until it becomes negligible.

An additional and interesting point concerns the asymmetric behavior if transformation to martensite and retransformation to austenite are considered. In order to focus on this matter, Fig. 5 shows, in the same figure, the variation of stress and strain parameters with the number of cycles for 3 different grain sizes. From Fig. 5, it can be noticed that not only is an asymmetric behavior present if stress induced transformations and retransformations are compared at the first stress induced transformation, particularly for smaller grain sizes as shown in Fig. 3, but also an asymmetry is present during pseudoelastic cycling. In fact, the smallest grain sizes show a stronger effect of cycling on critical stresses and hysteresis. Moreover, the decrease in critical transformation stresses as the number of cycles *N* increases. This is clearly noticed in Fig. 6 where only cycles 1 and 2 are shown for sample H



Fig. 4. Evolution of retained deformation per cycle (e_{rdc}) and accumulated retained deformation (e_{ard}) with pseudoelastic cycling for two samples, G (grain size=703 µm) and H (grain size=93 µm). (a) e_{rdc} for samples G and H, (b) e_{ard} for sample G and H.



Fig. 5. Variation of critical transformation and retransformation stresses, hysteresis and retained deformation per cycle as a function of number of cycles for samples G, E and H. (a) $\sigma^{tr}(\varepsilon_d)$ vs. $N_i(b) \sigma^{ret}(\varepsilon_d)$ vs. $N_i(c) \Delta\sigma(\varepsilon_d) = \sigma^{tr}(\varepsilon_d) - \sigma^{ret}(\varepsilon_d)$ vs. $N_i(c) \Delta\sigma(\varepsilon_d) = \sigma^{tr}(\varepsilon_d) + \sigma^{tr}(\varepsilon_d)$ vs. $N_i(c) \Delta\sigma(\varepsilon_d) = \sigma^{tr}(\varepsilon_d)$ vs. $N_i(c) \Delta\sigma(\varepsilon_d)$ vs. $N_i(c) \Delta\sigma(\varepsilon_d) = \sigma^{tr}(\varepsilon_d)$ vs. $N_i(c) \Delta\sigma(\varepsilon_d)$ vs. $N_i(c) \Delta\sigma(\varepsilon_d) = \sigma^{tr}(\varepsilon_d)$ vs. $N_i(c) \Delta\sigma(\varepsilon_d) = \sigma^{tr}(\varepsilon_d)$ vs. $N_i(c) \Delta\sigma(\varepsilon_d)$ vs. $N_i(c) \Delta\sigma(\varepsilon_d) = \sigma^{tr}(\varepsilon_d)$ vs. $N_i(c) \Delta\sigma(\varepsilon_d)$ vs. $N_i(c) \Delta\sigma(\varepsilon_d)$



Fig. 6. (a) σ -e curves for cycles 1 and 2 (sample H) (b) σ -e curves for cycles 1 and 2 (sample D). Test temperature=303 K and crosshead speed=0.1 mm/min.

and D. The morphology of the curve during the austenitemartensite transition is very different in cycles 2 and 1, whereas changes during retransformation are not nearly as pronounced.

Fig. 4a also shows that the smallest grain size leads to nearly closed loops after a smaller amount of cycles if compared with samples with larger grain sizes. One can observe that partial mechanical irreversibility is present from the first stress induced transformation and that this irreversibility shows an evolution during cycling. In fact, the first cycles show the most significant changes, although an asymptotic behavior is reached after approximately 100 pseudoelastic cycles. An interesting point here is that although cycles appear completely closed after N=100 cycles, a very small irreversible deformation is found in each cycle after a higher number of cycles. However, this effect is extremely small, only noticeable if an extensometer is used and we might consider that irreversibility in each cycle greater than 100.

In order to have a deeper understanding of the origin of this irreversibility, the microstructure of a sample before pseudoelastic cycling is shown in Fig. 7 and the effect of cycling is shown in Fig. 8 for sample H (the smallest grain size analyzed). The photographs were obtained by Transmission Electron Microscopy after 120 cycles. The images in Fig. 7 show grain boundaries in the austenitic phase with a very small amount of dislocations or even no dislocations at all.

A remarkably different microstructure is obtained after cycling. Attention was paid to the microstructure both close to grain boundaries and in the interior of the grains. Two features are clearly observed. Fig. 8a shows dense arrays of dislocations on one side of a grain boundary while retained martensite is clearly observed on the other side. Fig. 8b presents dislocations on both sides of a small angle grain boundary with a few plates of retained martensite. Martensitic variants correspond to the 18R structure. Two additional photographs presented in Fig. 8c and d show dislocation tangles and retained martensite quite far from grain boundaries. No significant crystallographic texture was observed in the studied specimen.

The critical stresses to start the transformation increase as the grain size decreases, as observed in Fig. 3. However, it is known that critical transformation temperatures can also be affected by grain size. It is then convenient to know if critical transformation temperatures do change with grain size in the range considered in the present manuscript and if this change might explain the measured effect on the critical stresses for transformation. For this purpose, several samples were submitted to the same thermal treatments as the tensile samples and the corresponding thermally induced transformations were determined by electrical resistivity measurements. Fig. 9 shows the curves obtained for samples GR, FR and HR (see Table 2).

As curves in Fig. 9 indicate, a decrease in M_s is observed as grain size decreases. In fact, the change in M_s reaches 10 K for the range of grain sizes used here. In order to determine the corresponding change in σ_s which should be expected according to the measured change in critical transformation temperatures, information on the Clausius–Clapeyron relationship is required. In fact, the relationship was determined for CuAlBe polycrystals with the same composition and a value equal to 2.2 MPa was reported for $d\sigma_s/dT$ [48]. An interesting point to mention here is that the Clausius– Clapeyron relationship obtained from polycrystalline materials results from some kind of average behavior, as thoroughly discussed in the literature [49]. This is understandable since the critical stress to induce martensite depends on the orientation of the structure. Additionally, the way in which the effect of



Fig. 7. Microstructure close to grain boundaries in a sample that was not submitted to cycling.



Fig. 9. Electrical resistivity curves for samples GR (703 μm), FR (347 μm) and HR (93 μm). Grain size for each sample is shown in each case.



Fig. 8. TEM photographs taken from sample H after 120 pseudoelastic cycles. (a) Mainly dislocations are observed in the grain on the left side. Martensite plates together with dislocations appear in the grain on the right. (b) Low angle grain boundary showing dislocations and martensite plate. (c) Dislocations arrays inside a grain. (d) Martensite microplates inside a grain.

temperature is determined might be affected by the effect of cycling, because if the same sample is used to obtain the effect of temperature on critical stresses, the marked decrease in these values due to the first stage of cycling would clearly affect the result. The effect of pseudoelastic cycling might be avoided either by using a different sample for each test at a different temperature or by the measurement of critical stresses at several test temperatures after an asymptotic stage is reached, i.e., after cycling. In fact, the second method was performed here for sample G and $d\sigma_s/$ dT=2.1 MPa/k was obtained. Using this result, a change of 20 MPa in $\sigma_s^{N=1}$ might be expected, if this variation were originated in the $M_{\rm s}$ change, while a change of 85 MPa was obtained between sample G and sample H to start the transformation (see Fig. 3). From these results, it is clear that the effect of grain size on the tensile induced transformation cannot be obtained merely from the information provided by thermally induced transitions and that the interaction between austenite-martensite interphases and grain boundaries is strongly a mechanical effect. An additional interesting result which focuses on the differences between thermal and mechanical effects can be obtained if the martensitic transformation is thermally obtained during several consecutive cycles. This experiment has been performed for two additional samples, named IR and KR, which were only prepared for resistivity measurements and which were both thermally treated for t=60 s (see Table 2). A complete overlap was obtained for the first 5 thermally induced cycles, indicating that critical transformation temperatures are reasonably stable for a thermally induced transformation, while critical tensile stresses to transform are strongly affected if the transition is repeatedly induced.

Concerning the mechanical interaction between austenitemartensite interfaces and grain boundaries, it has been reported that critical stresses to induce martensite do follow a Hall–Petch relationship [29]. Critical stresses to induce martensite obtained for cycle 1 at 0.02% deformation were plotted in Fig. 10 vs. $(d/e)^{-0.5}$ and a reasonably linear fit can be obtained with a slope equal to 32.6 MPa.

Finally, hysteresis plays a significant role if energy dissipation is to be considered. However, hysteresis, defined as the difference between the critical stresses to transform and retransform, changes with the amount of transformed material, i.e. deformation. Considering this fact, it is more convenient to quantify the area enclosed by the pseudoelastic cycle as the significant parameter associated to the dissipated energy during a complete mechanical reversible austenite-martensite transformation and the following



Fig. 10. Critical stress to start the martensitic transformation for cycle 1 ($\sigma_s^{N=1}$), plotted vs. $(d/e)^{-1/2}$. A linear fit is also plotted indicating a Hall–Petch behavior in this material.



Fig. 11. Area enclosed in the pseudoelastic cycle at the asymptotic stage of cycling vs. (d/e) for several samples. A linear fit is also plotted.

retransformation. However, it must be kept in mind that the mentioned enclosed area of the pseudoelastic cycle shows an evolution during cycling. We consider here that, during the first stage of cycling, a significant part of the mechanical work is used to create defects whereas, at the asymptotic stage, the enclosed area describes the dissipated energy which, in each cycle, is required to accommodate the shape change during transformation and retransformation. The enclosed area in the pseudoelastic cycle at the asymptotic stage (named H) is then the main parameter associated to dissipative phenomena in these alloys. The corresponding values have been obtained for several samples and plotted vs. *d/e* in Fig. 11. It should be mentioned here that the plotted values have been corrected taking into consideration the actual fraction of the material that transforms. In this way, H measures the dissipated energy per volume unit of the transformed part of the material.

A linear fit was performed with the results shown in Fig. 11, leading to the following relationship:

$$H = (2.7 \pm 0.2) \left[1 - (0.8 \pm 0.4) \frac{d}{e} \right] \frac{\text{MJ}}{\text{m}^3}$$
(1)

4. Discussion

The obtained results show that grain size clearly affects pseudoelastic properties as well as the mechanical evolution during pseudoelastic cycling. As shown, several parameters have to be used to characterize the pseudoelastic behavior: the critical stress to start the transformation, the slope of the stress-strain curve at the pseudoelastic stage and the mechanical hysteresis. Additionally, in case pseudoelasticity is not complete, information on the retained deformation after unloading the sample is also required. All these parameters change during cycling and some of them are not constant for an individual selected pseudoelastic cycle. An example of this last point is the increase of the critical stress to transform as the pseudoelastic deformation increases, a behavior intrinsically related to the positive slope of the stress strain curve at the phase transition stage. In order to analyze the obtained results, we will first consider some crystallographic aspects of the martensitic transition taking place in each individual grain.

Assuming for simplicity a cubic shaped grain as in Fig. 12a, the habit plane of the martensitic transformation passes along the horizontal diagonal of the cube, with the normal parallel to the y axis. The macroscopic shear direction is along the horizontal x axis. Let us assume now that the grain transforms freely to martensite



Fig. 12. Geometry of the transformation for a particular case. (a) A cubic grain with the normal of the habit plane along the *y* axis and the macroscopic shear deformation along the *x* axis. (b) Shape change after transformation with g = 1.1045d, h = 0.9055d, $\alpha = 5.19^{\circ}$ and $\delta = 88.8^{\circ}$. (c) Schematic representation to see more clearly the empty (E) and overlapping (O) areas.

following the indicated habit plane and shear direction; the shape of the grain will change into the parallelepiped drawn in Fig. 12b in thicker lines. There will be no changes in the direction perpendicular to the paper. Fig. 12c shows the shape the grain would have in case it could completely transform to martensite. In fact, neighboring grains will impede this possibility and regions O and E will be under compressive and tensile stresses, respectively. The amount of shear deformation can be calculated using the WLR crystallographic theory [50]. The shear deformation depends on the orthorhombic deformation of the basal plane, which is defined by a parameter ψ [50]. The parameter ψ is also linearly related to the martensite transformation $M_{\rm s}$ [51]. For the present case we obtain a macroscopic shear deformation s = 0.2. Using this shear deformation in Fig. 12b, we obtain that the grain is narrowed by about 10% and elongated by about 10% upon transformation (See Fig. 12b and c). Very low volume change is involved in this transformation. The contribution of the grains to the elongation of the specimen will depend on the Schmid factor. Not all grains will transform the same amount, i.e., for a fixed amount of deformation of the sample, those grains having a larger Schmid factor will transform a smaller amount. When the grains are embedded in the material they need to accommodate themselves according to the shape change of each one. There are regions void of material and regions where material overlaps, as shown in Fig. 12b and c. Since the amount of deformation is very large (about 10%), plastic deformation in addition to elastic stresses are to be considered. Therefore, plastic movements of material are necessary to compensate for this mismatch.

A problem of this kind has been treated by Roqueta et al. [38], in CuZnAl single crystals, while studying the hysteresis increase of the stress induced martensitic transformation, when small non transforming precipitates are absorbed by the martensite. In their problem, the work done by moving material from the overlapped areas to the empty ones, using elementary concepts of plasticity, successfully explained the asymptotic hysteresis width as a function of precipitate size. This internal plastic work was proportional to the precipitate volume. It was spent to accommodate each precipitate to the local surroundings. Defects like dislocations or second variants of martensite microplates are necessary to perform this internal work, they are created in the first stage of the mechanical cycling, leading to a pronounced decrease of the transformation stresses on cycling.

However, in the present case, little or no material can be removed from the overlapping areas to the empty ones (Indicated as O and E, respectively, in Fig. 12c), otherwise no elongation of the specimen would take place. This means that the changes of the grain shapes have to be arranged in another complex way, which is very difficult to calculate in detail. We will then consider some aspects related to the first stage of cycling where strong changes are observed in the main parameters which characterize the transformation and suggest a phenomenological treatment to describe the effect of grain size on the asymptotic hysteresis of the pseudoelastic cycling.

One of the noticeable features detected in all samples concerns a strong evolution during pseudoelastic cycling which leads to a significant decrease in hysteresis and in the stresses to transform. Additionally, the amount of required deformation directly influences the retained deformation on cycling, affecting the reversibility of the transformation. As stated above, an intermediate maximum deformation (approx. 4.3%) was selected in order to have reasonable energy dissipation in each cycle with a rather small (but not negligible) retained deformation. In fact, reported results indicate that retained deformation increases noticeably if the maximum deformation is larger than 2.0% [29], in agreement with our observations.

Plotted stress strain curves corresponding to cycle 1 for different grain sizes show several interesting facts. On the one hand, the critical stress to start the transformation is larger for smaller grain sizes. The pseudoelastic slope and hysteresis is also larger for smaller grain sizes. In fact, reported results show that σ_s increases as the grain size decreases [29]. Additionally, the same authors suggested a linear fit of σ_s as a function of $(d/e)^{-1/2}$ (Hall–Petch relationship), where the critical stresses were obtained at the second pseudoelastic cycle, since first cycles were considered anomalous. In the present work we do consider the critical stress already since cycle number 1, as the mechanical behavior shows no artifacts, mainly because an extensometer has been used. It is interesting to notice that the linear fit obtained for the relationship between σ_s and $(d/e)^{-1/2}$ in the present work gives a slope still larger than the reported value (32.6 MPa was obtained in this work, whereas 24.6 MPa was reported [29]). This difference can be understood if the effect of cycling is taken into account. It can be observed from Figs.1 and 2 that the effect of cycling on the critical stresses to transform is noticeably stronger at the very beginning of cycling, i.e., a decrease in the critical stresses to transform is observed in cycle N if compared with cycle N-1, but the mentioned decrease shows its maximum value between cycles 1 and 2 and diminishes with N as shown in Figs.1 and 2b.The decrease of σ_s with N is also affected by grain size, being stronger for smaller grains. The effect of grain size on the critical stress to transform will change then, according to which cycle is considered for the measurement. This seems to be reasonable since constraints are larger for smaller grain sizes, which leads to a stronger effect during the first pseudoelastic cycles for smaller grain sizes.

In the same way as precipitates lead to an asymmetric behavior between transformation and retransformation after pseudoelastic cycling [39], a similar result was obtained here, since a strong evolution is observed during the transformation to martensite in the first cycles, whereas the retransformation is only slightly affected. It is clear then that the main creation of defects (martensite microplates and dislocations) required to accommodate the shape change, occurs while martensite is being formed. During the retransformation, the same defects would be used (at least partially) to recover the initial shape on unloading. This will lead to a mechanical irreversibility which was detected during each cycle although the retained deformation in each cycle decreases as N increases. Two kinds of defects can explain this result, as it was undoubtedly observed by transmission electron microscopy: the creation of dislocations and the formation of secondary martensitic plates which do not retransform after unloading. Cycled samples observed by TEM have shown that grain boundaries concentrate both dislocations and retained martensite although dislocations and martensitic plates have also been observed far from grain boundaries. This can be understood considering that martensitic plates, when nucleated at grain boundaries due to the stress accumulation, will grow within the grains. The intersection of martensitic plates far from grain boundaries will also provide stresses high enough to form dislocation arrays which are, in fact, observed (see Fig. 8c).

5. The asymptotic hysteresis

As mentioned above, a nearly asymptotic reproducible behavior is reached after approx. 100 cycles. This happens once all the necessary defects for the accommodation of the grains were created. Hereafter, the accommodation of the grains proceeds by movement of material using such defects during transformation, and the same defects are used when coming back during load removal.

The slope of the asymptotic hysteresis cycles depends on the grain size. It can be observed in Figs. 1 and 2 that, in the asymptotic behavior, the transformation starts at the very beginning of the loading processes. This means that internal stresses and martensite nuclei remain in the cycled specimen in such a way that transformation can start at a very small applied stress. However, increasing applied stresses are necessary for the transformation to proceed. Disregarding the hysteresis for the moment, we can consider that elastic energy is increasingly stored in the material as the transformation of the specimen advances. The slope of the cycle would be determined by at least two contributions. (a) It would be related to the storage of elastic energy as the transformation proceeds. This energy will be released on unloading, giving a reversible path of the transformation (disregarding the hysteresis for a moment). It could be, in principle, evaluated as proposed in [27], for example, provided that a detailed knowledge of the microstructure at each level of the transformation is available. (b) In addition to the pure elastic energy, other phenomena may contribute to the slope of the transformation-retransformation cycles. The dislocations existing and formed during cycling are pure dislocations in the β phase (their Burgers vectors have translation symmetry in this structure). However, when these dislocations are absorbed by a growing martensite plate, the Burgers vector of many of them may lose its translation symmetry in the martensitic phase. A stacking fault will be trailed by the β /martensite interface for each of this kind of dislocations being absorbed by the growing martensite [52–54]. Thus, a growing plate would require an increasing applied stress to advance any further.

On the other hand, the hysteresis obtained at the asymptotic stage plays a significant role if applications are to be considered. It is the smallest obtained hysteresis, although still significant if dissipation of energy is considered. Below, we propose a mechanism to understand the effect of grain size on the hysteresis in this stage. As mentioned above, critical stresses change with the deformation of the sample. In this sense, it is more convenient to use the area inside the pseudoelastic cycle as the significant parameter to evaluate the dissipation of energy.

Let us assume, following the results of Roqueta et al. [38], that the plastic work to accommodate each grain is proportional to its respective volume. Furthermore, the plastic work will be averaged over all grains. Then, the total plastic work, after a given elongation of the specimen, due to $N_{\rm g}$ grains accommodation, can be written as

$$\overline{W}_{\rm T} = \langle C \rangle \overline{V}_{\rm g} N_{\rm g} - \overline{W}_{\rm FS} \tag{2}$$

where $\langle C \rangle$ is the average plastic work to accommodate the shape change of an inner grain, per grain volume, which thus becomes independent of the grain size. The value of $\langle C \rangle$ depends on several factors, such as: the mechanisms of plastic deformation and their corresponding yield stresses, the size, shape and crystallographic orientation of the grains, etc. [38]. \overline{V}_g is the average volume of the grains, which, for simplicity, are all considered equal, with a cubic shape as shown in Figs. 12 and 13. In Fig. 13, a specimen with a



Fig. 13. View of the specimen with cubic grains of size *d*, length *L* and thickness *e*, to show the amount of grain free surfaces.

square cross section is used as an approximation of the cylindrical specimens used in the experiments. \overline{W}_{FS} in (2) represents the amount of accommodation work that is not produced by the grains that are at the edges of the specimen. These grains have one or two free surfaces and no work will be performed when moving materials against the empty space. In particular cases, for some grains, depending on the crystallographic orientation, the free surface will not go into deformation (this is the case of those two surfaces being parallel to the page in Fig. 12a). However, for random crystallographic orientations, all faces of a cubic inner grain may be submitted to some degree of deformation. As a first approximation, we will formally assign, on the average, $(1/6)\langle C \overline{V}_g$ of the plastic work to each face of the cubic grains. Thus, the total amount of work that is not produced for the grains with free surfaces becomes:

$$\overline{W}_{FS} = \frac{1}{6} \langle C \rangle \overline{V}_g N_{FS} \tag{3}$$

where $N_{\rm FS}$ is the total number of grain free surfaces in Fig. 13.

Finally, the total plastic work to accommodate the shape change of $N_{\rm g}$ grains with $N_{\rm FS}$ free surfaces becomes

$$\overline{W}_{\rm T} = \langle C \rangle \overline{V}_{\rm g} N_{\rm g} - \frac{1}{6} \langle C \rangle \overline{V}_{\rm g} N_{\rm FS} = \langle C \rangle \overline{V}_{\rm g} \left(N_{\rm g} - \frac{1}{6} N_{\rm FS} \right) \tag{4}$$

From Fig. 13, we obtain

The volume of the grains as: $\overline{V}_g = d^3$. The number of grains as:

$$N_{\rm g} = \frac{e^2 L}{d^3} = \frac{V_{\rm T}}{d^3}$$
(5)

The total transformed volume as: $V_{\rm T} = e^2 L$ The number of free surfaces as: $N_{\rm FS} = 4(eL/d^2)$ Inserting in (4) the expressions given in (5), we obtain:

$$\overline{W}_{\rm T} = \frac{\overline{W}_{\rm T}}{V_{\rm T}} = \langle C \rangle \left(1 - \frac{2}{3} \frac{d}{e} \right) \tag{6}$$

Expression (6) gives the total work for grain accommodation, per volume unit of the transformed material. The same amount of work would be delivered during the retransformation, as the grains have to come back to their initial shape in the parent phase. Thus in a closed hysteresis cycle, in a (σ , ε)plot, the total irreversible work, per volume unit, that accounts for the enclosed hysteresis area will be:

$$H_{\rm chc} = 2\overline{w}_{\rm T} = 2\langle C \rangle \left(1 - \frac{2d}{3e}\right) \tag{7}$$

This work is finally delivered as heat.

Comparing (1) and (7) we obtain that $\langle C \rangle = (1/2)(2.7 \pm 0.2)(MJ/m^3)$. From here, the coefficient (2/3) of the variable (*d/e*) in (7) shows a good agreement, within the experimental scatter, with the experimental coefficient (0.8 ± 0.4) of the same variable given in (1).

6. Conclusions

- 1. The effect of grain size and mechanical cycling on transformation stresses and hysteresis has been studied.
- 2. An important difference in the morphology of the stress–strain curves is observed in the first cycles between the largest and smallest grain sizes; this difference decreases as the number of cycles increases.
- 3. An asymptotic behavior is found after about 100 of cycles. The microstructure of the specimen in the asymptotic regime has been observed by transmission electron microscopy, showing the presence of dislocations and martensite microplates at the grain interfaces and also inside the grains.
- 4. At the asymptotic stage of cycling, it is found that the total hysteresis, per volume unit of the transformed material, depends on the (d/e) ratio.
- 5. A simple model explains the observed relationship between the enclosed area at the asymptotic stage and (d/e).

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