Gómez-Cortés, J., Nó, M., López-Ferreño, I. et al. *Size effect and scaling power-law for superelasticity in shape-memory alloys at the nanoscale.* **Nature Nanotech** 12, 790–796 (2017). This version of the article has been accepted for publication, after peer review (when applicable) and is subject to Springer Nature's AM terms of use, but is not the Version of Record and does not reflect post-acceptance improvements, or any corrections. The Version of Record is available online at: https://doi.org/10.1038/nnano.2017.91

Size-effect and scaling power-law for superelasticity in Shape Memory Alloys at the nano-scale

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Abstract

Shape memory alloys are promising materials to be incorporated in new generation of smart micro electro-mechanical systems but, in order to guarantee a reproducible and reliable behaviour, a still open question must be answered: Whether the critical

stress for the stress-induced martensitic transformation during superelasticity exhibits a size-effect similar to the one observed in confined plasticity. In the present work the answer to this crucial question is offered. A large series of [001] oriented pillars, from 2 μm down to 260 nm in diameter, have been milled by focused ion beam on Cu-Al-Ni shape memory alloy single crystals. The superelastic behaviour at the nano-scale has been carefully characterized by nano-compression tests. Here we demonstrate that there is a remarkable size-effect on the critical stress for superelasticity. Even more, we have quantitatively determined, for the first time, the scaling power-law for superelasticity at small scale in shape memory alloys, and a model explaining the observed size-effect is proposed.

Shape memory alloys (SMA) are firm candidates to be used as sensors and actuators in new generation of micro electro-mechanical systems (MEMS). This is due to the specific intrinsic behaviour of SMA, which undergo a structural displacive phase transition, named martensitic transformation (MT), between a high-temperature phase called austenite and a low-temperature phase called martensite[1]. The basic mechanism of the MT is a shearing of the austenite atomic lattice, which stabilize at a lower energy state when reaching the atomic positions of the new martensite lattice[1]. This atomic shearing can be completely reversible and is responsible for a macroscopic shape change when cooling or heating, giving place to the well-known shape memory effect[2-4]. In addition the MT can also be induced by an applied external stress able to promote the atomic lattice shearing. When the stress exceeds a critical value σ_c the stress-induced transformation occurs, and martensite nucleates within the austenite lattice creating internal interfaces, which move through the material given place again to a large change of shape. Moreover, when the stress is withdrawn the reverse MT occurs and the material recovers its original shape, without any residual deformation. Such behaviour is referred to as superelasticity or superelastic effect[2-4]. These outstanding properties attracted the interest of both scientific and technological communities driven the research on new SMA like Ni-based magnetic shape-memory alloys[5], Fe-based superelastic alloys[6,7], superelastic ceramics[8] and even combinatorial techniques are being used to promote the development of advanced SMA[9,10]. SMA are particularly attractive at small scale because they offer the highest work-output density (about 10^7 J m^{-3})[11,12] becoming more competitive when decreasing the size of the device. Consequently, testing the behaviour of SMA at small scale is of paramount interest not only as a source of basic knowledge but also as a required step for reliable applications. Unfortunately, the worldwide most widespread SMA, Ti-Ni, do not exhibit a good behaviour at nanoscale and Ti-Ni pillars show a loss of reversibility during stress-induced MT[13]. On the contrary, pioneering works on Cu-Al-Ni SMA showed a completely reversible and reproducible superelastic behaviour during nano-compression tests on micro- and nano-pillars[14,15].

A fundamental question remains open, whether the critical stress for stress-induced transformation during superelastic effect in SMA exhibits a size dependence similar to that observed in crystal plasticity[16-18]. A recent review on size effects in plasticity[19] has also overviewed the state of the art on the critical stress for superelasticity at small scale in SMA, concluding that no apparent trend emerges from the scatter of the works to date. In fact a size independence on shape memory behaviour has been reported[20] for NiTi pillars, and further attempts to evaluate size-effects on shape memory properties in magnetic[21] NiFeGa and ceramic[22] ZrO_2 micropillars, were masked by plastic deformation, which prevent the observation of the onset for stress-induced transformation.

In the present work we provide the first quantitative assessment of the stress-induced transformation at small-scales and demonstrate that the critical stress for superelasticity does indeed exhibit a size effect. This effect leads to a strong increase of the critical superelastic stress when decreasing the diameter of the pillar below the micrometer in Cu-Al-Ni SMA, and the scaling power-law for the observed size-effect on superelasticity has been found. A new atomic and elastic model has been proposed to quantitatively explain the apparition and the behaviour of such size-effect.

To study the size-effects on the superelastic behaviour of SMA we used [001] oriented single crystal slides of Cu-Al-Ni SMA, which according previous studies[23] were selected to exhibit superelastic effect at room temperature. We will focus our presentation here on a single alloy Cu-14Al-4Ni (wt%) whose details are given in the Methods. A top-down approach was considered when designing the present study. Several tens of [001] micro and nano pillars were milled by focused ion beam (FIB) technique, with decreasing diameters. Then superelastic nano-compression tests were performed on such pillars by using instrumented nanoindentation[24,25]. The details of milling and testing procedures are given in the Methods. In what follows, we provide the first explicit assessment of a size effect on the critical stress for superelasticity in SMA at small scales.

Superelasticity at micro-scale

In Figure 1 (a-c) three pillars in the range of ~1 μm diameter, which were milled in each one of the three different laboratories participating in this study, are shown. The load-depth curves obtained during the instrumented nano-compression test on each pillar are presented just below in Figure 1 (d-f), and the critical load at which the stress-induced martensitic transformation starts, can be clearly appreciated in all cases. During loading the progress of the forward MT produces the compressive collapse of the pillars, giving place to a deformation of several hundreds of nm in depth, which is completely recovered during the reverse MT when unloading. As expected, the critical load to nucleate the stress-induced MT decreases with the section of the pillar, but we have to remark that in some cases it takes place suddenly as is shown in the inset of Figure 1e for the pillar of 1.1 μm diameter, whereas in other cases the transformation plateau is preceded by some previous small pop-ins as shown in the inset of Figure 1d for the pillar of 1.35 μm diameter. From the measured section of the pillars, and using the methodology described in the Methods section, the stress-strain curves have been obtained for the above pillars and presented below in Figure 1 (g-i). The values of the critical stress to induce the MT are indicated in each figure, and it is basically the same (around 185 MPa) irrespective of the pillar size. About one ten of pillars with different diameters have been tested in the range from 2 μm down to 0.9 μm, and the results are plotted in Figure 2a, where it has been indicated the values of the stress for the first pop-in (blue diamond), and those for the MT plateau (magenta dot). We have also included in the same plot, the values reported in previous works (green dots), which tested exactly the same alloy[14,26,27]; a remarkable good agreement of the whole set of results can be observed. However, in order to verify the reliability of the testing method and the reproducibility from one pillar to another, the same nano-compression tests have been carried out on each pillar of the array shown in Figure 2b. The nano-compression tests of these 25 pillars are presented in the supplementary information, and the critical stresses to induce the MT are presented in Figure 2c, with the corresponding error bars. The critical stress to induce the MT fits squarely in a band around the mean value 187 MPa ± 3% for 80% of the pillars, and taking into account the error bars, 92% of the pillars come into this band. An exceptionally good reproducibility is obtained for the pillars of the array, and the mean value has been also included in Figure 2a as the magenta dot surrounded by a cyan circle. We may conclude that in the diameter range of micrometer, just down to 0.9 μm, there is no apparent evidence of a size-effect on the critical stress σ_c to start the stress-induced MT.

Size-effect on superelasticity at nano-scale

Lets now move down to the nano-scale diameter range. In Figure 3(a-c) the SEM images of three small diameter pillars down to 262 nm are presented. The superelastic behaviour due to the stress-induced MT is still very well observed at this small scale and in Figure 3(d-f) the load-depth curves for such pillars are plotted. In these small pillars the critical load is reached just for a few tens of μN and the associated transformation strain is only of some tens of nanometres. The stress-induced MT takes place very fast, as shown in Figure 3(f,i), where a strain larger than 4% takes place in just 1.2 ms; the collapse of the pillar is faster than the motion of the indenter tip, given place to an apparent decrease of the load. At this scale a residual deformation of about 2 to 3 nm is observed during the recovery of the first cycle, Figure 3(e-f), which is probably linked to the flattening of the top surface roughness of the pillar beneath the indenter. The second superelastic cycle becomes completely closed during the recovery (see supplementary information) and no residual indent is observed after many cycles, evidencing that there is no plastic deformation of the pillars during the nano-compression cycles. From the above load-depth curves, the stress-strain plots can be obtained as shown in Figure 3(g-i). The reproducibility of the nano-compression tests continues to be remarkably good as can be seen in the supplementary information. The important point is that in this diameter range, the critical stress σ_c strongly increases when decreasing the diameter of the pillar, as illustrated in Figure 3(g-i) for the presented pillars.

Several series of small pillars have been milled and measured to obtain the Figure 4a, which clearly shows the trend of the critical stress measured during the first cycle, versus the diameter of the pillars. Red dots correspond to the stress-plateau and blue diamonds correspond to the first pop-in, as commented before. For comparison, we have included three points, green dots, from previous works[14,26,27] on the same kind of samples, as well as one point obtained by in-situ testing in another different equipment[28]. As explained in Methods, we studied the potential influence of Ga contamination on the critical stress, and several nanopillars were milled at 5 KV to minimize damage and eventual Ga implantation; the points corresponding to the tests on these pillars are also included in Figure 4a as cyan triangles. All the points match very well in a homogeneous trend that clearly demonstrates the existence of a size effect on the critical stress for the stress-induced MT taking place during superelastic behaviour, and from the cyan points and the analysis presented in Methods, we exclude the potential influence of gallium alloying as relevant to this dramatic size-effect on the critical stress for superelasticiy. In a first approach we may attribute this increase of the critical stress to the scarcity of defects constituting the preferential points for heterogeneous nucleation of martensite, for instance on dislocations[29], such as was previously suggested[15]. In absence of any preferential nucleation point, martensite plates must be homogeneously nucleated inside the austenite crystalline lattice. However, in a recent work[27] the decrease of the critical stress σ_c with cycling was reported and interpreted in terms of the development along cycling of a dislocation network in the plastically deformed area beneath the indenter, and constituting preferential nucleation points for martensite. Then, in order to verify if nano-compression cycling has a similar influence in the nanometre range, a series of selected pillars from those plotted in Figure 4a were systematically tested for more than 100 cycles and in many cases above 200 cycles. A slight decrease of the critical stress σ_c on cycling was observed along training cycles, which becomes completely stable for the first 100 cycles or before. An example of the series of superelastic tests along cycling is presented in the supplementary information. In Figure 4b the critical stress for the cycles 50^{th} (green diamonds) and 100^{th} (blue dots) has been plotted for comparison with the one measured for the first cycle (red dots). Indeed, a slight decrease on the critical stress is observed along cycling, until the stable behaviour is reached, but still an important size-effect is reported in Figure 4b after 100 cycles. This shows that cycling does not destroy the size-effect on the superelastic critical stress observed in the nanometre range.

Discussion and scaling power-law for superelasticity

To analyse the size-effect presented in Figure 4 we must consider that the atomic shearing on the $L2_1$ austenite phase, giving place to the new martensite lattice, is parallel to the <10-1> directions on the {101} planes, which are the basal planes of the martensite (obviously the symmetry equivalent systems must be considered). Then, martensite nucleation can be induced by a pure shearing of the atomic lattice (homogeneous nucleation), or promoted by the atomic configuration of some pre-existing defects (heterogeneous nucleation). In-situ transmission electron microscopy superelastic tests showed that martensite easily nucleates (and annihilates when reversed) on the <111> screw dislocations of the austenite[29,30]. This is because the core of the <111> screw dislocations in BCC metals (including B2 and derived ordered lattices) is spread in the three {110} planes containing the threefold symmetry axis[31,32], and each dissociated partial on such {110} planes promotes the motion of the atoms to a stable minimum at about 1/3 position of the ½ <110> direction (see Supplementary information for a schematic drawing of the above description).

As both, homogeneous and heterogeneous nucleation of martensite are closely related to the atomic configuration at the core of dislocations, we may consider, in a first approach, that the size effect on the critical stress σ_c for the stress-induced MT during superelastic behaviour could follow a law similar to the scaling law proposed by Dou and Derby[33] for the strength of metals at micro- and nano-scale. Then for stress-induced MT the following empirical law can be proposed:

$$\sigma_c = \sigma_0 + A \cdot d^n \quad (1)$$

where σ_c is the critical stress for the superelastic onset (instead of the yield stress σ_y considered in plasticity), σ_0 is the scale-independent stress for superelasticity, d is the pillar diameter and A and n are empirical constants. In our case, the scale independent σ_0 stress can be considered as the asymptotic value of the stress, when no size-effect is present, and can be considered as the final value after cycling in Figure 4b, σ_0=165 MPa, plotted as a blue line. Another option could be to consider the value measured in the bulk single crystal, σ_B=132 MPa, which is presented in the supplementary information, and plotted in Figure 4b as a grey line. At this point we have to note that no plastic deformation has been observed in any of the tested pillars below 900 nm in diameter, even after 100 cycles, and the bulk value is only reached after plastic deformation during cycling[27], when nucleation is clearly heterogeneous. So, in order to analyse the size-effect without losing generality, we have considered the asymptotic value as the scale independent σ_0 stress. As in the case of plasticity[19,33] a further refinement should consider the resolved shear stress on the direction and plane for the atomic shearing promoting the stress-induced MT, using the corresponding Schmid factor. Traditionally the Schmid factor for the selection rules of the growing martensite in macroscopic tests has been considered as the one provided by the habit plane between martensite and austenite[34]. However, superelastic in-situ tests at the TEM have shown that at small scale the selection rules for martensite nucleation are determined by the Schmid factor of the basal plane of martensite[35]:

$$m_{basal} = \sin\phi \cdot \cos\lambda \quad (2)$$

being ϕ the angle between the basal plane and the applied stress direction, and λ the angle between the shearing direction and the applied stress. Then the critical resolved shear stress $\tau_{c(RSS)}$ for nucleation of martensite must be given by:

$$\tau_{c(RSS)} = \sigma_c \cdot m_{basal} \tag{3}$$

and taking into account the above equations, the scaling law for the resolved critical stress on superelastic behaviour at small scale becomes:

$$\left(\tau_c - \tau_0\right)_{RSS} = A \cdot d^n \tag{4}$$

In our case the stress is applied on the [001] direction and for Cu-Al-Ni SMA the basal planes of martensite are parallel to the {101} planes and the atomic shearing takes place on the <10-1> directions (there are four symmetry equivalent systems). These shearing systems have the maximum m_{basal}= 0.5 and consequently are the ones controlling the stress-induced transformation. Then we have applied the above equations to the experimental results from Figure 4, to obtain the scaling power-law behaviour plotted in Figure 5. A remarkable good fitting is appreciated for both sets of experimental results; for the σ_c measured during the first cycle (Figure 4a) the slope is n =-2.02, and for the σ_c measured after 100 cycles (Figure 4b) the slope is n =-2.04. So a value of n =-2.00 ± 0.05 can be considered for the exponent of the scaling power-law. This is an outstanding result not only because it is the first time that the scaling power-law is determined for superelasticity at small scale, but also because this exponent exceeds in more than three times the mean observed exponent for confined plasticity, which ranges between -0.3 and -0.8 for non pre-deformed samples[19,33,36,37]. What is the physical meaning of this exponent? This is still an open question in confined plasticity, after hundred of works, and at this stage remains open for confined superelasticity, but in what follows a rationalized explanation for the physical meaning of the measured exponent n and the empiric parameter A, will be offered through an atomistic and elastic model.

Indeed, we may ask about the possible explanations for the observed size-effect on the critical stress for superelasticity. The concept of "dislocation starvation"[38] was used in confined plasticity to explain the size-effect on the crystal strengthening, because in dislocation starved crystals new dislocations must be created requiring an applied stress close to the theoretical one for the perfect lattice shearing. A similar concept than in plasticity was already invoked for the size-effet on superelasticity[15], the paucity of defects for heterogeneous nucleation of martensite in small volumes, leads to a situation in which the martensite must be homogeneously nucleated by direct shearing of the austenite lattice, requiring a much higher applied stress. In both scenarios, the development of a dislocation network by plastic deformation, destroys or strongly decreases, the observed size-effect[27,36]. However, even in absence of plastic deformation, the slight decrease of the critical stress for superelasticity σ_c along cycling, presented in Figure 4b, suggests that some irreversible structural change is taking place at atomic scale, making the nucleation of martensite easier than in previous cycles. In absence of plastic deformation, the creation of another kind of atomic defects, different from perfect dislocations, can be envisioned to explain an easier nucleation while maintaining the size-effect. Indeed, the formation of stacking-faults associated to individual partial dislocations, at sharp-edge of surfaces, has been considered in several works[39-41] conducted by molecular dynamics and in-situ TEM observations, as the mechanism responsible for the nucleation of the deformation twinning mode in defect-free FCC metallic nanowires. In addition, numerical simulations of dislocation nucleation in such pristine crystals show that in most of cases the preferred nucleating dislocation was a leading partial one[42]. Recently, in-situ TEM tensile tests in defect-scarce nanowires[43] evidenced a direct connection between incipient plasticity and nucleation of partial dislocations at free surfaces. In what concerns SMA, the formation of pre-martensitic stacking-faults initiated by correlated motions of a group of atoms in a short period of time has been described by molecular dynamics[44]. Then, at the light of the preceding works, we offer the following rationalization for the observed size-effect and its slight evolution during cycling. In defect-free crystals the first superelastic cycle should proceed by homogeneous nucleation of martensite, requiring a high stress. During the reverse transformation, when unloading the first cycle, the sheared martensite lattice transforms back to regenerate the initial austenite lattice, but in this process some residual stacking-fault of the martensite lattice could become stabilised at the surface of the pillar (for instance by oxide film covering the pillar). This atomic-scale stacking-fault will offer a preferential nucleating point for further cycles, decreasing slightly the stress required to induce the first atomic lattice shearing. However, as the austenite lattice continues to be defect starved, the progress of the stress-induced transformation, from the very beginning of the superelastic plateau, still requires a high stress to shear the perfect atomic lattice of the austenite being transformed to martensite. A quantitative model for homogeneous martensite nucleation, predicting the observed n=-2 exponent, will be presented as follows.

Atomistic and elastic model for the size-effect on superelasticity

The homogeneous nucleation of martensite can be stress-induced through the lattice distortion of the cubic β ($L2_1$) austenite parallel to the {011} planes, which constitute the basal planes of the orthorhombic γ' martensite. When an axial compression stress $\sigma_{zz}=-\sigma_{ap}$ is applied on the [001] direction of a pillar, a compression strain $\varepsilon_{zz}=-\sigma_{ap}/E$, as well as a lateral expansion strain $\varepsilon_{rr}=-\nu\cdot\varepsilon_{zz}= \nu\cdot\sigma_{ap}/E$, are produced according the rules of elasticity (in cylindrical coordinates and being ν the Poisson ratio). As a consequence, an expansion in [01-1] direction on the (011) plane will occur, and all bonds parallel to this direction will be elastically stretched, Figure 6a. When this atomic elastic displacement in β phase reaches the value U_M corresponding to the position of atoms in the b atomic planes of the martensite, some atoms will move forward to relax the stretched bonds on *b* planes, while some atoms on *a* planes spontaneously collapse back to relax the bonds, as indicated by grey arrows in Figure 6b. This shearing of the atomic planes parallel to (011) will be responsible for the nucleation of martensite, Figure 6c. This homogeneous nucleation mechanism explains the experimentally observed abrupt strain plateau, associated to the stress-induced MT, taking place suddenly from the elastically loaded austenite, see Figures 3d-i. The critical atomic displacement U_M on the (011) planes, to induce the MT, can be easily calculated from the crystallography of both phases, and taking the β ($L2_1$) lattice parameter *a*=0.58216 nm [35], it becomes $U_M=1/6\cdot(1/\sqrt{2}\cdot a)$=0.0686 nm. However, to reach this U_M value, which is the component of the displacement on the [01-1] direction, a displacement on the radial [010] direction U_{Mr} is required.

The above mechanism of homogeneous nucleation will exhibit a size-effect. Indeed, in absence of any crystal limitation and for an external applied stress σ_{ap} the radial displacement is given by $U_r=(\nu\cdot\sigma_{ap}/E)\cdot r$, being a lineal function of *r* as depicted in Figure 6d, and the displacement U_{Mr} will be reached at a radio r_0. This means that for radios above $r > r_0$, spontaneous nucleation can take place for a critical applied stress $\sigma_{apc}(r_0)$, and above the limit radio r_0 the stress for martensite homogeneous nucleation will be constant, being r_0 a parameter that should be determined by the model; we have to note here that the elastic strain $\varepsilon_{rr}= \nu\cdot\sigma_{apc}/E=\partial U_r/\partial r$ is the slope of the plot in Figure 6d. Now, let us consider the nucleation in a confined volume, like a pillar of radio $r_{P1} < r_0$. In this case, the displacement U_{Mr} have to be reached inside the pillar and then the imposed strain $\varepsilon_{rr}(r_{P1})$ must be higher than $\varepsilon_{rr}(r_0)$ and consequently $\sigma_{apc}(r_{P1}) > \sigma_{apc}(r_0)$, see Figure 6e. If we still reduce the size of the pillar $r_{P2} < r_{P1} < r_0$ it becomes $\sigma_{apc}(r_{P2}) > \sigma_{apc}(r_{P1})$, and consequently a size-effect appears on the critical stress to induce the MT. To quantify this size-effect we have to ask: What is the increment of the strain $\varepsilon_{rr}(r_P)$ required to reach U_{Mr} when the radio r_P is reduced? This is the derivative:

$$\frac{\partial \varepsilon_{rr}(r_P)}{\partial r_P} = \frac{\partial}{\partial r_P}\left(\frac{U_{Mr}}{r_P}\right) = -\frac{U_{Mr}}{r_P^2} = \frac{\nu}{E} \cdot \frac{\partial \sigma_{apc}(r_P)}{\partial r_P} \tag{5}$$

From (5) we find $d\sigma_{apc}(r_P)$, which can be expressed in increments, then changing radios r_P by diameters d_P and taking into account the corresponding projections, we finally get:

$$\sigma_{apc}(d_P) = \sigma_{apc}(d_0) + \frac{2\sqrt{2} \cdot E \cdot U_M}{m_b \cdot \nu} \cdot (d_0 - d_P) \cdot \frac{1}{d_P^2} \tag{6}$$

The above equation (6) accounts for the size-effect on the critical stress for the stress-induced MT and contains two terms, one quadratic on $1/d_P^2$ and another varying on $1/d_P$. When d_P approaches d_0 both terms become compensated and there is no size-effect. On the contrary, when d_P is much smaller than d_0, the quadratic term becomes dominant and there is a strong size-effect. To fit the theoretical equation (6) of the homogeneous nucleation model to the experimental values presented in Figure 4a, we have just considered the real numerical values of E=23.5 GPa [34], ν=0.47 [45], m_b=0.5 and U_M=0.0686 nm, as well as the exponent n=-2 predicted by the model. Only two parameters, $\sigma_{apc}(d_0)$ and d_0, have been let free, and from the fitting to the experimental values of Figure 4a, the diameter limit of d_0=1740 ± 40 nm is obtained. The fitting is exceptionally good and the result for d_0 is quite reasonable, allowing us to conclude that the proposed model explains quite well the size-effect on the critical stress for superelasticity at nano scale. For pillars with a diameter $d \geq d_0$ the homogeneous nucleation mechanism will still operate, provide that no plastic deformation occurs. For pillars with a diameter $d < d_0$, and in absence of plastic deformation, there is a size-effect that becomes dramatic for $d < d_0/2$ when the quadratic term firmly stands. The lower limit for the application of the size-effect model depends on the stress at which plastic deformation will occur. In several pillars that have been heavily loaded after the stress-induced MT, martensite became plastically deformed at stresses above 1200 MPa, what means that the size-effect should be still observed in pillars as small as 175 nm in diameter. This mechanism is consistent with the observed experimental results and obviously will be ruled by statistical local fluctuations on stress and temperature, whose importance on nucleation processes in incipient plasticity has been recently outlined[43].

In summary, we have demonstrated the existence of a remarkable size-effect on the critical stress for superelasticity during the stress-induced martensitic transformation in SMA. Our results provide new insights on the behaviour of SMA at small scale, and taking into account the good superelastic behaviour along cycling, which has also been reported in Cu-Al-Ni during thousand of cycles at micro-scale[46], we anticipate an exceptionally reproducible behaviour at nano-scale, where superelasticity is taking place in absence of plastic deformation. We have also quantified the size-effect on superelasticity, finding the scaling power-law that rule for Cu-Al-Ni SMA, and proposed a model for homogeneous nucleation of martensite that completely explains the observed size-effect. The above findings open new challenges to verify the universality of this power-law for the confined stress-induced martensitic transformation in other SMA, and even in another materials undergoing field-induced diffusionless phase transformations. Our results can ultimately be used to design new strategies of SMA applications for the development of the coming generations of MEMS and NEMS, as well as for smart devices to be used in flexible electronics.

Methods

Samples. In order to conduct a systematic and reproducible series of nano-compression tests to study the size-effect on superelasticity, we focused our study on a single alloy composition because of the strong dependence of the MT temperatures of Cu-Al-Ni SMA on Al concentration[23]. The selected alloy was Cu-14Al-4Ni (wt%), which transforms at the following MT temperatures: Ms=252 K, Mf=242 K, As=273 K and Af=285 K (martensite start and finish, austenite start and finish respectively), and consequently exhibits a fully recoverable superelastic behaviour at room temperature. Taking into account the high elastic anisotropy of this family of alloys[34], we used oriented [001] single crystals grown by the Stepanov method, from which several slides, some millimetre thick, were cut. Samples were annealed at 1173 K in argon for 1800 s and then quenched in ice water to frozen the metastable austenite phase. Sample slides were finally mechanically thinned and polished.

Focused Ion Beam machining. The micro- and nanometre diameter pillars were machined by focused ion beam (FIB) technique, from the above described slides, in order to obtain oriented [001] cylindrical pillars. The influence of gallium contamination, during FIB milling, has been a matter of controversy from the very beginning of the studies on confined plasticity[16-19]. After many hundred of works (see the overview[19]) even with alternative FIB-less production methods[47,48], there is a general agreement on the non relevance of the gallium contamination on the extensively observed size effects in plasticity at small scale. However, we were aware that, for a size-effect study, the reliability and reproducibility of the results must be guaranteed, avoiding any experimental artifact from the sample milling. Then, pillars of different sizes were milled in three laboratories with different FIB equipment and milling procedures: A FEI Quanta 200 3D DualBeam at the University of Cadiz, a FEI Helios 650 at Nanogune Research Centre and a FEI Helios 650 at the SGIKER of the Basque Country University. Nevertheless, it can be argued that the potential damage and contamination of the sample is not depending on the machine, but on the milling conditions, particularly ion accelerating voltage and milling current (dose). The standard conditions for milling were 30 KV for I-beam and decreasing currents for the different milling steps, 80 pA, 40 pA and 24 pA, followed by finishing steps with 15 pA and 7,7 pA as the diameter of the pillars becomes smaller; several pillars in different machining series were milled at 5 KV with similar currents for milling and finishing. The aspect ratio of the pillars fluctuates between 1/3 and 1/5, as recommended for micro-compression tests[49], and for small pillars it becomes practically not possible to avoid some taper (2º-4º) and a slightly rounded circular edge at the top of the pillar. Finally, as we are dealing with stress-induced MT, it could be also argued that perhaps a small amount of gallium could decrease dramatically the MT temperatures and consequently increase the critical stress for superelasticity at room temperature. This aspect has also been approached and presented in the last section of the supplementary information. The complete analysis of the potential influence of gallium on the critical stress is discussed in detail in this section of the supplementary information and we conclude that gallium is not responsible for the remarkable size effect on the critical stress for superelasticity seen in this work.

Nano-compression tests. Instrumented nanoindentation[24,25] has demonstrated to be a highly reliable technique for nano-compression experiments and has been successfully applied to address fundamental issues on crystal plasticity at small scale, including size effects[16-19], as well as on superelasticity at nanoscale[14,15]. In the present work a Triboindenter TI-950 (from Hysitron Inc.) was used to perform all series of nano-compression tests. The procedure to carry out such experiments has been extensively described in previous works[14,26,27]. A spheroconical diamond indenter tip with a 2-μm radius was used to obtain a contact image and after carefully positioning the apex of the indenter over the top of the pillar, the nano-compression test was performed. We carried out a multiple-cycle compression tests (typically 5 cycles) by using a load function at a constant loading-unloading rate; the tests were conducted in load control, to avoid any potential feedback artifact, at a loading rate of 250 $\mu N\ s^{-1}$ for pillars above 1-μm diameter and at a slower loading rate of 10 $\mu N\ s^{-1}$ for smaller pillars. The equipment is working in an air-conditioned room and during the tests the temperature was measured with the sensor incorporated at the bridge of the TI-950; 300 ± 1 K were maintained along all compression test series. Drift was analyzed and automatically corrected by the TriboScan software. The point from In-situ test, included in Figure 4a, has been measured with a Hysitron Pico-Indenter PI 85 with a flat indenter, inside a SEM-FEG JEOL 7000F. The nano-compression results on the pillars milled in the present work have been compared with previous works[14,26,27] on the same kind of samples, which were milled at the Center for Nanoscale Systems of the Harvard University with a FEI Dual Beam DB235 instrument and tested at the DMSE of the MIT. As shown in Figures 2 and 4, all series of milled pillars match up properly in the same behaviour trend.

Stress-strain analysis and errors. To convert the raw data load-depth into stress-strain curves, an analysis of the stress, the strain ant its error is required. The critical stress for the stress-induced MT, observed during superelastic tests, will be reached at the smallest section of the pillar and for pillars exhibiting some taper this will correspond to the top of the pillar. However, taking into account the rounding effect produced by FIB in small pillars, the use of the top section will give place to an overestimation of the critical stress, whereas the use of the mean diameter of the pillar will give place to an underestimation with no physical meaning. To overcome this dilemma, we measured a section close to the top of the pillar (but free of rounding effect) at a height below the top, equal to the radius of top circle of the pillar (which is easily measured in a 45º tilted view at the SEM). This criterion has been applied to all pillars giving comparable and consistent results for the complete set of pillars. The diameter of this section has been measured at the SEM-FEG JEOL 7000F, with an error smaller than ±10 nm. From the tests at the TI-950 the critical load is measured with an error of ±0.3% for small pillars exhibiting an abrupt plateau, and with an error of ±1% for big pillars with less abrupt start of the plateau. Using the classical theory of errors, the critical stress $\sigma_c=L_c/S_p$ (critical load / section of the pillar) has been estimated with an error of ±4% for small pillars (down to 262 nm of diameter) and with an error smaller than ±2% for the biggest pillar (2000 nm of diameter). Concerning the reproducibility of the tests, the critical stress for the array of 25 pillars, in Figure 2, has been measured with a standard deviation of ±3%. At the light of these data, an overall error of ±7% has been considered for the error bar of the critical stress on Figure 4, the size of the dots being larger than the error bar for the diameter of the pillars. Finally, to estimate the strain of the pillar from the displacement of the indenter, the height of the pillar must be used; once again, the shape of the pillars makes difficult the measure of the height to be considered. However, it is known from previous works that the $E_{[001]}$ elastic modulus measured in micropillars[14] is basically the same than in macroscopic single crystals with such orientation[34], $E_{[001]}$=23.5 GPa. Then, the effective height of the pillars has been evaluated as the one matching this value of the modulus during the elastic strain, as indicated in Figures 1i and 3i. With the above considerations, the superelastic strain takes the expected values, approaching in some cases the theoretical maximum value of 8.2% for γ' martensite in compression on the [001] direction[50].

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Acknowledgments

This work has been supported by the Spanish Ministry of Economy and Competitiveness, MINECO, projects MAT2009-12492, MAT2012-36421 and CONSOLIDER-INGENIO 2010 CSD2009-00013, as well as by the Consolidated Research Group IT-10-310 and the

ETORTEK-ACTIMAT project from the Education and Industry Departments of the Basque Government and Junta de Andalucía (INNANOMAT PAI research group TEP-946. J.F. G-C thanks the Ph.D. Grant from the MINECO. This work made use of the FIB facilities of the SGIKER from the UPV/EHU and of IMEYMAT-UCA. Co-funding from FEDER-EU and REACT project from H-2020, Grant 640241, are also acknowledged.

Author contributions

J.M.S-J and M.L.N. designed the experiments, developed the model and wrote the manuscript. I.L-F and J.M.S-J produced the alloys. J.F.G-C, J.H-S, S.I.M., A.C., M.L.N. and J.M.S-J performed the milling of the pillars by FIB and took the SEM micrographs. J.F.G-C and J.M.S-J performed the nano-compression tests. All authors discussed the results and reviewed the manuscript.

Competing financial interests

The authors declare no competing financial interests.

Figure legends

Figure 1 | Superelastic behaviour in micro-scale pillars. a,b,c, Scanning electron micrographs of three pillars milled by FIB with a measured diameter (see Methods) of (**a**) ϕ=1.35 μm, (**b**) ϕ=1.1 μm and (**c**) ϕ=0.9 μm. **d,e,f,** Nano-compression load-depth curves during superelastic tests performed on the above pillars (**a**) to (**c**). To be remarked the first pop-in in the inset of (**d**) in comparison with the abrupt onset of the superelastic plateau in the inset of (**e**). **g,h,i,** Stress-strain superelastic cycles corresponding to the above load-depth curves. The critical stress σ_c for superelasticity is reported in each graphic. In (**i**) the slope of the Young modulus $E_{[001]}$=23.5 GPa has been indicated.

Figure 2 | Critical stress for superelasticity in the micro-scale domain, and reproducibility of the nano-compression tests. a, Plot of the critical stress σ_c for superelasticity as a function of the pillar diameter, above 0.8 μm. Green dots are taken from previous works performed on the same kind of samples; ϕ=1.7 μm[14], ϕ=1.6 μm[26], ϕ=1,55 μm[27]. The magenta dot cyan encircled represents the mean value from the array of pillars of (**b**). **b**, Scanning electron micrograph of the array of pillars used to test the reproducibility of nano-compression tests, cyan encircled dot in (**a**). **c**, Critical stress measured for each one of the pillars from the array shown above (**b**) and mean value plotted in (**a**). See supplementary information for the individual load-depth cycles.

Figure 3 | Superelastic behaviour in nano-scale pillars. a,b,c, Scanning electron micrographs of three pillars milled by FIB with a measured diameter (see Methods) of (**a**) ϕ=435 nm, (**b**) ϕ=335 nm, and (**c**) ϕ=262 nm. **d,e,f,** Nano-compression load-depth curves during the first superelastic test performed on the above pillars (**a**) to (**c**) (second cycles are shown in supplementary information). **g,h,i**, Stress-strain superelastic cycles corresponding to the above load-depth curves. The critical stress σ_c for superelasticity is reported in each graphic. In (**i**) the slope of the Young modulus $E_{[001]}$=23,5 GPa has been indicated.

Figure 4 | Size effect on the critical stress for superelasticity. a, Critical stress for the stress-induced MT of the whole set of micro- an nano-pillars plotted as a function of the pillar diameter. The stresses for the plateau (red dots) and for the first pop-in (blue rhombuses) are presented for comparison. As in Fig. 2, we have included the results from previous works[14,26,27] (green dots), the point from in situ experiments[28] (magenta square) and the ones corresponding to pillars milled at 5KV (cyan triangles). The included error bars are evaluated in the Methods section. The continuous violet line represents the prediction, according the equation (6), from the model proposed to explain the size-effect on the critical stress for superelasticity. **b,** Evolution of the critical stress for superelasticity on cycling, plotted as a function of the pillar diameter; First cycle (red dots), 50th cycle (green rhombuses) and 100th cycle (blue dots). Nano-compression tests reach a stable behaviour for the 100th cycle (see supplementary information) and the stress measured for the asymptotic non-dependent on size effect stress, 165 MPa, is considered as the scale-independent critical stress σ_o and plotted as a blue line. The critical stress for bulk single crystals σ_B is also plotted, for comparison, as a gray line.

Figure 5 | Scaling power-law for superelasticity at the nano-scale. Logarithmic plot of the size-dependent resolved critical stress, according equation (4), as a function of the pillar diameter, for the whole set of pillars. Red dots correspond to the first cycle, from Figure 4(a), and blue dots to the 100th cycled pillars, from Figure 4(b). Red and blue lines correspond to the respective fitting of both plots to the equation (4), with the indicated slope.

Figure 6 | Atomistic and elastic model accounting for the size-effect on superelasticity. **a,** Atomic stacking sequence of the austenite β ($L2_1$) lattice parallel to the (011) plane. **b,** Lattice of the β phase when elastically stretched on the [01-1] direction by an applied stress σ_{ap}, which produce a displacement U_M. Grey arrows indicate the atomic relaxation motion during the shearing responsible for the MT. **c,** Lattice of the γ martensite after the relaxation of the atomic bonds parallel to the [01-1] direction. **d,** Schema of the dependence of the radial strain ε_{rr} on the radio of the pillars, $\varepsilon_{rr}(r)=\partial Ur/\partial r=U_{Mr}/r$, required to reach the critical condition for the lattice transformation.