Improvements in the mechanical properties of the 18R ↔ 6R high-hysteresis martensitic transformation by nanoprecipitates in CuZnAl alloys

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ABSTRACT

The 18R ↔ 6R martensite–martensite transformation in Cu-based alloys exhibits large hysteresis, large pseudoelastic strain and weak transformation stress dependence on temperature. However, concomitant plastic deformation taking place in the 6R phase inhibits the use of these properties for applications. A novel approach to minimizing or even suppressing 6R plastic deformation during the 18R–6R transformation in CuZnAl shape-memory alloy single crystals with electronic concentration $e/a = 1.48$ is presented. The method is based on a thermal treatment that introduces nanoprecipitates in the alloy. Results suggest that the role of CuZnAl shape-memory alloys in engineering should be reconsidered, as many energy damping applications could benefit from the huge hysteresis associated with the 18R–6R transformation, once the 6R plastic deformation is suppressed.

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1. Introduction

The potential application of shape-memory alloys (SMA) in damping devices for civil structures, like buildings and bridges, to smooth out the oscillations produced by earthquakes, winds, etc., has been a subject of increasing interest in recent years. The pseudoelastic effect and the hysteresis cycle associated to the martensitic transformation in SMA are used to dissipate the energy of the oscillations [1–9].

Several relevant parameters are to be considered in this kind of applications. Firstly, the hysteresis width associated to the pseudoelastic cycle. The wider the hysteresis, the larger the dissipated energy will be in each cycle, providing for a more efficient damping device. Secondly, the critical stresses to induce the pseudoelastic effect depend on the working temperature, through the Clausius–Clapeyron equation [10]. A strong variation of these stresses with temperature will change the stiffness and the resonance frequencies of structures. As a result, the performance of damping devices would also be ambient-temperature dependent. In addition, other important parameters to take into account are: the evolution of the pseudoelastic cycles during cycling, the num-

ber of cycles until fracture, the evolution of the material itself due to atom diffusion effects, with time and temperatures, etc.

So far, NiTi-based alloys have been the most extensively studied materials, using the B2 ↔ B19′ martensitic transformation as a pseudoelastic mechanism. The average hysteresis width in the first pseudoelastic pull–pull cycle ranges from about 200 MPa to about 400 MPa, depending on several factors, namely: specimen preparation method, crystallographic texture, wire diameter or specimen size, working temperature, amount of elongation, deformation velocity, etc. [5,11–15]. Ni–Ti wires textured along the $[1 1 1]_{B2}$ direction can undergo about 9% pseudoelastic strain [15]. However, the pseudoelastic behavior degrades rapidly in the first cycles towards an asymptotic behavior. The final reasonably steady state is reached after a few hundred cycles. The average hysteresis width drops to a value which is roughly (or sometimes less than) one half of its initial value. In addition, non-recoverable strain accumulates in the material during cycling, reducing the length of the pseudoelastic deformation by an amount that could reach up to about 4% of the initial useful length [7–16], depending on the several aforementioned factors. Both effects, i.e., the reduction in hysteresis width and the reduction in pseudoelastic strain, will result in a strong reduction in damping capacity during cycling.

Another important aspect to be taken into account for the use of SMA in damping devices is related to the temperature dependence of transformation stresses (σ). In NiTi alloys, transformation stresses depend strongly on the working temperature [9,14,15]. The

most acceptable value given for the B2 ↔ B19′ martensitic transformation is $d\sigma/dT = 6.3$ MPa/K [14].

On the other hand, some interesting studies have also been carried out in CuAlBe alloys as applied to damping devices. The β ↔ 18R transformation in polycrystalline CuAlBe alloys has been chosen for damping prototypes of applications for civil structures, such as family houses [7,8,17]. The average hysteresis width in the tensile pseudoelastic behavior of CuAlBe polycrystalline materials ranges from about 20 to 150 MPa, depending on grain size, amount of pseudoelastic deformation, previous thermal treatments, deformation velocity, etc. The pseudoelastic behavior in CuAlBe degrades rapidly in the first cycles towards an asymptotic behavior, similarly to NiTi alloys. The final reasonably steady state is reached after about a hundred cycles. The hysteresis width reduces to a value which is roughly (or sometimes less than) half of its initial value. The pseudoelastic strain in the first cycle can be about 6.5%. However, this recoverable deformation is reduced by cycling by an amount which depends on the several factors aforementioned [7,8,14,18,19]. The best value for the relation between transformation stresses and working temperature is $d\sigma/dT = 2.2$ MPa/K [14], which is much lower than the value for NiTi given above. Very little attention has been paid to the damping capacity in other Cu-based alloys, such as CuAlNi [20,21] or CuAlMn [22], and ferrous alloys such as FeMn-based alloys [23].

In this report, we consider the 18R ↔ 6R martensite-to-martensite transformation in CuZnAl alloys. These alloys, depending on their composition, can undergo several martensitic transformations between metastable phases, which are induced either by temperature changes or by mechanical stresses [10,24–26]. In alloys with electronic concentration $e/a = 1.48$ and β ↔ 18R martensitic transformation temperature M_s close to 273 K, when a single crystal is strained in tension at temperatures above M_s, two martensitic transformations can be observed. First, the metastable β phase, usually called austenite, transforms into the 18R martensitic phase. This transformation can be reversed, with relatively small hysteresis. However, if the sample is further strained, the 18R phase could transform into the 6R martensite, depending on the orientation of the tensile axis. The 6R martensite has an FCT-type structure [10]. This phase transition shows stress hysteresis of about 150 MPa [25,27], whereas the deformation associated to a complete 18R–6R transformation is about 10% for a completely transformed material. A noticeable fact which makes this transition extremely interesting for applications is that, starting from the β phase, a reversible deformation of up to approximately 20% can be obtained if a complete β–18R–6R transition is produced. In order to induce the 18R–6R transformation, the tensile axis must be within about 22° from the $[1\,0\,0]_\beta$ direction, otherwise the 18R phase undergoes brittle fracture without a noticeable yield point; occasionally, 2H martensite might be observed after fracture [28].

An important additional detail of this work is based on the fact that the 18R ↔ 6R transformation and retransformation stresses (σ) show weak temperature dependence. In [10,29–32], several reported values for the variation of the critical resolved shear stress with temperature $d\tau/dT$ are mentioned, ranging from −0.12 to −0.15 MPa/K. Considering the possible tensile orientations, $d\sigma/dT$ might reach an absolute value (as it is always a negative dependence) of up to 0.42 MPa/K. These values are considerably less than those found in the B2 ↔ B19′ transformation in NiTi (6.3 MPa/K) and also less than those found in the β ↔ 18R transformation in polycrystalline CuAlBe alloys (about 2.2 MPa/K), given above. The slightly negative $d\sigma/dT$ observed in the 18R–6R transformation gives the CuZnAl system unique and completely new functionality compared to conventional SMAs, as 10% pseudoelastic strain can be obtained with a stress plateau that is expected to stay almost constant in a wide range of temperatures. Therefore, the use of the 18R ↔ 6R transformation in damping devices or other applications

integrated into mechanical structures would be more advantageous, as ambient temperature changes would cause variations in structure stiffness and resonant frequencies which are smaller than those obtained with other alloys. In addition, it should be remarked that the hysteresis associated with the 18R ↔ 6R transformation in CuZnAl single crystals is greater than the hysteresis observed in polycrystalline CuAlBe and comparable to the asymptotic behavior of NiTi alloys after cycling. Moreover, the 18R ↔ 6R transformation is able to recover more than 10% strain, which is somewhat greater than the recoverable β ↔ 18R strain in Cu-based alloys and the B2 ↔ B19′ strain in Ni–Ti alloys.

Previous studies [30,33] show, nevertheless, that the 6R phase in Cu–Zn–Al single crystals suffers plastic deformation while it is being formed. This fact renders the mechanical behavior irreversible, creating difficulties for possible engineering implementations of this transformation. Cuniberti and Romero studied the 18R–6R transformation in Cu–Zn–Al single crystals with electronic concentration $e/a = 1.48$ and 1.41 and found, by trace analysis, that the 6R slip systems are $\{1\,1\,1\}_{FCT}[1\,1\,0]_{FCT}$ [33]. These authors also reported a slip system whose plane is parallel to the basal plane of the 6R martensite, with a slip direction parallel to $[0\,1\,0]_{18R}$, although the corresponding Schmid factor is very small. The $[0\,1\,0]_{18R}$ is inherited from the $[0\,1\,0]_\beta$ after the β–18R transition. As the 18R–6R transformation was associated with 6R plastic deformation, the yield stress of the 6R martensite was assumed to be less than or equal to the 18R–6R transformation stress.

Although both β ↔ 18R and 18R ↔ 6R martensitic transformations can be easily reverted by removing the load, 6R plastic deformation cannot be reverted. Studies in Cu–Al–Ni shape-memory alloys have shown that, without precipitation treatments, it is possible to induce the 6R phase in adequately oriented single crystals, without permanent deformation after removing the load. Particularly, it was reported that it is possible to avoid plastic deformation for Ni contents higher than 4 wt.%, whilst plastic deformation of the 6R structure takes place during the 18R–6R transition for lower contents of Ni [34,35]. However, Cu–Al–Ni alloys are more brittle and difficult to manufacture [36]. As a result, Cu–Zn–Al alloys can be better choices for certain engineering applications, providing that 6R plastic deformation is controlled.

So, one of the keys to successfully implement the 18R ↔ 6R transformation in engineering applications and profit from its huge hysteresis, large pseudoelastic strain and weak dependence of transformation stresses on working temperature is to isolate this transformation from the plastic deformation of the 6R phase. There are two theoretically possible ways to achieve it: either by increasing the 6R yield stress and/or by reducing the 18R ↔ 6R transformation stress. This study is focused on the former.

The objective of this work is to increase the 6R plastic yield stress by introducing nanoprecipitates into the alloy. This might isolate the 18R ↔ 6R martensitic transformation from the plastic deformation of the 6R phase, allowing for either 18R ↔ 6R or (β–18R–6R) complete mechanical cycles, with little or no plastic deformation. As no information is available on the interaction between the 18R–6R transformation and precipitates, this approach applies the knowledge obtained from the reported results of the interaction between nanoprecipitates and the β–18R phase transformation to the 18R–6R transformation. The effect of introducing γ precipitates on the transformation has been thoroughly analyzed [37–41]. The nanoprecipitates change the chemical composition of the matrix, which in turn changes the equilibrium temperatures between the phases involved and the stress associated with the transformation at a given temperature [41]; however, this is a minor effect for small precipitates. Moreover, nanoprecipitates are expected to interfere with dislocations, disturbing their movement and increasing the yield stresses of all alloy phases [38,42,43]. An interaction between transformation fronts and precipitates might also have an effect