Mechanical behavior under cyclic loading of the 18R-6R high-hysteresis martensitic transformation in Cu-Zn-Al alloys with nanoprecipitates

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ABSTRACT

Mechanical damping applications could benefit from the large hysteresis, large pseudoelastic strain and the fact that the transformation stresses of the 18R↔6R martensite–martensite transformation depend very little on temperature in Cu-based alloys. This work presents the 18R↔6R mechanical cycling behavior of CuZnAl shape-memory alloy single crystals with electronic concentration $e/a = 1.48$. A fine distribution of gamma phase nanoprecipitates is introduced to prevent plastic deformation of the 6R phase. Results show that, although significant 6R stabilization is observed at very low frequencies (below 10^{-2} Hz), it is possible to obtain more than 1000 stable pseudoelastic cycles with only minor changes in transformation stresses and hysteresis width at frequencies above 10^{-1} Hz. A more pronounced decrease in transformation stresses is observed after 1000 cycles. Nevertheless, the decrease in hysteresis is small up to 2000 cycles. Reported and present results indicate that pair interchange of atoms can explain the stabilization of 6R under quasistatic experimental conditions. However, at higher frequencies of cycling, stabilization of this martensite shows additional features, leading to a dynamic stabilization with slight effects on the mechanical behavior at the required frequency and number of cycles. On the whole, the behavior of this transformation is unique and very promising.

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1. Introduction

The 6R phase in Cu-base shape-memory alloys (SMA) can be mechanically induced by applying a tensile stress to the 18R martensite, which in turn can be induced in the same way from the austenitic β phase, i.e., the metastable ordered structure resulting from the rapid cooling of the bcc high temperature phase, in which the type of order depends on the alloy composition [1–6]. These martensitic stress induced transformations are characterized by a mechanical hysteresis which is suitable for damping applications [7–16].

Several studies have been carried out for many years to analyze the significant parameters that characterize the stress induced transformations. NiTi and CuAlBe have been considered as interesting options for this type of applications. Most reported studies have focused their attention on the austenite–martensite transition, i.e., B2–B19′ in NiTi [11,17–22] the DO₃-18R in CuAlBe [13,23–25] or the L2₁-18R [26] in CuZnAl alloys embedded in glass fiber composites.

In CuZnAl it was shown that, by applying a tensile stress, two sequential reversible martensitic transformations β–18R and 18R–6R can produce more than 20% strain as pseudoelasticity [1,2,5,27,28]. Moreover, the mechanical cycle can be restricted to the 18R↔6R transformation showing two major differences from the β↔18R pseudoelastic cycles:

(i) The transformation–retransformation stresses show a weak dependence on temperature; $d\sigma/dT$ in 18R↔6R transformation might reach up to −0.42 MPa/K, depending on the crystal orientation [1,29–31]. On the other hand, a value of $d\sigma/dT \geq 2$ MPa/K is obtained for the β↔18R transition in Cu-based SMA [21]. This advantage becomes even more evident when compared with the value of $d\sigma/dT = 6.3$ MPa/K in NiTi alloys [21]. This is a very important property regarding applications where the surrounding temperature can change several tens of degrees.

ii) The larger hysteresis in the 18R↔6R transformation cycle, with a recoverable strain of about 10%, can also be an important advantage for some applications, i.e. damping devices for civil structures, such as buildings and bridges, to smooth out the oscillations produced by earthquakes, winds, etc.; it has been a subject of increasing interest in the last decades [5,32,33].

Recently, huge superelasticity has been reported in Fe-base alloys [34,35]. A highly textured Fe-base superelastic alloy, with

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composition Fe-28.85Ni-17.59Co-5.45Al-7.94Ta-0.0095B (wt%) containing ordered Ni–Al bcc precipitates was presented by Tanaka et al. In a single cycle, the hysteresis of these alloys is greater than in the 18R–6R transformation in CuZnAl single crystals, which makes them potential candidates for seismic damping. However, shape recovery is not complete, and it is also important to assess the mechanical behavior of these textured alloys under cycling conditions. Some results concerning the cyclic behavior of a single crystal of an alloy very similar to the one invented by Tanaka et al. have been recently published by Krooss et al. [36], up to 100 cycles. In these Fe-base single crystals, hysteresis is considerably smaller than in the textured alloy and is comparable to the one observed in 18R–6R transformation in CuZnAl single crystals. Other interesting Fe-base alloy was reported by Omori et al. This alloy with composition Fe-34Mn-15Al-7.5Ni (wt%) shows pseudoelasticity in the temperature range from 223 K to 423 K, and a slight temperature dependence of the critical stress to obtain the martensitic transformation, in fact close to the one obtained for the 18R–6R transformation in Cu based alloys. These new Fe-base superelastic alloys are very promising for earthquake damping, but more studies are required for a thorough assessment of dynamic behavior under earthquake conditions.

One of the associated difficulties to consider the 18R–6R martensitic transformation in CuZnAl alloys is the reported plastic deformation of the 6R martensite, which happens at approximately the same stress level at which the martensite–martensite transformation takes place [37]. A first approach to solve this problem was presented in [38]. It was found that nanoprecipitates, due to precipitation hardening, can greatly improve the mechanical behavior of adequately-oriented CuZnAl single crystals. The plastic deformation of the 6R phase is minimized or completely suppressed. A new alternative can then be considered, taking into account the fact that the 18R–6R phase transition in Cu-based alloys shows certain features which are advantageous for potential applications, such as wide hysteresis and very weak dependence of the transformation stresses on temperature.

Another fact to be considered for applications of the 18R–6R transition in Cu-based shape-memory alloys is the martensitic stabilization effect. The stabilization of martensite is usually described as the increase in critical transformation temperatures or, equivalently, the decrease in critical stresses if the transition is mechanically induced [39–46].

It is clear that stabilization might affect any device using a shape memory alloy in case it is not controlled or well considered in the lifespan of an application. Very briefly, explanations on the martensitic stabilization might be classified in two different types: those which consider changes in atomic configuration of the martensite after aging and those which justify shifts in critical temperatures or stresses as a consequence of pinning phenomena [40,47–49]. Indeed, a large amount of results has been reported in the last decades concerning the effect of aging in the martensitic structure. Different phenomena have been considered; stabilization of martensite and the rubber-like effect are probably the main focus of these studies. An interesting and general approach to the problem was presented by Otsuka and Ren [50,51]. The proposition of these authors, named SC-SRO (from Symmetry Conforming-Short Range Order), mainly considers that, at the equilibrium stage, the probability of finding a second point defect around a first one possesses the same symmetry as the crystal symmetry. In this way, if a martensitic transition takes place and diffusion is allowed in the martensitic structure, an evolution of the short range order will take place to reach a stable atomic configuration which conforms to the symmetry of the martensite. This model allows of the comprehension of stabilization phenomena both in equilibrium martensitic structures and in non-equilibrium ones. The same authors consider that CuZnAl alloys constitute an example of martensitic transitions

which lead to a non-equilibrium martensite, which can lower its free energy by a significant contribution of long range order evolution in addition to their suggested mechanism. Particularly, the stabilization of 18R martensite in CuZnAl has been analyzed in depth by Abu Arab and Ahlers [42]. These authors explain the observed stabilization in stress induced martensitic single crystals by a pair interchange between Cu and Zn atoms which in fact decreases the free energy of the martensite, leading to a more stable structure. This mechanism, which requires diffusion to be activated and uses the available data of pair interchange energies, clearly explains the observed effects in this system. Additionally, an increase in the degree of disorder during aging in martensite has been experimentally measured in CuZnAl alloys by Hashiguchi et al., using a four circle diffractometer [52]. Due to the mentioned facts, taking into consideration that martensite in these alloys is not an equilibrium phase when it is thermally or stress induced, and considering the excellent agreement between experimental results concerning either kinetics or amount of stabilization and the model of Cu–Zn pair interchange, in the present manuscript we will consider the mechanism suggested by Abu Arab et al. as the main contribution to the stabilization effect.

As the present work focuses on the 18R–6R stress induced transformation, it is necessary to analyze the effect of 6R stabilization on the mechanical behavior associated with this transition. As a start point, similar considerations can be performed to analyze aging phenomena in 18R and 6R martensite. On one hand, neither the 18R nor the 6R martensite is a stable phase when it is induced, and an evolution of the free energy of the 6R structure is expected to take place if diffusion is allowed. On the other hand, the crystalline structure is sufficiently different if both martensites are compared. Only a reduced amount of works considering the stabilization of 6R have been published and some outputs will be briefly commented below.

Saule et al. [32,53,54] studied the stabilization of martensitic phases in CuZnAl alloys and found out that 6R stabilization is faster than 18R stabilization under static conditions. The main difference between the stabilization of 18R and 6R martensites arises from the higher symmetry of the 6R structure, which is close to an fcc structure if order is disregarded. This difference makes the interchange of Cu and Zn atoms possible on additional planes with the same symmetry of the basal plane [32,55]. This is potentially troublesome if one intends to avoid 6R stabilization altogether, as the time spent in 6R should be minimized.

However, it should be noted that most of the reported results on stabilization of martensite were obtained under experimental conditions far from the required ones at seismic events. Just as an example, most of the results obtained by Abu Arab and Ahlers [42] and by Saule et al. [32,53,54] were obtained by tensile inducing transitions to obtain either an 18R single crystal or a 6R single crystal and letting the martensite age under stress, at constant temperature, for different times. The amount of stabilization in these martensitic single crystals has been determined mainly by measuring the decrease in the critical stress to obtain the retransformation to austenite, in the former transition, or to 18R, in the latter one.

A previous study [56] has found that the kinetics of dynamic 18R martensite stabilization observed under mechanical β–18R cycling in CuZnAl alloys cannot be satisfactorily described by static stabilization models. Several physical phenomena are involved in the dynamic stabilization of martensite during transformation–retransformation cycling, making it considerably more complex than static stabilization [56–58]. As an example, we can mention that pseudoelastic cycling between the $L2_1$ austenitic phase and the 18R structure at temperatures higher than room temperature can be well explained by considering just two phenomena: the stabilization of martensite and the recovery of the order of the austenitic structure [56]. Yawny et al. reported that the kinetics of