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Thermomechanical behavior of a CuAlBe shape memory alloy

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Abstract

The deformation of a Cu–11.4 wt%Al–0.5 wt%Be polycrystalline alloy induced by compressive stress at room temperature (RT) was analyzed. The different contributions to the total strain were considered and its evolution with the stress was examined. The macroscopic plastic limit was determined at around 600 MPa of stress and 8% of strain. This strain is associated with induced martensite, which transforms to β phase with a flash heating. Higher stress–strain levels introduce irreversible strain, and it would correspond to plastic deformation of martensite. Slip dislocations make difficult the mechanically as well as the thermally β-martensite transformation, leading to a hyperstabilization effect.
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1. Introduction

The martensitic transformation (MT) is responsible for the shape memory (SM) properties exhibited by a group of alloys based on the noble metals. In the Cu–Al system, β phase is stable at high temperatures, although it can be retained at temperatures below the stability region by rapid cooling. The Cu–Al–Be alloy is an alloy derived from the Cu–Al system. Upon quenching from the β phase, alloys containing more than 11 wt% Al become ordered and then transform martensitically. The martensitic phase is 18R for alloys containing less than 13 wt% Al [1]. The martensitic transformation (MT) can be induced by cooling or by the application of mechanical stress. Transformation on cooling, spontaneous transformation, begins at a temperature, M_s, and it is completed at the temperature M_f. The spontaneous transformation occurs without macroscopic shape change with the formation of 24 self-accommodated 18R variants. Typical values of $A_f − M_s$ are around 10 K in Cu–Al–Be alloys [2,3]. On heating, transformation to β phase starts at the temperature A_s and it is completed at the temperature A_f. Applying mechanical stress to the β phase, 18R martensite is induced, both on tension and compression [4,5], resulting in a macroscopical shape change. Under appropriate conditions, a hysteretic loop is formed removing the load, and the strain is almost fully recovered leading to the pseudoelastic (PE) behavior. Studies about the thermomechanical behavior of Cu–Al–Be alloys have been performed [4,6–8]. Nevertheless, a detailed analysis of the stress–strain relationship and the different components of the total strain reached under compression has not been reported. The advantage of compression test compared to tension test is that the first one allows a direct and precise evaluation of the involved deformations. In the present study, we analyze the deformation of a Cu–11.4 wt%Al–0.5 wt%Be polycrystalline alloy induced by compression cycles up to increasing loading at room temperature (RT). The evolution of the strain components is examined, determining the macroscopic plastic deformation limit. The influence of plastic deformation on the thermally induced martensitic transformation is studied.

2. Experimental procedure

The Cu–11.4 wt%Al–0.5 wt%Be polycrystalline alloy under study was provided by TREFIMETAUX S.A. (France), as 5 mm diameter bars and $M_s \sim 238$ K. The chemical composition was determined by atomic absorption spectrophotometry. Cylindrical samples for compression were prepared, consisting of cylinders around 5.1 mm diameter and 14 mm length, with a length/diameter ratio of 2.75. All the specimens were betatized during 5 min at 1073 K, water quenched at room temperature, and a heat treatment of 1 h at 373 K, obtaining a mean grain size of 0.5 mm. A Shimadzu Autograph-DSS-

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10T-S deformation universal machine was used for compression tests at room temperature and a constant cross-head speed of 1 mm/min. To reduce the friction during the tests, the end faces were covered with a thin teflon film and lubricated with grease. The samples length was measured with a digital caliper with precision $\pm 10^{-2}$ mm. The strain was evaluated as the relative difference of the sample length with regard to the initial length in each cycle. For light microscopy observations, the samples were electropolished with a solution of trioxide of chromium in phosphoric acid at 4 V, in sequences of 60 s each one and cleaned in methanol. Calorimetric measurements were performed by means of a Rheometric DSC calorimeter, with a heating/cooling rate of 10 K/min.

3. Results and discussion

Fig. 1 shows typical stress–strain curves obtained at RT ($T - M_s \approx 319$ K), a single cycle and repeated cycles up to increasing levels of maximum stress, σ_m. Concerning the loading curve, the first linear part corresponds to the elastic regime of the β phase, while the linearity deviation is associated with the β to martensite transformation start; thus, the stress corresponding to the end of the initial lineal part will be referred to hereafter as the martensite-start stress, σ_s. The final almost constant stress–strain slope corresponds to the progress of the martensitic transformation, although another deformation mechanisms could act as will be discussed; later this slope will be called the pseudoelastic slope, PES. On removing the load, a hysteretic loop is formed in the first cycles, for the lowest maximum stresses and the strain is almost fully recovered leading to the PE behavior. As σ_m increases, the strain retained on unloading is increasingly accumulated and the pseudoelastic behavior is lost. The single cycle corresponds to the envelopment of the successive cycles. It can be seen that the stress–strain path in each cycle depends on the loading history. The material "remembers" the maximum point ($\varepsilon_{max}, \sigma_m$) of the previous cycle, at which unloading began, and returns to this point upon the subsequent loading. Once this point is crossed, the deformation follows the original path, i.e. the deformation path of the single cycle. This behavior has been analyzed in detail in CuZnAl single crystals under partial loading–unloading loops [9]. The cycles show an almost complete strain recovery up to around 3% of applied strain. From therein more, strain is increasingly
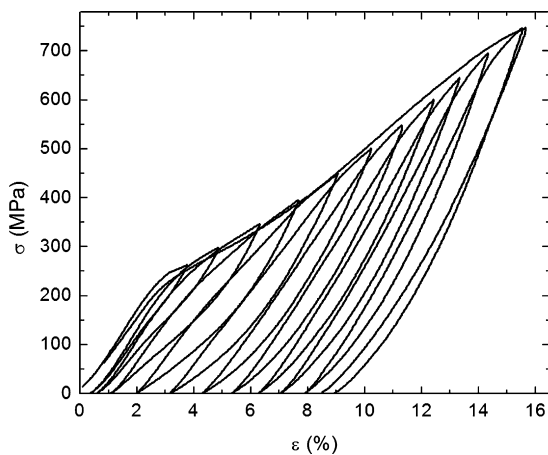
retained on unloading as the applied strain increases, leading to open cycles and a continuous decrease of the PE capacity. Similar behavior is observed in the alloy subject to tension tests [10].

With the purpose of analyzing the deformation processes occurring under loading, the different contributions to the total strain have to be considered. The maximum strain can be written as:

$$\varepsilon_{max} = \varepsilon_{el} + \varepsilon_{ps} + \varepsilon_{pl} \tag{1}$$

where ε_{el} corresponds to the elastic regime of the β phase, ε_{ps} the pseudoelastic strain produced by the stress-induced martensite and ε_{pl} is the strain associated with plastic deformation. When no perfect strain recovery occurs, a retained strain ε_{ret} is observed on unloading. Fig. 2 shows a stress–strain cycle up to σ_m where the considered strain components are indicated. We define the total applied strain, ε_{app}, as $\varepsilon_{ps} + \varepsilon_{pl}$, discounting the ε_{el} contribution. If martensite does not completely revert to β phase, the associated strain is reversible by heating as the transformation to β phase occurs, and the one way SM effect is obtained. If plastic deformation takes place, the associated strain is irreversible and it is not recoverable by heating. In order to distinguish the reversible and irreversible strain components, a flash heating was made. The specimens were kept for 30 s in a resistance furnace at 1073 K, reaching a temperature of 660 K, and water quenched. The remaining strain after heating, ε_{TT}, is considered irreversible and it is attributed to plastic deformation, ε_{pl}.

Fig. 3 shows the measured strain components as a function of the maximum imposed stress, σ_m, for samples subject to (a) a single cycle up to σ_m and (b) cycles up to increasing σ_m with an intermediate flash heating. The alloy presents a pure pseudoelastic behavior up to around 3% of ε_{app}, the cycles are closed and ε_{ret} is almost zero. Major levels of ε_{app}, with the increase of σ_m, lead to the continuous increase of ε_{ret} up to ε_{app} around 8% and $\sigma_m \approx 600$ MPa. Until that, the heat treatment produces a high recovery degree with ε_{TT} values lower than 0.5%. The strain increasingly retained on unloading can then be attributed to the increase of retained martensite, which transforms to β phase with the flash heating, and produces the almost total recovery
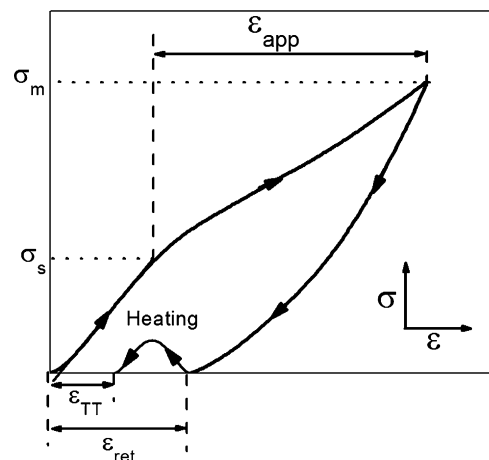

Fig. 1. Stress-strain cycles obtained for samples in β phase subject to compression tests at RT: a single cycle and repeated cycles up to increasing levels of maximum stress, σ_m.

Fig. 2. Stress-strain cycle up to σ_m and subsequent heating (see text).
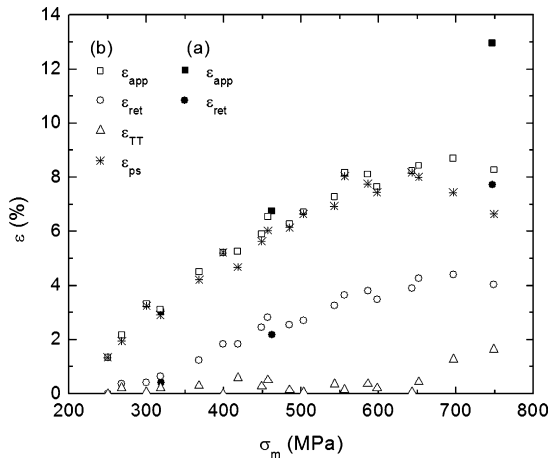
Fig. 3. Measured strains corresponding to samples subject to different thermo-mechanical treatments: a) a single cycle up to the highest σ_m; b) cycles up to increasing σm with a flash heating.

of the original length of the sample. Therefore, ε_{app} would be composed only of ε_{ps}. This is also suggested by microscopy observations of the samples surface before and after a heating up to 923 K, Fig. 4. As can be seen, some martensite needles remain within the β phase under unloading, and disappear after the flash heating. SEM observations have also shown the increase of retained martensite with the σ_m increase [5]. According to Fig. 3 and for σ_m lower than 600 MPa, sample b shows similar behavior than that one under a single cycle (sample a). It indicates that the flash heating between cycles does not introduce significant changes in the stress–strain behavior.

For σ_m higher than 600 MPa, both ε_{app} and ε_{ret} show a visible flattening, denoting that a strengthening mechanism starts to act. Moreover, ε_{TT} shows an increase with the σ_m increase. Therefore, plastic deformation is increasingly introduced. Fig. 5 shows an optical micrograph of a sample subject to σ_m of 747 MPa. After a heating up to 923 K the surface looks very irregular due to the presence of plastic deformation.

We can then note that there is a limiting stress which determines the maximum fully recoverable strain for this alloy, the plastic limit and it is around 600 MPa. Above the plastic limit, irreversible processes occur in the material, which manifest as retained strain after the heat treatment, inhibiting the one way SM effect. Plastic deformation also produces an increasing inhi-

bition in the formation of martensite, denoted by the decrease in the strain due to the creation of martensite, ε_{ps}. Kaouache et al. [8] have attributed the retained strain after applying a stress of 350 MPa to plastic deformation of the martensite for a similar alloy. The present study shows that the retained strain is recovered after a heat treatment for that stress level, which indicates that the retained strain corresponds principally to retained martensite.

According to Fig. 3, the maximum measured strain associated with the transformation, reversible by unloading and heating, is slightly lower than 8%. This is the limiting strain the material is able to recuperate. The deformation produced by the formation of a single variant, obtained in a Cu–Al–Be single crystal with a Schmidt factor 0.482 is 9.7% [4]. In a polycrystal, the transformation occurs due to the creation of plates of the martensitic variants more favored by the distribution of tensions in each grain. The self-accommodated character of the martensitic variants [1], and the different degree of transformation between the different grains, lead to a smaller deformation value in the polycrystal than in a single crystal. The influence of texture on the deformation behavior seems to be not significantly marked in polycrystalline CuAlBe alloys [11].

The irreversible deformation introduced in the material could be plastic slip in the β phase or in the martensitic phase. Studies in Cu–Zn–Al single crystals show that 18R phase deforms at lower stress than β phase by a factor ≈1/3 [12,13]. The yield stress of the β phase in polycrystalline Cu–Al–Be is 572 MPa at 533 K, and 228 MPa at 593 K [4]; indicating that this phase presents a normal plastic stress–temperature relationship like β Cu–Zn–Al alloys [13]. According to that, the yield stress at room temperature would be very much higher than 572 MPa. These features strongly suggest that the plastic slip, here determined starting at around 600 MPa, corresponds to plastic deformation of martensite.

While the stress–strain cycles up to 600 MPa are similar in test types (a and b), higher σ_m leads to marked differences, as can be seen for $\sigma_m = 747$ MPa in Fig. 3. Fig. 6 shows the individual curves obtained for that level of σ_m, that is, above the plastic limit, for both tests: (a) a single cycle of a fresh sample, (b) a cycle of a sample subjected to previous cycles at increasing σ_m with intermediate flash heatings. In order to interpret these curves, it is necessary to describe the initial microstructure in each one. In the curve (a) the sample is β phase, and in the curve
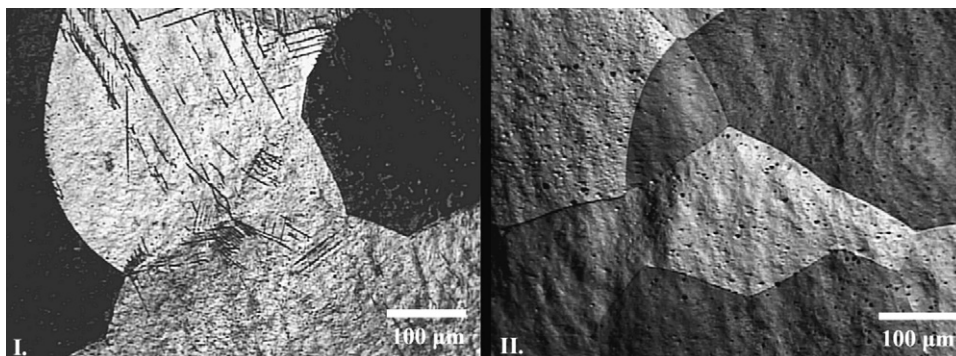

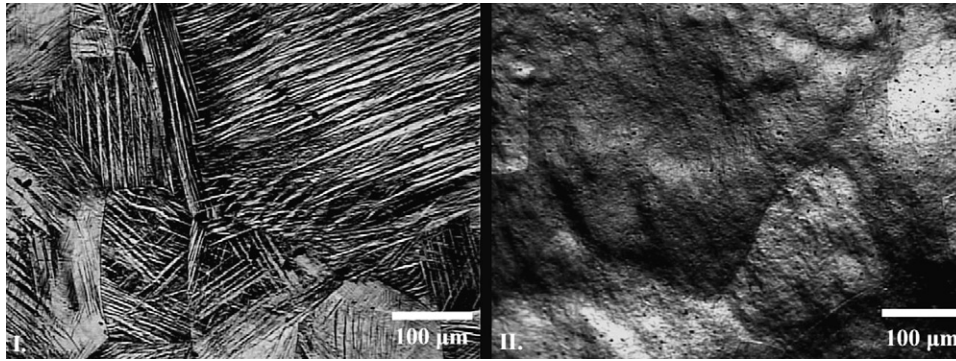Fig. 4. Optical micrograph of the sample with $\sigma_m = 319$ MPa (I), and after a heating up to 923 K (II).

Fig. 5. Optical micrograph of the sample with $\sigma_m = 747$ MPa (I), and after a heating up to 923 K (II).
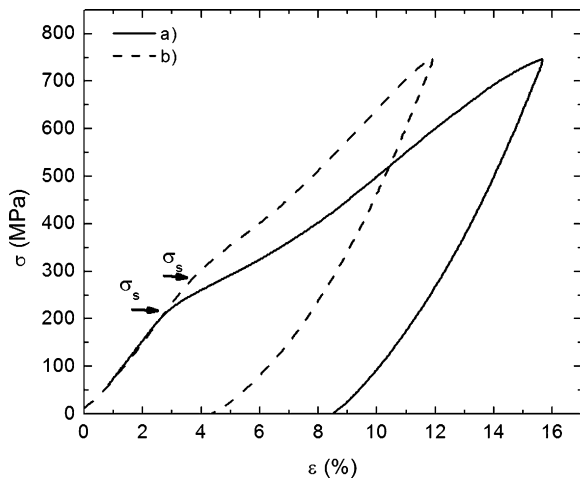

Fig. 6. Applied stress-strain σ-ε cycles obtained for the different kind of tests: a) and b), for $\sigma_m = 747$ MPa (See text).

(b) the sample is β phase with dislocations introduced by plastic deformation. As can be seen, plastic deformation produces a higher martensite start stress σ_s, and a higher pseudoelastic slope PES. These features indicate that dislocations make difficult the beginning of the martensitic transformation as well as its progress.

Fig. 7 shows the σ_s of the successive cycles against the maximum stress σ_m applied in the previous cycle, for samples with
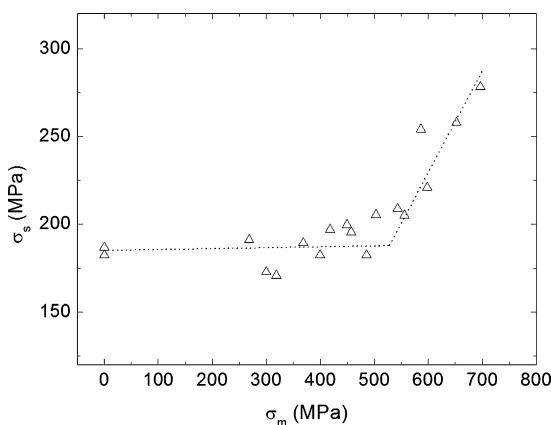

Fig. 7. Evolution of σ_s with σ_m of the previous cycle, for test type (b). The dot lines are only a guide for the eyes.

intermediate flash heating (sample b). σ_s is almost invariable with σ_m up to around 600 MPa, but beyond this stress, a σ_s increase is observed.

The irreversible strain effect on the SM behavior has been studied in other SM alloys like NiTi [14,15] and CuZnAl [16]. In order to study the effect of the stress–strain history on the thermoelastic $\beta \rightarrow$ M transformation, a DSC study was done. From samples subject to compression up to different σ_m, small discs were appropriately cut for calorimetry, with mass $\approx 145 \times 10^{-3}$ g. Fig. 8 shows the thermograms obtained for the first and second cycles. Subsequent cycles show great repeatability. Samples denoted A, B and C correspond to samples with (0 MPa, 0%), (319 MPa, 0.65%) and (747 MPa, 4.03%), maximum applied stress and strain retained on unloading (σ_m, ε_{ret}) respectively. Sample A is the reference sample, sample B is a β-martensite mix and sample C is a β-martensite mix plus plastic deformation. The heat exchanged on the transformation Q, proportional to the area under the transformation cycles, gives an approximation to the amount of transforming material. In the first cooling run, as σ_m and ε_{ret} increase, the heat involved in the first cooling decreases. This occurs because more mechanically formed martensite is present when ε_{ret} is higher, and then less β phase is available for the thermally induced MT. The subsequent heating corresponds to the reverse transformation of the martensite induced a part mechanically and a part thermally. The reverse MT is similar for samples A and B, while the sample C, with plastic deformation, behaves strongly different. Sample C shows two peaks with a second reverse MT stage at around 630–700 K. The amount of martensite transformed at the first peak is very small for this sample, but more martensite transforms at the second MT stage. This second stage has been investigated in Cu–Al–Be single crystals, and it is associated with the so-called hyperstabilization effect of the stress-induced martensite due to the jamming of the interface motion and the renucleation of the lamellar β phase [7,17]. We have found that the hyperstabilization is appreciable only in those samples with plastic deformation. The slip dislocations induced by deformation seem to produce the strong inhibition of the interfaces motion. The analysis of the second and subsequent cooling-heating cycles permits examine the influence of the stress–strain history on the pure thermally induced MT. Samples A and B show similar direct and reverse MT, with critical transformation temperatures and transformation heats comparable to the first reverse
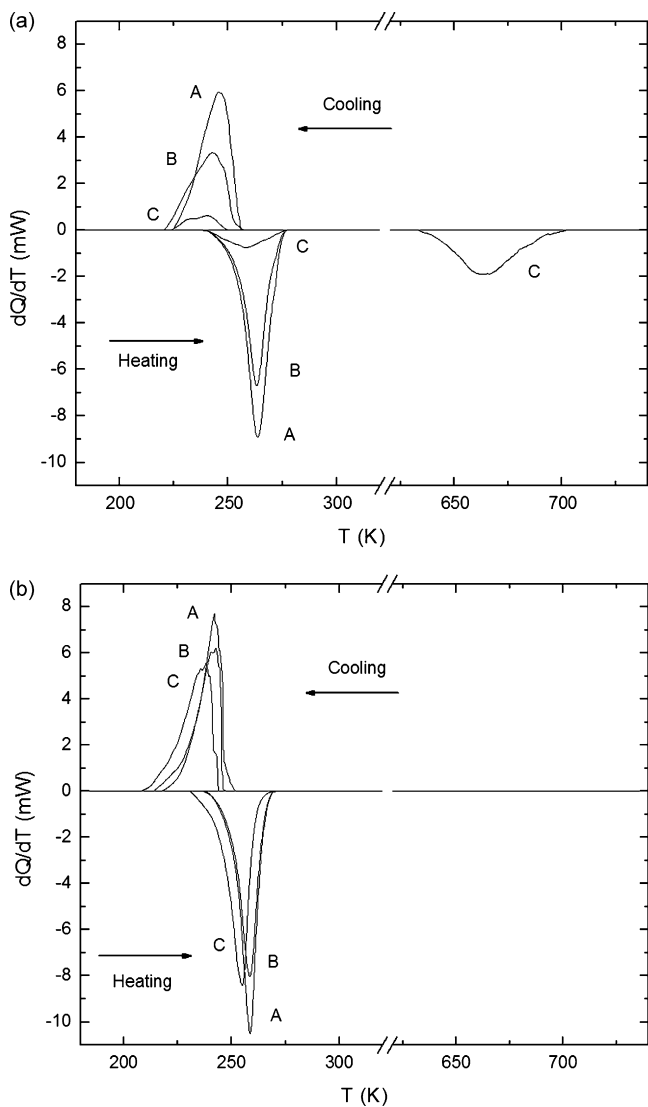
Fig. 8. Cooling and heating DSC cycles of samples subject to compressive test at a specified maximum stress: 0 MPa (A), 319 MPa (B), 747 MPa (C). (a) First cycles. (b) Second cycles.

transformation. Once again, sample C behaves clearly different. In this case, the peaks remain flatter, and the transformation is completed in a wider range of temperatures. However, the hyperstabilization effect disappear in the second cycle, and the reverse MT temperatures are almost recovered. Kustov et al. reported similar behavior for CuAlBe single crystals [7]. Upon the first excursion in the β phase, the second and subsequent heatings correspond to the transformation of self-accommodated martensitic variants. In this case, fully elastic accommodation prevail, and the material shows the typical thermoelastic behavior.

4. Conclusions

The deformation of a Cu–11.4 wt%Al–0.5 wt%Be polycrystalline alloy induced by compression cycles up to increasing loading at room temperature has been analyzed.

In stress–strain curves, as σ_m increases, the cycles show an almost complete strain recovery up to around 3% of ε_{app}. From therein more, strain is increasingly retained on unloading. The retained strain up to ε_{app} around 8% (and $\sigma_m \approx 600$ MPa) can be attributed to the increase of retained martensite, which transforms to β phase with a flash heating. There is a limiting stress which determines the maximum fully recoverable strain for this alloy, the plastic limit and it is around 600 MPa. Above it, irreversible processes occur in the material, which manifest as retained strain after the flash heating, inhibiting the one way SM effect. The irreversible deformation introduced in the material would correspond to plastic deformation of martensite. The dislocations difficult the beginning of the stress-induced MT as well as its progress. The thermally induced MT is also strongly affected by plastic deformation, leading to an hyperstabilization effect of the compression induced martensite.

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