J. PHYS. IV FRANCE **7** (1997)
Colloque C5, Supplément au Journal de Physique III de novembre 1997 C5-227

Stability of γ'_1 Martensite in Cu-Base Alloys

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Abstract: The analysis of the nonequilibrium $\sigma - T$ diagrams constructed from the results of tension/compression thermomechanical tests with [001] Cu-based shape memory alloy/SMA/ single crystals was found to be a good way how to understand complex path dependent phenomena exhibited by SMA single crystals. Particularly, it has been shown that the γ'_1 martensite phase forming in Cu-based SMA may exist in much wider range of stress-temperature conditions than would be expected just from the results of thermal cycles or tensile loading-unloading tests with single crystals usually presented in the literature.

1. INTRODUCTION

Martensitic transformations/MT/, induced by the applied stress and temperature in SMA's are responsible for peculiar properties of those materials (superelasticity and shape memory effects/SME/). Though phase transitions between one high temperature, parent austenite phase, and one low temperature martensite phase are typically considered as a microphysical deformation mechanism of SMA's, in fact, mutual phase transformations between three or even more solid phases typically occur in transforming SMA polycrystals. Each among the solid phases involved may exist in a particular range of applied stress-temperature conditions. So called stress-temperature, $\sigma - T$, maps, in which lines denote phase transformation conditions, were constructed on the basis of thermomechanical tests performed on single crystals of various SMA's loaded in uniaxial tension [1, 2, 3]. Martensitic transformation is, however, orientation and stress state dependent - various martensitic phases may be induced by different applied stress states [1, 4] (uniaxial tension, compression, biaxial loading). It is thus clear that stress-temperature diagrams of SMA single crystals should cover various load axis orientations and at least tension/compression stress states. We have performed such experiments recently on CuAlNi and CuAlZnMn SMA single crystals and the obtained orientation dependent $\sigma - T$ diagrams can be found in [5].

Transitions between solid phases are expected in the vicinity of transformation lines in $\sigma - T$ diagrams (when external $[\sigma, T]$ conditions approach the transformation lines).

Nucleation and friction effects intrinsically associated with martensitic transformations, however, cause broadening of the transition regions (transformation hysteresis). As a result, regions of existence of individual phases in the diagram frequently overlap. What kind of solid phase then actually exists in such overlapped multiphase regions, depends in a large extent on the recent transformation history. The macroscopic thermomechanical behavior of the single crystal, which strongly depends on the kind of the formed martensite phase, is, consequently, also affected by the transformation history at $[\sigma, T]$ conditions corresponding to the multiphase regions of the $\sigma - T$ diagram. Results of recent experiments [4] with CuAlZnMn SMA polycrystals suggest that the history dependencies may have serious consequences even for polycrystalline SMA behaviors of engineering interest.

In this work, martensitic transformations taking place in [001] single crystals of Cu-based SMA's were experimentally studied in tension/compression thermomechanical tests and the results are discussed with respect to the stability of individual transforming phases. A solid phase is considered stable in a region of the $\sigma - T$ space if it exists at corresponding $[\sigma, T]$ conditions regardless of the stress-strain-temperature history just passed by the specimen.

2. EXPERIMENTAL

[001] oriented single crystals were grown from Cu-14.3Al-4.1Ni [wt.%] and Cu-10Al-5Zn-5Mn [wt.%] SMA by the seeded Bridgman technique. Cylindrical specimens, 50 mm long, 4 mm in diameter, were machined from the as grown crystals, and their central part, 12 mm long, was electrolytically thinned to a diameter of 3.3 mm. The specimens were given a standard thermal treatment by annealing at 923 K - CuAlZnMn (1175 K - CuAlNi) for 2 hours in an argon atmosphere and quenching into ice water. Tension/compression stress-strain tests, as well as thermal cycling tests at constant applied load, were performed in an Instron 1362 testing machine equipped with a heating/cooling chamber consisting of an electrical furnace and a cooling system by nitrogen vapors. Experiments were performed in the position or load control mode in the stress range [-500MPa, 500MPa] and temperature range [150 K, 450 K].

3. RESULTS AND DISCUSSION

3.1 Basic tests

Two kinds of basic tests were used to determine the $[\sigma, T]$ transformation conditions between the austenite and martensite phases forming in the single crystals: - i) stress-strain curves at constant temperature (figure 1a) and ii) thermal cycles at constant applied stress (figure 1b). Since both forward and reverse martensitic transitions proceed typically at constant applied stress or temperature in these tests, transformation conditions can be evaluated as plateau stresses or temperatures at which the length of the specimen changes suddenly (figure 1). Moreover, transformation strain, ε_t, characteristic for each transformation, can be evaluated directly from the length change of the specimen undergoing stress induced MT - i.e. from the lengths of the corresponding plateaus on the $\sigma - \varepsilon$ or $\varepsilon - T$ curves.

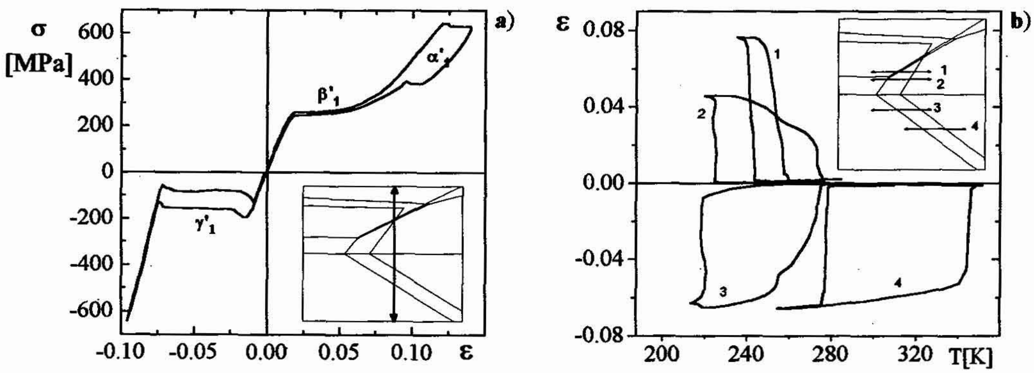

Figure 1: CuAlNi - a) tension/compression stress-strain cycle at room temperature, b) thermal cycles at constant applied stress. Stress-temperature paths prescribed in individual cycles are shown by double arrow line segments in $\sigma - T$ diagrams.

Stress induced transformations between one β_1 parent and three γ_1', β_1' and α_1' martensitic phases may be recognized on pseudoelastic curve of the [001] CuAlNi single crystal in figure 1a. There is no symmetry in transformation characteristics $(\sigma_t, \varepsilon_t)$ measured in tension/compression at all and each transformation is associated with very different hysteresis width. The strain response of the specimen in the thermal cycles (figure 1b) also depends sensitively on the kind of the low temperature martensite phase. Wide hysteresis in the thermal cycles under large compressive as well as small tensile stresses correspond to the $\beta_1 \leftrightarrow \gamma_1'$ transformation, while narrow hysteresis at larger tensile stresses is observed for $\beta_1 \leftrightarrow \beta_1'$ transformation.

Stress-strain behavior of the [001] CuAlZnMn single crystal is shown in figure 2. If the specimen is loaded in tension directly from the parent phase, highly reversible β_1' martensite phase forms. When, however, the specimen was at first loaded in compression, the γ_1' phase forms and remains stable even upon unloading. When stress-strain test continued by loading in tension, the γ_1' was only reoriented. Depending on the transformation history β_1' or γ_1' may thus exists at room temperature under tensile stress.

Similar behavior was observed in more complex thermomechanical cycles as well (figure 2b). The specimen was transformed to martensite by cooling under various applied stresses as the curves with arrows 1-4 in figure 2c show. Although the reverse transformation path was identical in all four cases, the temperatures, at which the reverse transformations completed - austenite finish, A_f, differed as much as 60K. The progress of the reverse martensitic transformation thus depends on the forward transformation history.

Effects of the transformation history as discussed above did not clearly appear in simple thermal cycles or loading-unloading tests in uniaxial tension. Nevertheless, they should be studied since other than uniaxial stress states must be considered for local stress conditions in transforming SMA polycrystals. Construction and, particularly, analysis of the nonequilibrium $\sigma - T$ diagrams (figure 3) is extremely useful for such purpose and will be done below for both alloys studied.

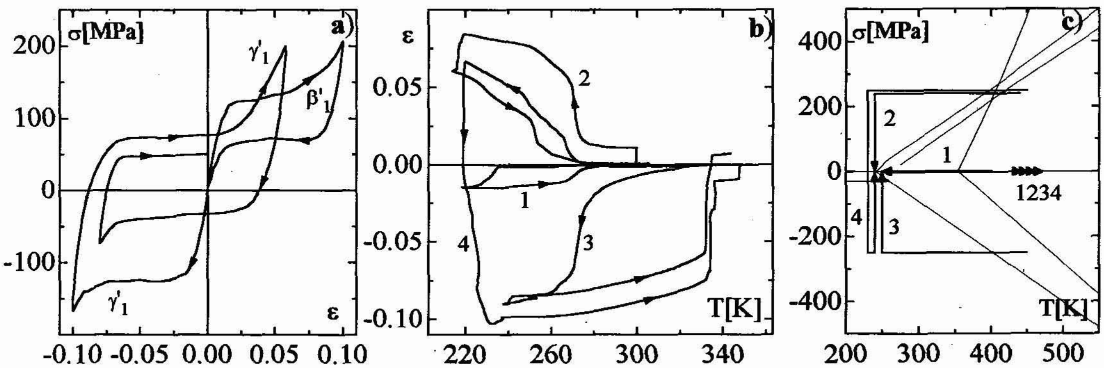

Figure 2: a) CuAlZnMn - tension/compression stress-strain curve at room temperature.
b) CuAlZnMn - strain response of the single crystal in four thermomechanical cycles 1-4 presented schematically as a path in the $\sigma - T$ map (c).

3.2 σ-T maps

Stress-temperatures, σ-T, maps were constructed from the experimental data taken from thermomechanical tests. In this work, only transformations between three low stress phases $\beta_1, \beta_1', \gamma_1'$ are discussed (transformations involving α_1' phase are omitted). Therefore, only parts of the obtained $\sigma - T$ maps are presented in figures 3, 4, 5. Regions of stability of individual phases $\beta_1, \beta_1', \gamma_1'$ in [001] $\sigma - T$ diagrams are marked by filled areas in figure 3 a,b. Given phases are stable in these regions, which means that they exist at corresponding $[\sigma, T]$ conditions independently on the recent stress-temperature history. However, when looking for the whole areas of $\sigma - T$ diagrams, in which the above phases may exist - **regions of existence of the $\beta_1, \beta_1', \gamma_1'$ phases** - a completely different picture is obtained (figure 4). Regions of existence of individual phases partially overlap and **multiple phase regions** can be identified in nonequilibrium $\sigma - T$ diagrams. Formation of martensite phases in multiple phase regions is thus not uniquely determined by the current stress state and temperature conditions, but depends on the transformation history in a complex way. Let us have a more careful look on the $\sigma - T$ diagrams of both alloys.

3.2.1 CuAlNi

Lots of important information about martensitic transitions in the CuAlNi single crystal can be easily read from the nonequilibrium $\sigma - T$ diagram. While highly reversible $\beta_1 \leftrightarrow \beta_1'$ transformation characterized by very narrow hysteresis (7K, 20MPa) occurs only at higher applied tensile stress, the $\beta_1 \leftrightarrow \gamma_1'$ transformation associated with larger hysteresis (40 K, 100MPa) proceeds at compressive or small tensile stress. By far largest hysteresis (220MPa) is exhibited by the $\beta_1' \leftrightarrow \gamma_1'$ martensite to martensite transformation. Temperature dependence of the transformation stress for this transition is extremely weak, and there is thus no thermally induced $\beta_1' \leftrightarrow \gamma_1'$ transformation. When forward (reverse) transformation path of a thermomechanical test passed through an area near the triple point at [250K,100MPa], a transformation involving mixture of β_1', γ_1' phases was typically observed. In such a case, the transformation did not proceed at a constant stress (temperature) anymore, and complex pseudoelastic curves [6] or multistage transitions upon heating/cooling at a constant stress were usually observed.

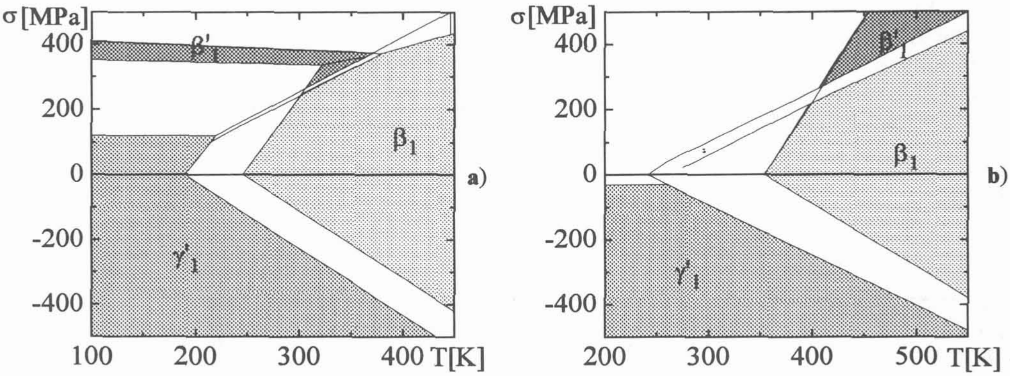

Figure 3: Nonequilibrium $\sigma - T$ diagrams with marked regions of stability of β_1, β_1' and γ_1' phases a) CuAlNi, b) CuAlZnMn.

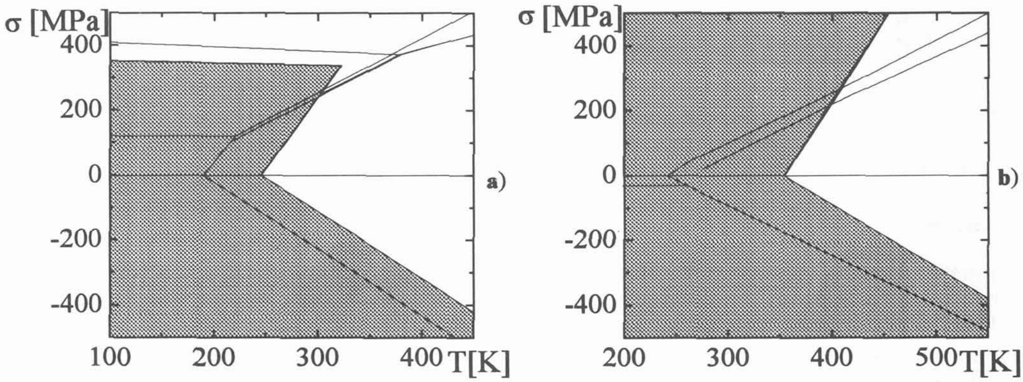

Figure 4: Nonequilibrium $\sigma - T$ diagrams with marked regions of existence of the γ_1' martensite phase - a) CuAlNi, b) CuAlZnMn.

3.2.2 CuAlZnMn

Nonequilibrium $\sigma - T$ diagram of the CuAlZnMn single crystal is qualitatively similar to the CuAlNi but there are some differences. Particularly, the widths of hysteresis accompanying MT in this system seem to be higher for all transitions. This has important consequences. For example, following a suitable transformation history, the γ_1' martensite phase may exist at very high applied tensile stresses, where it would be never expected on the basis of the tensile loading-unloading tests. One way how to do it is clearly demonstrated by figure 2. On the other hand, β_1' martensite phase may exist at zero applied stress besides of the γ_1' phase, something that was not possible with the CuAlNi single crystal. The reverse martensitic transformation of the CuAlZnMn single crystal heated back to the parent phase thus depends significantly on the transformation history as shown by the experiments in figure 2b. This is in accord with the fact that low temperature stress-free conditions belong to the multiple phase region of the $\sigma - T$ diagram. Depending on the fraction of the β_1' and γ_1' martensites in the mixture of phases undergoing reverse MT, the reverse MT completes at a relatively low temperature (curve 2, A_f=270K, high fraction of β_1'), medium temperature (curve 1, A_f=300K, equal fractions of both martensite phases) or at quite high temperature (curves 3,4, A_f=335K, low fraction of the β_1').

3.3 Equilibrium $\sigma - T$ diagrams

Comparing the equilibrium $\sigma - T$ diagrams presented in figure 5 with the nonequilibrium ones (figure 3), we find out the differences between thermodynamic equilibrium phases and actually observed phase composition of the specimen following various transformation histories. As a consequence of the transformation hysteresis two-phase and three-phase regions appear in the non-equilibrium diagrams. The lines and triple points in the diagrams denote equilibrium between interacting phases. Stress (temperature) centers of experimental hysteretic loops (see figures 1a,b) were usually considered as experimental data for construction of these diagrams. In some cases, experiments with partial stress or partial thermal cycles were performed to find out the equilibrium transformation conditions more precisely (e.g. CuAlZnMn [4]). Again, only parts of the $\sigma - T$ diagrams, where β_1, β_1' and γ_1' phases occur are shown in figures 4a,b. The equilibrium temperature between the β_1 and β_1' at zero stress is denoted as $T_0(\beta_1')$ and, similarly, the equilibrium temperature between β_1 and γ_1' as $T_0(\gamma_1')$. Since the latter is located at a higher temperature, the γ_1' phase preferably forms upon cooling when no stress is applied.

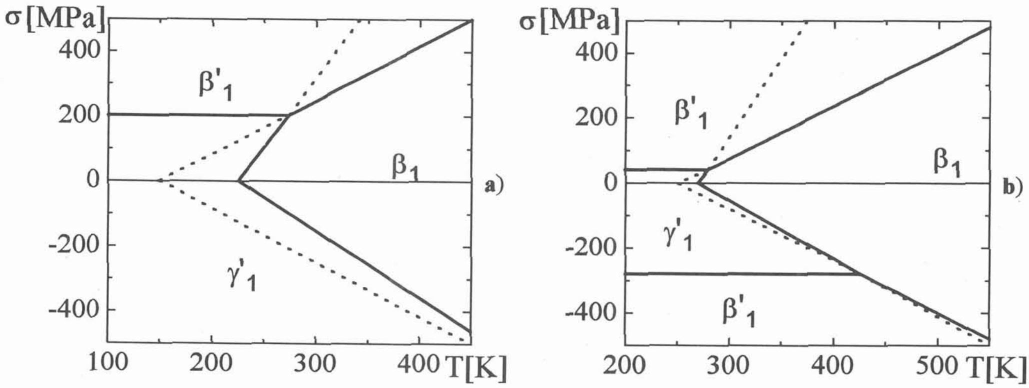

Figure 5: Equilibrium $\sigma - T$ diagrams - a) CuAlNi, b) CuAlZnMn.

The stress dependence of equilibrium temperatures can be described by Clausius-Clapeyron equation[8]. The slope of this dependence is inversely proportional to the magnitude of the orientation dependent transformation strain ε_t. This proportionality was proved experimentally and may be even used to determine the transformation strain in cases, in which it can not be evaluated directly [5]. There is a large asymmetry in the transformation strains ε_t corresponding to the $\beta_1 \to \gamma_1'$ transformations under tension and compression loads. The difference in slopes of the transformation lines of $\beta_1 \leftrightarrow \gamma_1'$ in tension and compression represents this asymmetry as well.

Intersection of three lines in a triple point represents the phase equilibrium among all three phases. There is no symmetry between the locations of the triple points in tension and compression. Looking at the diagrams, we find out that the locations of the triple points in $\sigma - T$ diagrams are actually determined by the difference in stress-free equilibrium temperatures $\Delta T_0 = T_0(\beta_1 \leftrightarrow \beta_1') - T_0(\beta_1 \leftrightarrow \gamma_1')$ and also by the mutual relation of the slopes of two competing phase transformations. In particular, the slopes of the $\beta_1 \to \gamma_1'$ and $\beta_1 \to \beta_1'$ transformation lines in compression are very close in the case of the [001] orientation, and, consequently, the triple point is shifted to high temperatures and compression stresses. Direct consequence is a higher stability of the γ_1' phase in compression, clearly demonstrated by the comparison of nonequilibrium $\sigma - T$ diagrams of both alloys. On the other hand, these slopes are quite different in tension (transformation strain $\varepsilon_t(\beta_1')$ is about two times higher than $\varepsilon_t(\gamma_1')$), and the triple point lies at a relatively low stress level. Consequently, the triple point is located at lower stresses and the region of existence of the β_1' phase in tension is markedly larger than in compression.

Single crystals of both investigated alloys transform to the same austenite and martensite structures. It is thus not surprising that similar habit plane orientations, transformation strain ε_t, and slopes of transformation lines were observed for both alloys. Different, however, are the equilibrium temperatures $T_0(\beta_1 \leftrightarrow \beta_1')$ and $T_0(\beta_1 \leftrightarrow \gamma_1')$ between austenite and martensite phases. The temperature difference is as large as $\Delta T_0 \approx 50K$ for the CuAlNi alloy but only $\Delta T_0 \approx 20K$ for the CuAlZnMn alloy. The magnitudes of the T_0 equilibrium temperatures of phase transformations are governed mainly by the alloy compositions. Shifts due to the composition change are, however, not generally equal for various transformations. This has a tremendous impact on the shape of the nonequilibrium diagrams, on the response of the single crystal in thermomechanical cycles and, ultimately, on the SMA polycrystal behaviors. In a particular case of the CuAlZnMn alloy, the triple points on the diagrams are shifted to lower stress levels as a consequence of the close T_0 equilibrium temperatures of both $\beta_1 \rightarrow \gamma_1'$ and $\beta_1 \rightarrow \beta_1'$ transformations. The region of existence of the β_1' martensite is thus shifted to even lower stresses and, due to the hysteresis accompanying MT, the β_1' martensite phase may exist and does exist together with the γ_1' phase at zero stresses. This is the main origin of the complicated path dependence phenomena exhibited by the single crystal of the CuAlZnMn alloy (see also [7]).

4. CONCLUSIONS

CuAlNi and CuAlZnMn [001] oriented single crystals were investigated in tension/compression thermomechanical tests. Stress-temperature $\sigma - T$ phase diagrams were constructed from experimentally determined $[\sigma, T]$ transformation conditions.

Regions of existence of austenite and martensite phases mutually interacting upon thermomechanical loading of the single crystals were found and marked in the diagrams. It is shown that history dependence phenomena associated with the martensitic transformation occur at stress-temperature conditions inside the multiphase regions and can be understood on the basis of $\sigma - T$ diagrams.

On the other hand, individual phases were found stable, i.e. existing independently on the stress-strain-temperature history, in limited ranges of $[\sigma, T]$ conditions - regions of stability of individual phases in the $\sigma - T$ diagram.

A careful analysis of the $\sigma - T$ diagrams has clearly shown that the γ_1' martensite phase forming in Cu-based SMA may exist in much wider range of stress-temperature conditions than would be expected from the results of simple thermal cycles or tensile loading-unloading tests with single crystals usually presented in the literature.

Acknowledgement

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic under Contract No. A1010621.

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