Statistical Description of Mechanical Stabilization of Cu–Al–Ni Martensite

Victor A. L'vov¹, Catalina Picornell², Jaume Pons² and Eduard Cesari²

¹Taras Shevchenko University, Dept. of Radiophysics, Glushkov str. 2, Build. 5, Kiev 03127, Ukraine

²Departament de Física, Universitat de les Illes Balears, Cra. de Valldemossa km 7.5, E-07122 Palma de Mallorca, Spain

A statistical description of the superelastic behavior of martensitic alloys has been applied to the stress–strain curves obtained for a Cu_{69.6}Al_{26.8}Ni_{3.6} at% single crystal under compression which shows a mechanical stabilization effect of the stress-induced γ' martensite. In order to analyse very different stress–strain behaviours, the same model has been applied to a Cu_{68.3}Zn_{15.4}Al_{16.3} (at%) single crystal showing the β – β' transformation under tension with almost “ideal” superelasticity.

The model, which reproduces accurately the experimental σ – ε curves, allows to compute the volume fractions of martensite at every stage of the loading–unloading cycle by introducing a probability distribution function or, if the elastic stiffness coefficients are known, by performing some calculations directly from the experimental stress–strain loops.

The mechanical stabilization of γ' martensite in the Cu–Al–Ni alloy is manifested through the large differences in the probability distributions between the forward and reverse transformations. The dependence of the mechanical stabilization degree on the amount of previous deformation is also quite well reproduced by the model.

(Received February 2, 2005; Accepted March 24, 2005; Published May 15, 2005)

Keywords: martensitic transformations, copper-based shape memory alloys, superelastic stress–strain cycles, statistical model, mechanical stabilization

1. Introduction

Mechanical stabilization of the martensitic phase is observed in several shape memory alloys as Ni–Ti, Ni–Ti–Nb, Cu–Al–Zn–Mn, Cu–Al–Ni and others.^{1–7)} This phenomenon occurs when the martensite is stress-induced from the parent phase and results in the decrease of the stresses at which the reverse transformation takes place, leading to an enhanced stress hysteresis of the σ – ε loop. If the martensitic transformation (MT) is stress-induced at temperatures not high enough, the reverse martensitic transformation upon unloading is inhibited, the specimen remaining in deformed martensitic state at zero stress. In this case, a subsequent heating is needed to return to the parent phase, the mechanical stabilization of martensite being manifested by an increase of the temperature of the reverse martensitic–austenitic transformation (*i.e.* the “nominal” temperature of the austenite start A_s is shifted to the value $A_s^* > A_s$ by the preliminar mechanical loading of the specimen).

The mechanical stabilization of martensite in the axially compressed Cu–Al–Ni alloys has been observed so far only when the γ' (2H) martensite is stress induced.^{6,7)} Starting from the parent β phase, small β' martensite needles arise in the austenitic β state at the initial stage of loading, which work as a “catalyst” for the subsequent $\beta \rightarrow \gamma'$ transformation.^{8,9)} The β' needles allow for the formation of a habit plane between the parent β phase and the non internally-twinned γ' martensite (from pure β phase, an undistorted habit plane with the γ' martensite is only crystallographically compatible provided the martensite is internally twinned).⁹⁾ In the course of the forward austenitic–martensitic transformation, the β' phase needles are absorbed by the non-twinned γ' martensite, making difficult the reverse martensite–austenite transformation, and therefore, resulting in the stabilization of the resultant γ' phase.^{5,7)}

As it was emphasized in Ref. 7), the mechanical stabilization of martensite occurring in the course of stress-induced

martensitic transformation (MT) can be recognized by the peculiar shape of partial stress–strain loops. The detailed study of superelastic loops under compression up to different strains, and the reverse transformation behavior monitored by DSC in the stabilized samples after compression, allowed concluding that the stabilization degree is increasing with the applied deformation and that the stabilization can not be attributed to the stored elastic energy only. It is worth to mention that the formation of martensite in Cu–Al–Ni alloy by applying the stress immediately results in the stabilization of stress-induced γ' phase, therefore mechanical stabilization does not involve any thermally activated process (*i.e.* reordering) as in the case of thermal stabilization induced by ageing in martensite.

In this paper a model for the superelastic behavior^{10,11)} will be applied to stress–strain results obtained in both a Cu–Al–Ni alloy exhibiting $\beta \rightarrow \gamma'$ transformation and mechanical stabilization under compression and a Cu–Zn–Al alloy showing $\beta \rightarrow \beta'$ transformation in tension with almost ideal (quasi-reversible) superelastic behavior. In addition to discuss and bring out a better understanding of some specific features of the stress–strain loops, the model contains a probability distribution through which the volume fractions of martensite are computed. It will be shown that the probability distributions are characteristic functions of the stress-induced martensitic transformations, therefore significant differences appear when comparing stabilizing and non-stabilizing alloys under mechanical loading. The specific features of probability densities are consistent with both situations, including the main characteristics of stabilized γ' martensite in Cu–Al–Ni, outlined above.

2. The Model of Superelastic Behavior of Alloy under the Axial Stress

A simple model of superelasticity was proposed in Refs. 10) and 11). According to the model, the deformation

Fig. 1 Scheme of a martensite unit formed in a column of the austenitic specimen.

of the alloy depends linearly on time during the loading/unloading cycle, assuming constant crosshead speed. The growth of martensite is modeled through the successive appearance of martensitic phase elements of equal shape and volume occurring in different spatial domains of the specimen at some strain values $\varepsilon = \varepsilon_n$. The number/volume of the units appearing in the specimen is expressed through statistical distributions $P_{f,r}(\varepsilon_n)$, which are the probabilities of appearance/disappearance of martensite units at the different stages of loading (forward)–unloading (reverse) cycle.

The martensite units are modeled by plane-parallel platelets with the dimensions l_x , l_y and l_z . The platelets are assumed to be coplanar with the shear planes corresponding to the maximal Schmid factor. The dimension of the specimen in the direction of compression is denoted as L_z . In this case, the columns with dimensions $l_x \times l_y \times L_z$ can be outlined inside the specimen (see Fig. 1).

The value $N_z = L_z/l_z$ is assumed to be integer. In this case the strain ε is expressed through the number n_z of martensitic nuclei in a column of the compressed specimen as

$$\varepsilon = N_z^{-1} [n_z \varepsilon^{(m)} + (N_z - n_z) \varepsilon^{(a)}], \quad (1)$$

where $\varepsilon^{(m)}$ and $\varepsilon^{(a)}$ are the absolute values of strain for the martensitic and austenitic domains in the column, respectively. The deformation of martensite is the sum of the elastic and transformation strains, while the deformation of austenite is completely elastic, *i.e.*

$$\varepsilon^{(m)} = \varepsilon_M + \sigma_{zz}/S^{(m)}, \quad \varepsilon^{(a)} = \sigma_{zz}/S^{(a)}, \quad (2)$$

where σ_{zz} is the mechanical stress applied to the column cross-section, ε_M is the absolute value of the spontaneous lattice distortion in z direction, $S^{(m)}$ and $S^{(a)}$ are the stiffness coefficients of martensite and austenite, respectively. In the case of uniform uniaxial stressing, the equations for strains $\varepsilon^{(m)}$ and $\varepsilon^{(a)}$ involve the same stress value σ_{zz} . The deformation of the specimen is expressed, therefore, as

$$\varepsilon = N_z^{-1} \left[n_z \left(\varepsilon_M + \frac{S^{(a)}}{S^{(m)}} \varepsilon^{(a)} \right) + (N_z - n_z) \varepsilon^{(a)} \right] \quad (3)$$

or as a function of σ_{zz} using $\varepsilon^{(a)} = \sigma_{zz}/S^{(a)}$. Strictly speaking, eq. (3) describes a nonlinear stress–strain characteristic of the mixed austenitic–martensitic state in a certain column outlined in the specimen. As it was argued in Ref. 10, in the case when $N_z \gg 1$ the number of transformation units in the different columns is approximately equal to each other. This

can be rationalized by the fact that the formation of each martensite element causes a local stress relaxation around it, which makes more probable the formation of the subsequent elements in different columns, in order to relax the stress homogeneously across the whole specimen. Hence, the discrete value n_z can be expressed through the volume fraction of martensite in the whole specimen $X(\varepsilon)$ as

$$X(\varepsilon) = n_z(\varepsilon)/N_z \quad (4)$$

and eq. (3) can be presented in a simple form

$$\sigma_{zz}(\varepsilon) = [\varepsilon - \varepsilon_M X(\varepsilon)] S(\varepsilon), \quad (5)$$

where

$$S(\varepsilon) = \frac{S^{(a)} S^{(m)}}{S^{(m)} + (S^{(a)} - S^{(m)}) X(\varepsilon)} \quad (6)$$

is the variable stiffness of mixed martensitic–austenitic state in a column. As far as the number N_z is large, the values $X(\varepsilon)$ and $S(\varepsilon)$ may be considered as continuous.

The volume fractions of martensite are expressed through the probability distributions as

$$X^{(f)}(\varepsilon) = \int_0^\varepsilon P_f(x) dx \quad (7)$$

for compression and

$$X^{(r)}(\varepsilon) = X^{(f)}(\varepsilon_{fin}) - \frac{1}{Z} \int_\varepsilon^{\varepsilon_{fin}} P_r(x) dx \quad (8)$$

for decompression. The value ε_{fin} is the deformation value in the final point of compression cycle, the factor

$$Z = \frac{1}{X^{(f)}(\varepsilon_{fin})} \cdot \int_0^{\varepsilon_{fin}} P_r(x) dx \quad (9)$$

provides for the further application of the model to the reversible cycles featuring the superelasticity phenomena.

Equations (5)–(9) enable the computation of the superelastic stress–strain characteristics of martensite if the statistical distributions $P_{f,r}(\varepsilon)$ are given. This computation can be referred to as the *direct problem solution*.

On the other hand, the function $S(\varepsilon)$ can be excluded from the eqs. (5) and (6) and then the volume fractions of martensite can be related to the stress function by the elementary algebraic relationship

$$X^{(f,r)}(\varepsilon) = \frac{S^{(m)} [S^{(a)} \varepsilon - \sigma_{zz}(\varepsilon)]}{(S^{(a)} - S^{(m)}) \sigma_{zz}(\varepsilon) + S^{(a)} S^{(m)} \varepsilon_M} \quad (10)$$

Equation (10) enables the computation of the volume fractions of martensite from the experimental stress–strain loops if the elastic stiffness coefficients of pure martensite and pure austenite are known in addition to the spontaneous MT strain. Let it be the *inverse problem solution*. It should be emphasized that the knowledge of the probability distributions is not needed for the inverse problem solution.

3. The Direct Problem Solution

The results of the direct problem solution for Cu–Al–Ni

Fig. 2 (a): Experimental superelastic cycles taken for $\text{Cu}_{69.6}\text{Al}_{26.8}\text{Ni}_{3.6}$ alloy (solid lines) in comparison with the cycles computed with the use of smoothed trapezium probability distributions (dashed lines). (b): Graphical presentation of the smoothed trapezium probability distributions used for the computation of superelastic cycles. The solid line shows the distribution corresponding to the forward paths; other lines correspond to the reverse paths. (c): “Projections” of the partial superelastic cycles on P – ϵ plane.

martensite are presented in Fig. 2(a). The solid lines display the experimental superelastic loops of a $\text{Cu}_{69.6}\text{Al}_{26.8}\text{Ni}_{3.6}$ at% single crystal compressed along [001] direction at $T = 440$ K, which was homogenized for 15 min at 1120 K and then quenched in water at room temperature. For this alloy composition and loading mode, the stress-induced MT is $\beta \rightarrow \gamma'$. The theoretical curves computed from eqs. (5)–(9) are shown by the dashed lines. The values $\epsilon_M = 8.1\%$ (taken from the lattice parameters of austenite and martensite),

$S^{(a)} = 7.5$ GPa and $S^{(m)} = 11.5$ GPa (determined from the slopes of the initial parts of the forward and reverse complete cycles, respectively) were used. The computations showed that experimental stress-induced MT curves in $\text{Cu}_{82.5}\text{Al}_{13.5}\text{Ni}_{4.0}$ alloy could not be fitted with the Gaussian statistical distribution considered in Ref. 10). Instead, “smoothed” trapezium distributions (everyone being constructed as two Gauss distributions with the tops connected by an horizontal line) were used for computations. The distributions leading to the theoretical curves of Fig. 2(a) are presented graphically in Fig. 2(b). All forward cycles (complete and partial) are described by the same statistical distribution (which means that the undeformed state is reproducible), while the distributions corresponding to the reverse paths are different in each partial cycle. It means that the kinetics of the reverse MT depends on the maximal strain value achieved during the compression branch.^{6,7)}

Both experimental and theoretical partial loops shown in Fig. 2(a) exhibit abrupt segments at the beginning of unloading of the specimen. All these segments are almost parallel to each other, both in the partial cycles and the global one. It means that the beginning of all reverse partial branches corresponds mainly to recovery of elastic deformation, without noticeable reduction of the volume fraction of martensite. This conclusion is explicitly illustrated by Fig. 2(c). This figure shows the “projections” of stress–strain loops on the P – ϵ plane. According to the figure, the probability function falls from the maximal value almost to zero at the beginning of every reverse partial cycle and begins to rise again only after a substantial decrease of the (elastic) deformation. This result of the model clearly illustrates that the mechanical stabilization takes place at *every* partial cycle, and therefore, *has a permanent character*. This conclusion is in perfect agreement with the experimental results.⁷⁾

Moreover, it has to be noticed that more than 1% reduction of the deformation is needed to start the reverse MT in the course of the longest partial cycle (dashed line in Fig. 2(c)) and only about 0.5% reduction in deformation (and correspondingly a smaller decrease in the applied stress) is enough to start the reverse MT in the course of the shortest partial cycle (solid line in Fig. 2(c)). Therefore, the dependence of the mechanical stabilization degree on the amount of previous deformation is quite well reproduced by the model.

In order to explicitly reveal the effects of mechanical stabilization in the frame of the proposed model, a comparison with the behaviour of the non-stabilizing $\beta \leftrightarrow \beta'$ stress-induced transformation (in tension) was performed. Figure 3(a) shows the experimental loops for a $\text{Cu}_{68.3}\text{Zn}_{15.4}\text{Al}_{16.3}$ (at%) single crystal under tension along [001] direction together with the corresponding computed curves. In this case, the stress–strain curves have not the abrupt segments corresponding to the recovery of elastic deformation at the beginning of reverse transformation paths. It means that the reverse MT starts practically immediately after the beginning of unloading. This conclusion is supported by the analysis of the probability distributions that give the most satisfactory agreement between the experimental and theoretical stress–strain curves: all reverse paths are approximately described by the same probability distribution (shown in Fig. 3(b) by the dashed line) which is very close to the probability

Fig. 3 (a): Experimental superelastic cycles obtained in a Cu_{68.3}Zn_{15.4}Al_{16.3} at% alloy (upper plot) in comparison with the cycles computed with the use of smoothed trapezium probability distributions (lower plot) for the appropriate values of ϵ_{fin} . (b): Graphical presentation of the smoothed trapezium probability distributions used for the computation of forward (solid line) and reverse (dashed line) superelastic cycles. (c): "Projection" of the partial superelastic cycle with $\epsilon_{fin} = 5\%$ on the P - ϵ plane.

distribution of the forward path (solid line in Fig. 3(b)). It is worth to note that, contrary to the case of Cu–Al–Ni alloy, the probability of formation of martensite at the end of the forward paths is very close to the probability of disappearance of martensite at the beginning of reverse paths (see Fig. 3(c)). The small shift of the reverse probability function with respect to the forward one may be attributed to the stored elastic energy, as it was proposed in Refs. 2, 4). It should be emphasized once more that the probability distribution $P_r(\epsilon)$ used to compute the reverse path was the same both for the global and all the partial loops presented in Fig. 3(a). Thus, only the maximal value of deformation achieved in the course of the forward paths was varied when the different partial cycles were modeled. The values of the other parameters of the model are: $S^{(a)} = 9$ GPa, $S^{(m)} = 13.5$ GPa (obtained as in the Cu–Al–Ni case) and $\epsilon_M = 5\%$. The later one is lower than the transformation strain deduced from crystallographic data, which means that the larger loop shown in Fig. 3(a) does not correspond to the complete stress-induced MT.

The comparison of Fig. 2(c) and Fig. 3(c) leads to the conclusion that the effect of the stored elastic energy is not sufficient for the explanation of mechanical stabilization of Cu–Al–Ni martensite in view of both qualitative and quantitative difference in the partial superelastic loops and probability distributions describing transformational behavior of Cu–Al–Ni and Cu–Zn–Al alloys. Therefore, the theoretical modelling supports the minor role of stored

elastic energy in the mechanical (or stress induced) stabilization, as it was mentioned in the introduction, and shows that the statistical distribution describing the probability of formation/reversion of martensite at every stage of alloy transformation can be considered as a characteristic function for the stress-induced MT. The mechanical stabilization of γ' martensite in the Cu–Al–Ni alloy is manifested by a strong modification of the probability function for the reverse transformation, compared to the forward one. The physical origin of the mechanical stabilization effect and, hence, of the differences between direct and reverse probability distributions, has been attributed to the difficulties in the formation of a habit plane between the non-twinned γ' martensite and austenite, as internal twins are essential for crystallographic compatibility of the habit plane with the two phases.^{5,7)} For the direct stress-induced transformation, the small needles of β' phase formed at the beginning make possible the formation of the habit plane with non-twinned γ' martensite.^{8,9)} On unloading, the β parent phase needs to be nucleated from the non-twinned γ' phase which is crystallographically difficult. This nucleation depends on the initial state of the sample before unloading, that means, it depends on the amount of parent and non-twinned martensite phases existent after a certain applied strain.

The statistical model of superelasticity enables a very simple computation of the volume fraction of martensite induced at every stage of compression/decompression process. The graph of the volume fraction of martensite

Fig. 4 Volume fraction of martensite vs. stress computed for the complete and partial stress–strain cycles performed in $\text{Cu}_{69.6}\text{Al}_{26.8}\text{Ni}_{3.6}$, (a), and $\text{Cu}_{68.3}\text{Zn}_{15.4}\text{Al}_{16.3}$, (b), alloys using the probability distributions shown in Figs. 2(b) and 3(b), respectively.

versus strain can be plotted immediately from eq. (7), for the forward path, and eq. (8), for the reverse one. Moreover, the systems of eqs. (5)–(7) and eqs. (5)–(8) assign an implicit form to the dependence of volume fraction of martensite on the mechanical stress. The dependencies computed for the Cu–Al–Ni and Cu–Zn–Al alloys are presented in Fig. 4. The figure illustrates that the decrease of the volume fraction of martensite and formation of austenite in the Cu–Al–Ni alloy starts only after a substantial decompression of the specimen, while the formation of austenite in the course of the partial cycles performed in Cu–Zn–Al occurs immediately at the beginning of the reverse paths.

4. The Inverse Problem Solution

In this section the volume fractions of martensite are obtained from the experimental stress–strain loops using eq. (10), *i.e.* without use of the model probability distributions. These dependencies can be referred to as the semi-empirical ones. The computations are performed for the $\text{Cu}_{69.6}\text{Al}_{26.8}\text{Ni}_{3.6}$ at% alloy characterized by the values of the MT strain and stiffness coefficients reported above.

Figure 5 shows the obtained results, which enable the evaluation of the volume fraction of martensite at every stage of the stress–strain cycle with the exception of the beginning

Fig. 5 Volume fraction of $\text{Cu}_{69.6}\text{Al}_{26.8}\text{Ni}_{3.6}$ martensite vs. strain (a) and stress (b) computed from eq. (10) using the experimental stress–strain loops. The dashed lines for comparison show the dependencies computed for the complete cycle with the use of the model probability distributions.

of decompression process, where the semiempirical volume fractions take “nonphysical” values exceeding the maximum value obtained in the corresponding loading branch. This nonphysical behavior of the semiempirical dependencies of the volume fractions of martensite explicitly reflects the existence of unwanted apparatus effects at the beginning of decompression. These effects result in the wave-like deflections of the experimental stress–strain curves in the vicinity of the turning point. Therefore, computation of the martensite fraction within the frame of the inverse problem solution, even though it is very simple, suffers from the defects which can appear in the experimental stress–strain loops due to lack of accuracy in measuring the strain (and/or the stress). On the other hand, the evaluation of the martensite fraction through the direct problem approach, although a bit more complicated in computing, gives results of much better quality (compare Figs. 4 and 5). This is due to the fact that the probability distribution functions needed in the direct problem solution are free from any non-physical effect, therefore a proper physical behaviour is obtained both in the modeled stress–strain loops and in the martensite fraction vs. stress.

It is worth to note the particular shape of the curves corresponding to the reverse transformation in Figs. 4(a) and 5(b), which show multi-valued $X^{(r)}(\sigma_{zz})$ functions. This is due

Fig. 6 Semiempirical (solid line) and model (dot-and-dashed line) derivatives of the volume fractions of stress-induced martensite in comparison with the heat flow vs. "temperature related stress" σ_T (dashed line).

to the form of the reverse paths of the experimental σ - ε curves (Fig. 2(a)), which evidence an increase of the stress upon unloading. This behaviour (which indeed contradicts the Equilibrium Thermodynamics conditions) seems to be related to the explosive character of the reverse transformation of the mechanically stabilized martensite. A detailed study about this effect will be published elsewhere.

The inverse problem solution makes possible, in a simple way, to show the relationship between stress-induced and temperature-induced MT. To this end the semiempirical $X^{(f)}(\sigma)$ function was differentiated numerically and then interpolated with help of standard software tools. The result of interpolation is shown in Fig. 6 together with the derivative obtained using the model probability distribution. Then, the experimental temperature dependence of the critical stress needed for the start of the forward martensitic transformation, $\sigma_{ms}(T)$, was considered and the experimental value $d|\sigma_{ms}|/dT \approx 2.5 \text{ MPa/K}^{(12)}$ was used as a conversion coefficient from the variable temperature to the variable stress. Finally, the experimental DSC peak obtained for the $\text{Cu}_{69.6}\text{Al}_{26.8}\text{Ni}_{3.6}$ at% specimen exhibiting the $\beta \rightarrow \gamma'$ MT on cooling after the thermal treatment and posterior ageing (2 hours at 570 K) was depicted as a function of the "temperature related stress" $\sigma_T = T(d\sigma_{ms}/dT)$ and the top of DSC peak was matched with the center of $dX(\sigma)/d\sigma$ curve (see Fig. 6). This figure illustrates that the amount of overcooling needed for the completion of the temperature-induced MT is comparable to the stress difference between the final and

starting points of the stress-induced MT through the transmission coefficient ($d\sigma_{ms}/dT$). As far as at the actual experimental conditions both stress and temperature linearly depend on time, the difference in the shapes of the solid and dashed curves explicitly illustrates the difference in the kinetics of the formation of the self-accommodated poly-variant martensite (on cooling) and (almost) single-variant martensite (under stress).

5. Discussion and Conclusions

As it was shown above, the statistical approach proposed in the Refs. 10, 11) not only enables for the quantitative description of superelastic behavior of martensitic alloys but also clearly illustrates the effect of mechanical stabilization of martensite. This approach is considerably simpler than the thermodynamic models elaborated by other authors (see *e.g.* Refs. 13–15), because it is based on the probability distributions $P_{f,r}(\varepsilon)$ and simple Hooke's law (see eq. (2)) instead of the Gibbs potential and a rather complicate system of constitutive equations involved in the formalism of non-equilibrium thermodynamics.

The probability distributions needed "*a priori*" in the direct method approach are unknown functions, which could make difficult a proper initial choice and further optimisation in order to reproduce the experimental stress-strain loops. However, the forward and reverse probability distributions can be numerically determined from the experimental stress-strain loop corresponding to the complete transformation cycle through the inverse problem solution, by the following procedure:

1st. The stiffness coefficients $S^{(a)}$ and $S^{(m)}$ should be found from the slopes of the initial and final straight segments (respectively) of the forward stress-strain curve.

2nd. The transformation strain ε_M should be found by the extrapolation of the final straight segment to zero stress value.

3rd. The volume fractions of martensite $X^{(f,r)}(\varepsilon)$ should be found numerically by the substitution of the experimental dependence $\sigma(\varepsilon)$ into the simple algebraic eq. (10).

4th. The probability distributions can be computed by the numerical differentiation of $X^{(f,r)}(\varepsilon)$ functions, according to eqs. (7) and (8).

The steps 1st and 2nd can be performed graphically and points 3rd and 4th can be carried out using standard software for personal computers.

As long as the final straight segments of experimental stress-strain curves were not reached for the alloys examined above to avoid the possible fracture of the specimens, we performed the steps 3rd and 4th for the maximal experimental cycle presented in Fig. 3(a) using the values ε_M , $S^{(m)}$, and $S^{(a)}$ estimated in the course of the direct problem solution. The resultant (semiempirical) values of the probability density are shown in Fig. 7 by triangles. The figure illustrates the feasibility of the proposed procedure and a good agreement between the semiempirical and theoretical probability distributions. The local minimum of the semiempirical probability function at $\varepsilon \approx 2.5\%$ is attributed to the deflection of experimental stress-strain loops easily noticeable in Fig. 3(a) and seems to be related to the microstructure

Fig. 7 Semiempirical probability distributions obtained from the experimental stress-strain loops for the compressed (solid triangles) and decompressed (open triangles) $\text{Cu}_{68.3}\text{Zn}_{15.4}\text{Al}_{16.3}$ at% alloy specimen. (The model curves extracted from Fig. 3(c) are shown for comparison).

of the specimen and its influence on the course of stress-induced MT, while the anomaly displayed by this function in the vicinity of turning point may be related to the apparatus effects.

Finally, the obtained results can be summarized in the following way:

- (1) The probability distributions $P_{f,r}(\epsilon)$ for the events of appearance/disappearance of martensite elements in the austenitic matrix in the course of complete compression/decompression cycle can be considered as the characteristic functions of stress-induced martensitic transformation.
- (2) The characteristic functions can be unambiguously determined from the experimental stress-strain loop measured in the course of complete transformation cycle if the loops have pronounced linear segments corresponding to the reversible elastic deformation of pure austenite and pure martensite, while the absence of straight segments results in some ambiguity in the determination of the values of MT strain and stiffness coefficient of martensite. To avoid this ambiguity one of the two values mentioned above could be determined from an independent experiment.
- (3) The characteristic functions enable the determination of the volume fraction of martensite in the mixed austenitic-martensitic state at every stage of the compression/decompression cycle, *i.e.* for every stress and/or strain value.
- (4) The characteristic functions of the stress-induced martensitic transformation in the $\text{Cu}_{82.5}\text{Al}_{13.5}\text{Ni}_{4.0}$ wt% alloy illustrate the effect of the mechanical stabilization of martensitic phase and demonstrate the

following features of this effect:

- (i). The mechanical stabilization of γ' martensite in Cu–Al–Ni alloy has a permanent character: the larger is superelastic deformation of the alloy, the more pronounced is stabilization of the γ' phase.
 - (ii). The mechanical stabilization of γ' phase in Cu–Al–Ni alloy manifests itself in the large probability differences $P_f(\epsilon_{fin}) - P_r(\epsilon_{fin})$ inherent to the turning points of the partial superelastic cycles; these differences cannot be attributed to the stored elastic energy only (in accordance with the microscopic features studied in the Ref. 6).
- (5) A close interrelation between the processes of formation of stress-induced and temperature-induced γ' martensites exists; the commonly studied value $d\sigma_{ms}/dT$ (where σ_{ms} is critical stress necessary for the start of the forward stress-induced MT) measured with independent experiments is an adequate conversion coefficient from the temperature range of MT observed on cooling to the stress range where the stress-induced MT takes place.

Acknowledgements

V.A.L. is grateful to the UIB for financing his stay at Departament de Física. Partial financial support from Spanish DGI (project MAT2002-00319) is also acknowledged.

REFERENCES

- 1) M. Wang, Z. Yin, X. Sun and Y. Huang: *Proc. Shape Memory Materials-94*, ed. by C. Youi and T. Hailing, (International Academic Publishers, Beijing, 1994) pp. 412–417.
- 2) M. Piao, K. Otsuka, S. Miyazaki and H. Horikawa: *Mater. Trans., JIM* **34** (1993) 919–929.
- 3) Y. Liu, Y. Liu and Van Humbeeck: *Acta Mater.* **47** (1999) 199–209.
- 4) Y. Liu and D. Favier: *Acta Mater.* **48** (2000) 3489–3499.
- 5) P. Sittner, V. Novak, N. Zarubova and V. Studnicka: *Mater. Sci. Eng. A* **273–275** (1999) 370–374.
- 6) P. Sittner, V. Novak and N. Zarubová: *Acta Mater.* **46** (1998) 1265–1281.
- 7) C. Picornell, J. Pons and E. Cesari: *Acta Mater.* **49** (2001) 4221–4230.
- 8) H. Sakamoto, M. Tanigawa, K. Otsuka and K. Shimizu: *Proc. Int. Conf. of Martensitic Transformations (ICOMAT-79)* ed. by C. M. Wayman *et al.* (Cambridge, 1979) pp. 633–638.
- 9) J. Pelegrina and M. Ahlers: *Acta Metall. Mater.* **40** (1992) 3221–3227.
- 10) V. A. Chernenko, V. A. L'vov, E. Cesari, J. Pons, A. A. Rudenko, H. Date, M. Matsumoto and T. Kanomata: *Mater. Sci. Eng. A* **378** (2004) 349–352.
- 11) V. A. L'vov, A. A. Rudenko, V. A. Chernenko, E. Cesari, J. Pons and T. Kanomata: *Mater. Trans.*, in press.
- 12) C. Picornell, J. Pons and E. Cesari: *Mater. Trans.* **45** (2004) 1679–1683.
- 13) M. Achenbach: *Int. J. Plast.* **5** (1989) 371–395.
- 14) R. Aberayathne and S. Kim: *Int. J. Solids Struct.* **34** (1997) 3273–3289.
- 15) S. Govinjee and G. J. Hall: *Int. J. Solids Struct.* **37** (2000) 735–760.