Journal of Thermal Analysis, Vol. 38 (1992) 593-602

SHAPE MEMORY ALLOYS: LOCAL AND GLOBAL TRANSFORMATIONS BY HIGH RESOLUTION THERMAL ANALYSIS

A. Amengual, A. Isalgué, F. C. Lovey⁺, F. Marco and V. Torra*

APPLIED PHYSICS DEPT., UNIV. POLITECNICA CATALUNYA, JORDI GIRONA SALGADO 31,
E-08034 BARCELONA, SPAIN
* PERMANENT ADDRESS: PHYSICS DEPT., UIB. E-07071 PALMA DE MALLORCA, SPAIN
⁺ PERMANENT ADDRESS: DIV. METALES, CAB, 8400 S. C. BARILOCHE, ARGENTINA

The use of high resolution automatised equipment (HRTA, conduction calorimetry, stress-strain-temperature) allows to study, locally and/or globally, the martensitic transformations of the alloys with memory (Cu–Zn–Al). The observations allow to establish the phenomenology of the effects of the cycling on the crystalline structure. Particularly, the formation of defects, the interactions between the interphases and the precipitates that change the relative stability of the phases, the effects of the nucleation and the growth. The experimental research of the area of coexistence of the two phases allows to set a phenomenological model coherent with the experimental observations.

Keywords: high resolution thermal analysis, shape memory alloys

Introduction

Shape memory alloys (SMA) have promising fields of application in sensors and robotics. However, in order to apply them properly in predictive conditions about their performances, it is necessary to know in detail their behaviour, their surface of state stress-strain-temperature in the martensitic transformation and the conditions of reproducibility and ageing [1–4]. Right now, the state of the art for Cu-based SMA (which are interesting because of economic reasons) is that devices for a limited number of cycles are more reliable for immediate applications.

It is important to stress that the interesting domain is set in the area of coexistence of the two phases. Furthermore, in both the single crystals and the polycrystals the transformation is done through the formation of a great number of little domains of martensite, so that the material in the working area becomes a

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

complex heterogeneous system. In particular, the need to use a water-quenching from high temperature ($T > 650$°C) to avoid the precipitation of the α phase in the standard alloys, introduces an initial important concentration of dislocations. The associated intrinsic thermoelasticity helps the formation of little domains of martensite. All this phenomena make the behaviour of the alloy harder to describe and fit into a model. Moreover, the alloy changes in an unpredictable or stochastic way. As a result the available models, theoretical or numerical, do not give an accurate or predictive description of the behaviour of the alloy.

Lately some systematic observations have been done to establish the paths that should be followed to achieve a predictable behaviour. This observations have established that the values of the transformation temperatures depend on the kind of thermomechanical treatment (TTM), in addition, to each treatment corresponds a scale in the time of evolution [5–8]. It has also been noticed that the causes of the memory effect are closely related to the dislocation concentration initially present in the crystalline network of the parent phase. The evolution of the calorimetric thermograms with the cycling and their comparison with the observation through transmission electronic microscopy has established a first relation between the changes of the thermograms and the creation of dislocations.

The use of high resolution automatised equipment allows to analyse accurately and repetitively the global and partial cycles of transformation-retransformation and to separate the different processes that take place [9, 10]. In particular, we can analyse the process of growing-shrinking of a single plate and estimate the relevant parameters. This analysis has allowed to establish the importance of the concentration of dislocations that generates the intrinsic thermoelasticity. That is the most important cause for the existence of the memory effect. The analysis of the behaviour of a single plate allowed the preparation of a phenomenological model that described the movement of an interface and the asymmetrical effects of the pinning points.

We present here some results we have obtained in the detailed study of the martensitic transformation in Cu–Zn–Al SMA. A detailed study needs good control of external fields acting on the samples. We used previous experience on high resolution thermal analysis systems, to monitor the behaviour of the martensitic transformation in Cu–Zn–Al, without external mechanical stress, and in transformation to a single martensite variant, with simple interphases. Also, we used a computer controlled stress-strain-temperature system, in order to study the stress induced martensitic transformation.

In particular we present the effects of the interaction of an interphase with γ precipitates that radically change the width of the hysteresis loop by changing the characteristic temperatures. This means there is a change in the relative stability of the phases (parent and martensite phases). We make some quantitative observations of the entropy production associated to the changes in the calorimetric thermograms with the cycling. If there are changes in the production of entropy it means that the driving force linked to the transformation has been changed and that the structure of the material has been modified.

The analysis of the behaviour of one or more plates of martensite under mechanical stress allows us to take quantitative measurements of the friction work (with or without nucleation) and to compare them with some recent works based on dubious thermodynamic hypothesis. In this way, the systematic analysis of a group of stress – strain cycles allows us to build a phenomenological model based in the relevance of the processes of nucleation and growth that is coherent with the experimental observations.

Experimental

To study the transformation-retransformation processes we have used a group of automatised systems based on the HRTA (High Resolution Thermal Analysis) basic equipment [9–11]. The system has a resolution in temperature higher than ±0.01 degree. The use of thermomicroscopy associated with HRTA is decisive to be able to establish a connection between the quantity of martensite and the external fields (temperature, mechanical stress). For the transformations with one or more martensite plates we have used a stress-strain-temperature equipment and for the global spontaneous transformations a calorimetric system that allows us to achieve the characteristic temperatures, the exchanged energies, the hysteresis loops and the entropy productions [12].

Results and discussion

The observations can be separated into two groups. First, the observations of the growing/shrinking of a single domain of martensite. Secondly the processes associated to the spontaneous temperature induced transformations. The first group is to analyse the relevant parameters in the simple processes and the second to analyse the complexities associated to the spontaneous processes and in particular the formation of defects.

Single martensite plate

Single variant single martensite plates were usually induced by stress in necked samples, and then the stress released with simultaneous decrease of temperature, in order to stabilize one martensite plate and avoid the nucleation processes.

It has been established that for the transformations exclusively induced by temperature and stress free, the concentration of defects is very important. This is the reason why alloys with electronic concentration 1.48 have been used, and after 10 minutes at 850°C a quenching with different temperature rate has been done. The use of an air-quenching (TT1) has produced samples with little initial concentration of dislocations. The use of a water-quenching (TT2) produces material with a high concentration of defects. In the first case (TT1) the growth of the martensite is relatively easy and with coolings of ≈ 1 degree the interphase moves about 1 mm. In the second case (TT2), the growth is much harder – the intrinsic thermoelasticity dT/dx is much more important – and when the temperature is reduced new phases nucleate. Similarly, an evolution of the transformation temperatures, increasing with time more rapidly in the case of TT2, can be seen. Their evolution depends on the cycling process and is associated to the intensity of the stabilising effects and the evolution of the width of the hysteresis loop. Furthermore, the temperatures are different, so that, for example we could find $M_s(\text{TT1}) \approx M_s(\text{TT2})+10$ K, ($M_s \approx 280$ K).

The intrinsic thermoelasticity implies the need of a progressive cooling to increase the quantity of martensite. This generates a progressive instability of β phase and an energy rise of the obtained martensite. It is associated to the growth and to the continued formation of new stacking faults by the displacement of the interphase and by the interaction with the dislocations. The progressive instability helps the nucleation of new domains of martensite in other areas of the material. The changes in temperature and their evolution are associated to the atomic order (B_2, $L2_1$) and to the transport of vacancies that seems to be activated by the presence of the interphase [7–8].

a) Nucleation and friction measurements

We used the force – displacement – temperature system described in reference [12] before to trace elementary transformation-retransformation cycles at constant temperature, in force-displacement coordinates, the enclosed area in one cycle, $\oint \vec{T} d\vec{l}$ corresponds to work given to the sample (the friction energy) in order to complete the transformation.

From the results it can be seen (Fig. 1) that nucleation plays a very important role, but, in all cases the mechanical energies involved are very small compared to enthalpy changes in the martensitic transformation (around 6 J/g). For a Cu–Zn–Al sample, electronic concentration e/a=1.48, air cooled from 1123 K to room temperature, a single plate transformation cycle, with nucleation included, show a specific mechanical work done on the sample of about 0.03 J/g at 293.88 K, while for an internal cycle, nucleation free (growth-shrinkage of a single plate), we have a specific mechanical work of 0.005 J/g.

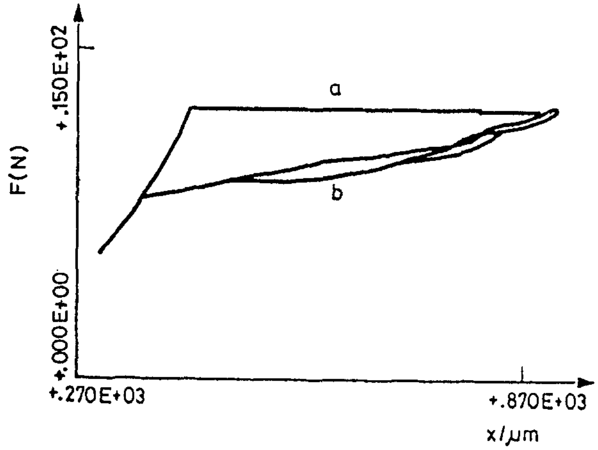

Fig. 1 Force (N) *vs.* displacement (μm) for an air-quenched sample from 1123 K: a, nucleation effect; b, growing /shrinking without nucleation (cross section near 1 mm^2)

The preceding results of $\oint \vec{T}\,\mathrm{d}\vec{T}$ are coherent with the width of the hysteresis loop (around 0.3 degree) seen through a stress free temperature programming and the entropy production. They are different from the ones found in recent literature (Ref. 13 and references therein) where the premises used are not correct.

The intrinsic pseudoelastic effect can be clearly appreciated in the internal cycle (Fig. 1.). In order to continue the transformation, an increasing force is needed. An intrinsic pseudoelastic coefficient can be defined as the differential resolved stress $\mathrm{d}\tau$ on the habit plane needed to increases the quantity of martensite in $\mathrm{d}x$, $ge=\mathrm{d}\tau/\mathrm{d}x$. The value we obtained for the air cooled sample, is around 3 kPa/μm and this corresponds quite well to the intrinsic thermoelasticity coefficient ($gT\equiv \mathrm{d}T/\mathrm{d}x$ [7] via the Clausius-Clapeyron relation, $\mathrm{d}\tau/\mathrm{d}T$ nearly equal to 1 MPa/K [14]: $ge=gt\cdot \mathrm{d}\tau/\mathrm{d}T$, taking into account the behaviour produced by pinning effects, and the margin implied in the value of gt (the value above mentioned of 0,005 degμm would imply 5 kPa/μm.

b) Samples with small γ precipitates

Small gamma precipitates were produced on a 16.7 Al, 14.6 Zn, 68.7 Cu (atom %) sample by the following thermal treatment: 1123 K for 10 min, air cooled to 290 K, 803 K for 10 min, and water-quenched to 293 K. From TEM, the size of the precipitates obtained was around 100 Å with mean distance between precipitates about 500 Å. A single variant plate of martensite was obtained in a necked sample, following the procedure previously indicated, from which it was possible to observe the temperature induced transformation behaviour free of external applied stress.

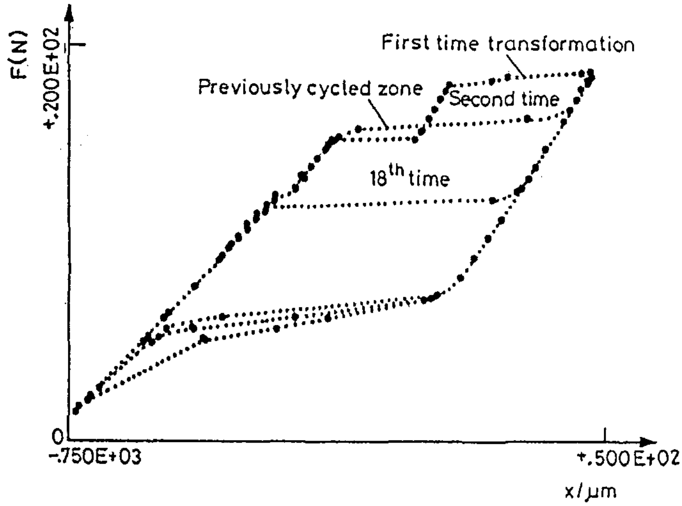

Fig. 2 Force (in N) *vs.* displacement (in μm) for a Cu–Al–Zn sample with small γ precipitates. Hysteresis width changes strongly by cycling

When a part of the sample transforms to martensite for the first time, its cycle presents a temperature hysteresis width much larger than for successive transformations. Hysteresis width progressively decreases with cycling (see Table 1). If the transformation is driven to an area that has not transformed before (by lowering the temperature), the first cycle hysteresis width is found again. If the domain of martensite is relatively important this situation helps the spontaneous nucleation of β phase to the previously cycled area. The overheatings observed for the nucleation of phase β are small (near 0.5 degree)

Table 1 Hysteresis width (ΔT_h in K) *vs.* cycle number (N)

N	1	3	4	19
ΔT_h	7.6	4.6	3.3	2.23

The observation of the behaviour with precipitates has been conducted at constant temperature for the action of an external stress. The results are coherent with the ones obtained by the action of the temperature. The cycling (growing-shrinking) reduces the width of the hysteresis cycle through a decrease (50%) of the transformation stress and a little increase (5–10% of the retransformation stress (Fig. 2). The results establish that there is an important change in the material through the interaction between the interphase and the precipitates. The most important change corresponds to the adaptation of the precipitate to the martensite phase (change of 50%) and a lesser adaptation in the retransformation. That is to say, the cycling changes the equilibrium conditions of the phases by displacing the characteristic temperatures. The calorimetric results obtained so far do not visualise this evolution. This shows that the nucleation of other phases is easier in the spontaneous transformations.

A larger friction work appears in the first cycle at 288.66 K in a single plate transformation: near 0.1 J/g. In successive mechanical cycles at constant temperature the specific work decreased to near 0.05 J/g after 20 cycles.

Global transformation and entropy production

The repetitive cycling after 24 h of a TT1 treatment has an important evolution, and the observation through TEM establishes that the concentration of dislocations increases. The study of the transformation bursts that can be seen on the thermograms of a series of complete cycles β phase to martensite [10] enables estimation of the associated entropy production ΔS_u. The values are shown on Table 2. The values of the expression:

$$|\Delta G_{S_U}| = (\Delta S_U(1) - \Delta S_U(\infty))\cdot\bar{T} \approx 0.043\,\mathrm{J\cdot cm^{-3}}$$

stands for the change of driving force linked to the cycling. In fact it is associated to the ease in the nucleation of martensite that, in the first cycle, needs a supplementary cooling of 2 K. For the temperature T an average of the temperatures of the cycle can be used. The value of ΔG_{S_U} is near the necessary energy to create the dislocations [15].

Table 2 Entropy production ΔS_u in $\mu\mathrm{J\cdot K^{-1}\cdot cm^{-3}}$ *vs.* N (cycle number) in β to martensite. Initial heat treatment: TT1 Temperature induced transformation.

Cycle number	1	2	3	4	6	10	14	17
ΔS_u / $\mu\mathrm{J\cdot K^{-1}\cdot cm^{-3}}$	214	158	98	86	75	68	54	55

Cycling in stress — strain representation and modelling

Some mechanical cycles were also measured on a microcrystalline water-quenched sample with electronic concentration e/a=1.48 (16.7 Al, 14.6 Zn, 68.7 Cu atom %). The F–x cycles were reproducible to near 0.4 μm in displacement while the force was within 0.001 *N*, even in the transformation area, if the temperature was constant.

The cycles on a water-quenched sample showed always a slope in the transformation area. However, this slope cannot be assigned directly to an intrinsic pseudoelastic effect. Nucleation is soon involved even with small displacements (changes in the length of the sample of some micrometers). From an initial state of nearly 8 plates, the optical microscopy showed (at the final state) the traces of around 50 plates in the 5 mm narrowest part of the sample. The cycling process used, which needed more than a week, is close to 500 cycles, nearly equivalent to the one shown on Fig. 3.

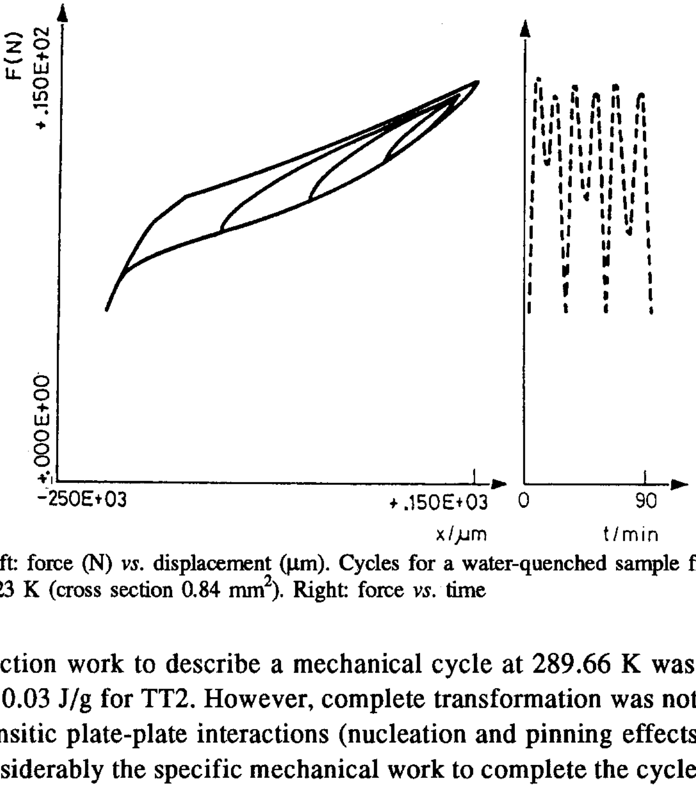

Fig. 3 Left: force (N) *vs.* displacement (μm). Cycles for a water-quenched sample from 1123 K (cross section 0.84 mm^2). Right: force *vs.* time

The friction work to describe a mechanical cycle at 289.66 K was found to be around 0.03 J/g for TT2. However, complete transformation was not reached, and martensitic plate-plate interactions (nucleation and pinning effects) will increase considerably the specific mechanical work to complete the cycle. Internal cycles showed also a friction work dependent on the width of the cycle.

The comparative analysis of the observations of a material under a mechanical tension establishes that in the process of transformation and retransformation these factors are relevant:

a) the nucleation of beta and martensite

b) the intrinsic thermoelasticity

c) the maximum size of the martensite plates
d) the intrinsic friction
e) the growth of the plates starts (and shrinking ends) through microplates
f) unsimultaneous formation of the plates
g) the pinning effects

The set of experimental conditions helps the construction of a numerical model in which a group of potential domains of martensite are under an external mechanical stress. The characteristics of the model provide stress-strain curves like the one shown on Fig. 4 that are very close to the one obtained through the tests. The model also allows to diagram the behaviour of the material for more simple situations like the ones shown on Figs 1 and 2. At present it seems possible to use numerical techniques of identification with physical image to, through experimental curves, obtain an approximate model to describe the behaviour of a material.

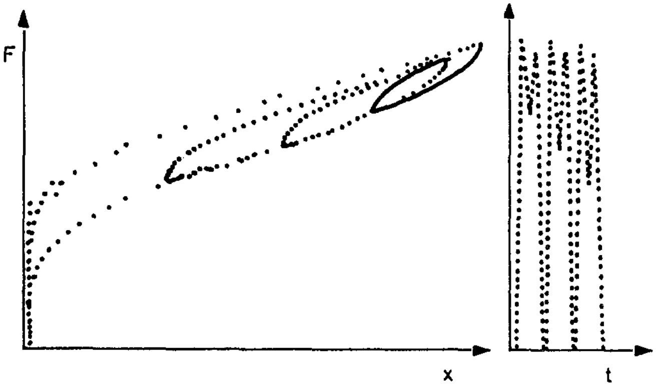

Fig. 4 Model results; left: force *vs.* displacement; right force *vs.* time

Conclusion

The use of high resolution equipment is a new approach to work in shape memory alloys that, along with the structural observations, helps to understand the elementary mechanisms that take place in the alloy or in the process of transformation. The observations point out the importance of the presence of the interphase and, in particular, its interaction with the precipitates. The production of entropy linked to the transformation burst is coherent with the processes of generation of dislocation in the spontaneous transformations. It seems an easy to measure sensitive thermodynamic parameter. The use of stress-strain-temperature equipment of high resolution allows to operate with cyclings of different length and to reach a reproducible situation visualising the different parameters relevant in the description of the transformation. This allows to build a phenomenological approximation that can be numerically solved and to get close to the hysteretic loop.

* * *

The financial aid from CICYT (project MAT89 – 0407 – CO3) is gratefully acknowledged. F.C.L. acknowledges the DGICYT (sabatic program) and the EEC (third countries program) for financial aid in the stay at Spain.

References

1 Science and Technology in Shape Memory Alloys, Proc. COMETT Course 1989 (Barcelona, Spain), V. Torra, Ed. Universitat de les Illes Balers (1989) (Spain).

2 Martensitic Transformations I and II, Proc. of the ICOMAT 89, B.C. Muddle Ed. Materials Science Forum Vol. 56–58 (1990), Trans. Tech. Publications, Zürich (Switzerland).

3 Proc. of the ICOMAT 86; I. Tamna Ed., The Japan Institute of Metals (1987), Sendai (Japan).

4 The Martensitic Transformation in Science and Technology; E. Hornbogen and N. Jost Eds., DGM, Obernsel (FRG) 1989.

5 A. Planes, J. Viñals and V. Torra, Phil. Mag., A 48 (1983) 501.

6 J. Viñals, V. Torra, A. Planes and J. L. Macqueron, Phil. Mag., A50 (1984) 653.

7 A. Amengual, F. C. Lovey, and V. Torra, Scripta Met. Mater., 24 (1990 2241.

8 L. Buffard, PhD 1991, Ecole Centrale de Lyon, France.

9 A. Amengual, V. Torra, A. Isalgué and F. Marco, Thermochim. Acta, 155 (1989) 115.

10 V. Torra and H. Tachoire, J. Thermal Anal., 36 (1990) 1545.

11 A. Amengual and V. Torra, J. Phys. E., Sci. Instr., 2 (1989) 433.

12 A. Amengual, A. Isalgué, F. Marco, H. Tachoire, V. Torra and V. R. Torra, Automatic equipment with improved performances (ATD and DSC) in shape memory alloys studies, J. Thermal Anal. (submitted).

13 A. Planes, J. L. Macqueron and J. Ortin, Phil. Mag. Lett., 57 (1988) 291.

14 W. Arneodo and M. Ahlers, Acta Metall., 22 (1974) 1475.

15 J. Pons, F. C. Lovey and E. Cesari, Acta Metall. Mater., 38 (1990) 2733.

Zusammenfassung — Unter Anwendung einer hochauflösenden automatisierten Apparatur (HRTA, Leitfähigkeitskalorimetrie, Zug-Dehnungstemperatur) können sowohl lokal als auch global die martensitischen Umwandlungen von Legierungen mit Erinnerungsvermögen (Cu–Zn–Al) untersucht werden. Die Beobachtungen gestatten die Feststellung der Phänomenologie des Einflusses von periodischen Schwankungen auf die Kristallstruktur, insbesondere Fehlstellenbildung, Wechselwirkungen zwischen Zwischen-phasen und Fällungen, die die relative Stabilität der Phasen verändern sowie der Einfluß von Keimbildung und Keimwachstum. Die experimentelle Ergründung der Gebiete mit zwei koexistenten Phasen erlaubt die Schaffung eines phänomenologischen Modelles, welches mit den experimentellen Beobachtungen übereinstimmt.