JOURNAL DE PHYSIQUE IV
Colloque C4, supplément au Journal de Physique III, Vol. 1, novembre 1991

PROBLEMS ASSOCIATED TO NUCLEATION AND GROWTH IN THE Cu-Zn-Al SMA

A. AMENGUAL, F.C. LOVEY* and V. TORRA**

Departament de Fisica, Universitat de les Illes Balears, SP-07071 Palma de Mallorca, Spain
**Division Metales, Centro Atomico de Bariloche, RA-8400 San Carlos de Bariloche, Argentina*
***Dep. Fisica Aplicada, ETSECCP - UPC, SP-08034 Barcelona, Spain*

Abstract - We have studied the characteristics of single-interface single-variant martensitic transformations in Cu-Zn-Al shape memory alloys with a high resolution thermal device (temperature resolution 0.003 K, optical resolution up to 1 μm) Two observations are presented: the appearence of an intrinsic thermoelasticity and the possibility to get two β-variants from a martensite single-crystal. The first phenomena is a phase growth problem (the interaction between interface and dislocations), whilst the second depends on the nucleation of the β phase and permits the breakdown of the SME.

1.- Introduction.

The study of the single-interface single-variant transformation in Cu-Zn-Al shape memory alloys is of paramount importance. The reason is that it is the nearest transformation to the pure phase change between the martensite and the β-phase. However, the study of this kind of transformation needs a very careful experimental work due to the resolution required.

In the literature of some years ago (at the end of the 70') it is possible to find experiments in β to γ' single-interface single-variant transformations [1]. However, these were performed with a temperature control that, looking backwards, appears very poor. In the afore mentioned work it was established that the single-interface single-variant DO_3-to-2H transformation proceeds at a constant temperature (with their resolution near 0.5 K). This corroborated the previous idea that no thermoelasticity would appear in that kind of transformations [2]. Moreover, this idea was accepted to be generally true: a single-interface single-variant transformation should proceed at constant temperature since no elastic strain energy was stored [1].

Detailed studies of the stochasticity of the transformation, carried out with the acoustic emission techniques, have shown that a more rigorous temperature control was necessary in order to obtain a reproducible transformation path [3].

Reproducibility could be achieved with an experimental set up where the temperature was computer controlled with a resolution of 0.003 K. This is a key point, since without this resolution the phenomena we are showing here could not have been separated from background perturbative effects (martensite stabilization, time scales, β recovery, and so on).

The symmetries of the parent and product phases determine the amount of variants which can appear after a free transformation (external fields modify this number). When a single crystal of the B2 or $L2_1$ transforms to martensite, 24 differently oriented variants of 9R or 18R martensite can appear [4]. From the symmetry point of view the retransformation should produce a phase compatible with the superimposition group of symmetry of the coexisting variants and this is the original matrix itself. This can be understood as the reason for the shape memory effect in multivariant transformations [5]. A single crystal of martensite has a symmetry point group $C2_h$ [6] and two differently oriented variants of the β phase could appear [7]. However, the coexistence of a martensitic phase and the two β equivalent phases was not experimentally observed.

The aim of this work points out to the phenomenological analysis of the elementary processes in the martensitic transformation. We have observed, first, that the intrinsic thermoelasticity prevents a growth of the same plate because the temperature has to be lowered continuously and other plates nucleates. Second, we have observed the appearence of the second β phase. This can be understood as a kind of breakdown of the shape memory effect which can appear only under very special conditions.

2. Experimental data and results.

Samples with two alloy compositions were used: alloy 1 (Cu-16.7% Al-14. 6% Zn (M_S= 290 K)); alloy 2 (Cu-16.0% Al-15.8% Zn (M_S= 253 K)). Planar specimens were cut with a low speed saw and a necked shape was produced with a fine file (length ~1.5 cm, hight ~0.1 cm, width at the necked region ~ 0.1 cm). Two thermal treatments were used: Ageing at 1120 K for 30 minutes followed by: cooling in air to room temperature (TT1) or quenching in water at room temperature (TT2).

A single martensite microplate was forced to appear combining stress and temperature changes. The stress was gradually removed while cooling (in addition the microplate attained to some degree of stabilization) until the sample was stress free. This operations were perfomed by using a device described elsewhere [8]. It allowed us to program and control the temperature (with a resolution ~0.003 K) and to apply a constant load (up to ~20 N). The transformation was followed with an optical microscope with a video tape recorder.

A) The intrinsic thermoelasticity.

The hysteresis cycle for a single-interface single-variant transformation can be plotted as x(T). T is the temperature of the sample and x is the interface position related to an imaginary axis on the surface of the sample.

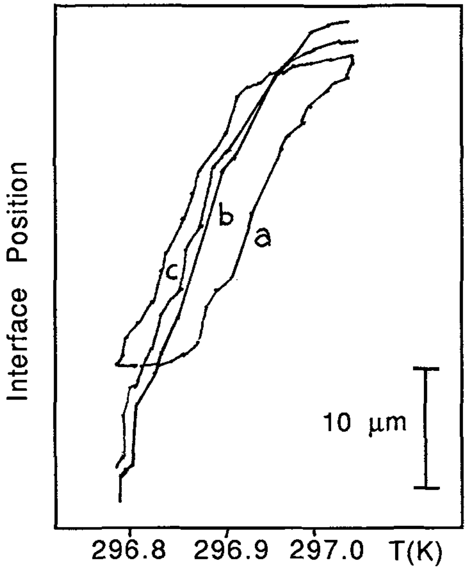

Figure 1. a) hysteresis cycle when a cooling rate $\dot{T}$= 0.2 K/min was used; b and c) cooling branches using $\dot{T}$= 0.02 K/min and $\dot{T}$= 0.002 K/min.

$T_g(x)$ will be the temperature at which the slice between x and x+dx transforms to martensite. In Figure 1, it is shown the hysteresis cycle for a TT1 thermal treated sample (alloy 1). The presence of a finite slope is apparent: an undercooling/overheating is needed to force the forward/reverse transformation. In figure 1, it is also shown the forward transformation of the same sample using slower cooling rates.

This undercooling (or overheating) needed to induce the continuous growth of the plate can be measured from the mean slope of the cycle as $\mu_{th} = dT_g/dx$. Samples of alloys 1 and 2 were subjected to thermal treatments TT1 and TT2 [9]. The slopes of the hysteresis cycles between similar samples showed a scatter up to a factor of two. Nevertheless, a systematic difference was observed between TT1 and TT2 thermally treated alloys. For TT1 treated materials we found: μ_{th}= 0.005 K/μm, whilst, for TT2 treated materials we found: μ_{th}= 0.05 K/μm.

B) The second β-phase.

Figure 2 shows schematically the experiment with which the second β-phase was obtained from a single-crystal of martensite. At the beginning (fig 2a) a small plate of martensite was present in the sample. Cooling carefully, the interfaces were forced to move until one side of the sample was completly transformed into martensite (fig 2b). Before the interface on the left could reach

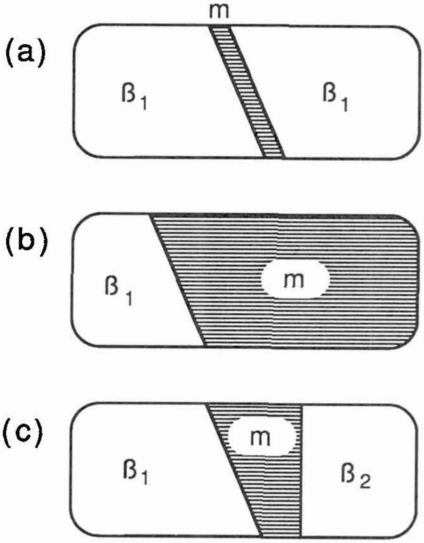

Figure 2. Appearence of the second β-phase from a martensite single-crystal (see text for details).

the other end, the sample was heated up. In figure 2c, a new interface had appeared. This was cycled, showing the same characteristics, slope and hysteresis, than the interface on the left. It was assumed that the new interface was the trace of the habit plane between martensite and the second β variant. Therefore, the label β_2 has been used for it.

Macroscopically, the right side of the sample was rotated. The sample surface direction **s** and the tensil axis **t** were determined by the back Laue X-ray diffraction technique. On the cubic basis of the β-phase (this is the basis used troughout this text) one have: **s**= (0.215, 0.000, 0.976) and **t**=(0.42, 0.93, -0.14). As the initial plate was obtained by slightly stressing the sample, the initial martensite plate was deduced to have the habit plane: $\mathbf{hp}_1$= (0.156, 0.726, 0.670).

The angle between the interface β_1-m and m-β_2 was measured to be 21.5° ± 1.0°. The angle between the interface β_1-m and the edge of the sample (**t**) was measured to be 64°.

3.- Discussion

The intrinsic thermoelasticity means that the single-interface transformation does not progress at a constant temperature but a continuous undercooling is needed, which provide an increasing driving force. This phenomenon can be explained as produced by the interaction of the transformation with dislocations existing in the material [9]. More specifically, it is due to the dragging and progressive formation of stacking faults because of the loss of translation symmetry of the dislocations Burgers vectors when absorbed by the martensite.

In a global transformation the intrinsic thermoelasticity is hindered by other contributions such as intervariant interactions, which are stronger than martensite-dislocation interactions. Nevertheless, the intrinsic thermoelasticity could be important in determining the number and size of the variants, which in turn determine the hysteresis width and the evolution of the hysteretic behaviour on cycling [10]. In this respect, the density of dislocations is an important parameter which depends strongly in the way the specimen was prepared by the various thermomecanical treatments commonly used. For example, the density of dislocations is higher after quenching in ice water, which is a necessary procedure for those alloys close to the α or γ region in order to avoid precipitation.

The symmetry operation relating the two β-variants compatible with a martensite single-crystal are C_2, a rotation around the two-fold b-axis, or σ, a mirror plane perpendicular to the b-axis in the orthorhombic unit cell of the 18R structure [4]. The crystallographic characteristics of the double transformation β_1-m-β_2 can be calculated [11] using the phenomenological theory [12]. The habit plane m-β_2 is calculated to be (-0.124, -0.578, 0.806). Hence, the angle between the interfaces should be 19.9° ± 2° in agreement with the observed value. Moreover, the angle between the interface β_1-m and the tensil axis should be 65.3° The lattices of the two β-phases are rotated, the axis and rotation angle being: (0.978, -0.210, 0.000), $\theta = 11.7°$. The results obtained from the phenomenological theory agree with the observed characteristics of the transformed material.

We suggested [11] that the appearance of the first or second variant of β depends on nucleation. In a multivariant transformation the β_1 is the only orientation compatible with the superimposition summetry group of any set of martensite variants [5]. When the martensite single-crystal is obtained through different plates of the same variant planar defects appear where the plates join each other. It was frecuently observed that the β_1 grows from these joinning interfaces [13] which serve as preferential nucleation sites. The β_1 variant can also nucleate inside a single martensite plate as it was recently observed [14]. All these observations show that the β_1 phase can be nucleated in any configuration of martensite variants and plates from multivariants to single-plate. This is the reason why the shape memory effect is always observed.

However, when the material has transformed to an extended single martensite plate without vestiges of the β_1, there is not reason for the preferential nucleation of the original parent phase. In this special case the β_2 would have a chance to appear as it is indeed observed. It should be emphasized the critical experimental conditions for this phenomenon to be observed. The control of the specimen temperature should be better than 0.01 K. The sample should be as free of dislocations as possible in order to reduce the intrinsic thermoelasticity, thus favouring the growth of a large unique martensite plate which is a necessary condition.

We have presented two phenomena associated to the martensitic transformation that can only be observed if the temperature during the experiment is rigorously controlled. Despite one of them, the intrinsic thermoelasticity, does not appear macroscopicaly clear due to stronger effects as intervariant interactions, it seems to be very important. The interaction of martensite and dislocations which gives rise to it, determines the morphology of the transformation and thereby the macroscopic thermoelastic behaviour and evolution with cycling. On the other hand, the actual possibility to get a second β-variant is a data which would have to be taken into account when working with single martensite plates.

Aknowledgements

Research made by CICYT PPA 86-0079 and CICYT MAT89-0407-C03 contracts. F.C.L. acknowledges the DGICYT, DGU (Catalonia) and CEE (Third Countries Program) for financial aid. A.A. acknowledges the DGICYT of Spain for the grant of a fellowship (PFPI program).

References

/1/ OLSON, G.A. and COHEN, M. Scripta metall. **91** (1975) 1247.
/2/ SALZBRENNER, R.J. and COHEN, M. Acta metall. **27** (1979) 739.
/3/ AMENGUAL, A. , MAÑOSA, Ll., MARCO, F., PICORNELL, C., SEGUI, C. and TORRA, V. Thermochim. Acta, **116** (1982) 195. PICORNELL, C., SEGUI, C., TORRA, V., LOVEY, F.C. and RAPACIOLI, R. Thermochim. Acta, **113** (1987) 171
/4/ TAS, H., DELAEY, L. and DERUYTTERE, A. Metall. Trans., **4** (1973) 2833.
/5/ PORTIER, R., and GRATIAS, D., J. Physique, **43** (1982) C4-17.
/6/ DELAEY, L., CHANDRASEKARAN, M., ANDRADE, M. and Van HUMBEECK, J. Proc. Int. Conf. Solid to Solid Phase Transformations, 1981 New York, American Insitute of Mining, Metallurgical and Petroleum Enginers (1982) 1429.
/7/ LOVEY, F.C., Van TANDELOO, B., Van LANDUYT, J., DELAEY, L. and AMELINCKX, S. Phys. Stat. Sol. (a), **86** (1984) 553.
/8/ AMENGUAL, A. and TORRA, V. J. Phys. E: Sci. Instrum, **22** (1989) 433.
/9/ LOVEY, F.C., AMENGUAL, A., TORRA , V. and AHLERS, M. Phil. Mag. A, **61**, (1990) 159.
/10/ PONS, J. , LOVEY, F.C. and CESARI, E. Acta Metall. et Mat., **38** (1990) 2733.
/11/ LOVEY, F.C., AMENGUAL, A. and TORRA, V. "Experimental and crystallographic evidence for the growth of two equivalent β-variants from one single martensite plate in a Cu-Zn-Al single crystal", Phil. Mag. A. (In Press)
/12/ WECHSLER, M. S. , LIEBERMANN, D.S. and READ, T.A. , Trans. AIME **197** (1953) 1503.
/13/ AMENGUAL, A. and TORRA, V. Unpublished (1989)
/14/ TORRA, V., ISALGUE, A. and LOVEY, F.C. To be published.