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AUTOMATIC EQUIPMENT WITH IMPROVED PERFORMANCES (ATD AND DSC) IN SHAPE MEMORY ALLOYS STUDIES

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We describe an experimental set-up of high resolution thermal analysis (HRTA) activated by Peltier effect and computer-controlled by the signal processing that allows a high resolution programming of the temperature and a reproducibility better than ± 0.01 deg.

The basic equipment is suitable for studying the behaviour of the shape memory alloys (i.e. Cu based alloys). We also describe the applications of the system, which allows to build up a calorimetric system (heat flux or conduction calorimetry) (resolution 1.5 μW) or a stress-strain-temperature system of 20 N of maximum charge (resolution around 1 mN and 0.1 μm.

Keywords: shape memory alloys

Introduction

The traditional instruments in Material Sciences allow us to determine the structure, the composition and, if required, the evolution of the sample. As a general rule, materials (and their uses) are not found in the thermodynamic equilibrium, usually a 'frozen' and unchangeable state is required. The situation of the shape memory alloys is quite different. To exploit their potential for robotical appliances it is necessary to maintain the coexistence of the two phases present and, only by the influence of the external fields, to change the relative quantity of one phase to the other. In this way, a radical change of the stress and/or the associated strain can be achieved [1].

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The study of the material shows that it is remarkably affected by the external forces and that its evolution is related to changes in atomic order because of diffusive processes in atoms and vacancies. It is obvious that to assure a high predictability it is necessary for the alloy not to spontaneously change by itself and it is also necessary that the processes of transformation and re-transformation are clearly described and fitted by a representative model. To achieve this, the equipment used for the analysis of the phenomenological behaviour of the transformation has to have the required resolution to sort out the different phenomena that take place simultaneously [1–4].

Previous measurements have shown that in order to study the elementary processes in the martensitic transformation – growth or shrinkage of one or a few martensite plates – and in order to describe the macroscopic processes it is necessary to have a resolution and control of temperature that conventional equipment lacks [5].

In this paper we introduce the High Resolution Thermal Analysis (HRTA) equipment and the related systems [6–8] used for the study of shape memory alloys (Cu–Zn–Al). The study of the material is done from two complementary points of view. On one hand the single interface or single martensite domain transformation of which we analyse the growing shrinking of one martensite plate. This allows us to obtain the elementary behaviour of the movements in the interfaces. On the other hand we analyse the more complex situations linked to the movements and to the nucleations of one or more isolated or interacting plates. In this second group we include the processes linked to the spontaneous transformations induced by temperature.

The observation corresponding to the first group are the ones we can achieve with the HRTA equipment and partly with the traction-strain-temperature system. The observations for the second group are done with calorimetric measurements. We describe in particular the outline of the algorithms used to achieve a resolution in temperature higher than $\pm$ 0.01 deg and the structure of the system necessary to reach a predictive description of the behaviour of the alloy. This resolution is necessary for taking calorimetric measures and for the local study of the state surface in coordinates stress (α), strain (ε) and temperature (T).

Experimental set up, performances and auxiliary equipment

The working space of the HRTA equipment is shown on Fig. 1. The system (computer-controlled) is based on Peltier effect and the measuring of temperature with the help of a Pt-100 resistance. The DC intensity $I(t)$ is related to the temperature – measured by the Pt-100 directly in Ω – through a semiquantitative

approximation. This approximation can be obtained from the linear systems equations via the extended RC models. A preliminary approximation of the direct relation between the intensity current and the temperature of the working space reads

$$I(t) - I_r = \frac{1}{S(x)}\left[\frac{dx}{dt}\cdot\tau + x\right]; \quad x = R(t) - R_r \tag{1}$$

R_r is the reference resistance and I_r the associated DC intensity. Usually R_r is related to the temperature of the external thermostat and in this case the I_r is practically zero. $S(x)$ is the sensitivity of the system and its dependency on x is approximately linear. R is the resistance measured for the instant t.

The system has an adapted software that help to automatically take some calibrating measurements and so to obtain an approximation of $S(x)$ for each temperature of the room thermostat. The use of Pade approximants is especially illustrative. In this way $S(x)$ reads

$$S(x) = [M, N] = P(x) / Q(x)$$

where $P(x)$ and $Q(x)$ are polynomials of grade M and N respectively. The study of the experimental curves establishes that a [1, 3] Pade is sufficient. The group of programs can give an approximation to the value of τ and, if necessary, more sophisticated approximations can be used.

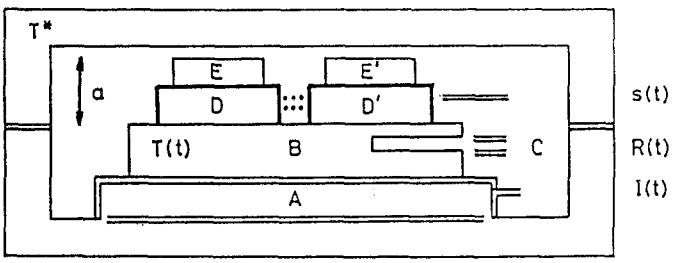

Fig. 1 High resolution thermal analysis (HRTA), CTT-UPC patent; T^* temperature of the external thermostat (thermal bath); A Peltier effect plate powered by a variable current intensity, and controlled $I(t)$; B working area made up of a copper plate at temperature $T(t)$ (working space); C resistance Pt-100; a calorimetric system situated in the working space and operating at temperature $T(t)$; D and D' calorimetric thermobatteries; E and E' sample and reference

The measurements use a predictor-corrector temperature control system. A computer measures the temperature of the working space (Cu-working plate) to 0.001 Ω by the Pt-100 platinum resistance, and gives current to a Peltier element (Dr. NEUMANN PELTIER-TECHNIK) in order to follow the desired tempera-

ture programmation (see Fig. 2). A preliminary programming of the DC current in open loop is achieved through the Eq. 1 from the desired temperature profile. Afterwards, the continuous comparison of the experimental values of the actual resistance with the ones set in the program introduce a predictive correction of the DC current (a feedback loop) using the expression 1 to achieve the desired value. The working space is used to observe (by direct thermomicroscopy) the behaviour of the material under temperature programming or the evolution of the electrical resistance of the sample.

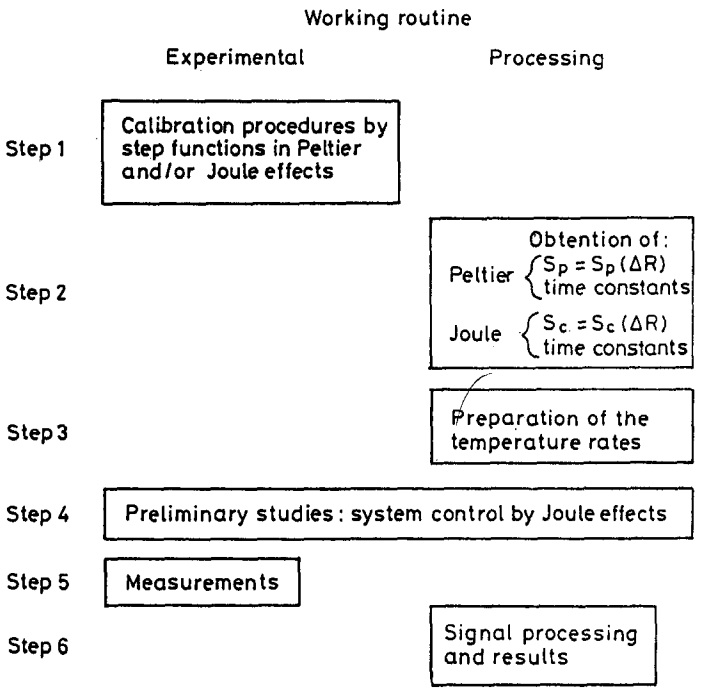

Fig. 2 Flow diagram for the calorimetric routines. Using only the High Resolution Thermal Analysis eliminates the unnecessary steps (Joule effect studies and so on). Using stress-strain-temperature equipment stiffness estimation implies supplementary steps

A heat flux or conduction calorimetric system is set putting two thermobatteries over the thermocontrolled plate [6, 8]. The operative diagram is shown on Fig. 2. In this case the effect of the intensity corrections introduces some causal deviations that can be suppressed with the adequate calibration and numeric processing. The mechanism set inside a sheath made of brass is submerged in a thermostatic bath (LAUDA RL6) so that the temperature T_r can be set below the room temperature. The working temperature $T(t)$ can be pro-

grammed using a reference temperature T_r, inside a domain of 80 deg with a certain asymmetry (T_r–25 deg < $T(t)$ < T_r+55 deg). The kind of the thermobatteries used (MELCOR) make it impossible to use the system in a temperature over 80°C but they have a high sensitivity (around 600 $mV \cdot W^{-1}$ at room temperature). The use of Dr. Newman's thermobatteries allows the temperature to rise to 110°C.

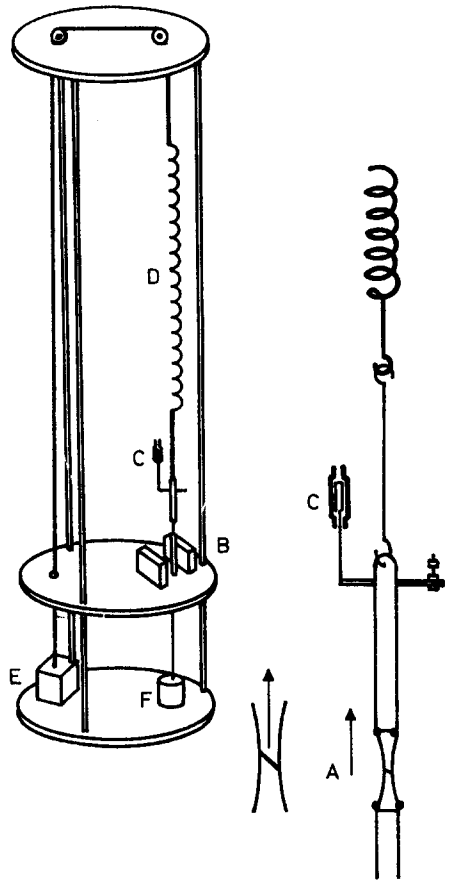

Fig. 3 Schematic representation of the stress-strain-temperature measuring system: A sample; B temperature controlled plates (section); C LVDT displacement transducer; D spring; E stepper motor; F load cell

Introducing a traction system we can measure the relevant coordinates of the material and analyse its behaviour in stress-strain-temperature state surface (see Fig. 3). The HRTA equipment is used to control the temperature. Two twin plates that surround the sample make sure that the temperature value is correct.

In the system, a computer controls the temperature of two plates surrounding the sample to ±0.003 deg, following the procedure indicated above.

The computer controls also a stepper motor which, through a spring (near 2 $N \cdot cm^{-1}$ from LUSAI – Spain), applies tensile force to the sample. Force is acquired by the computer from a load cell (U1 and MVD2405A from HBM – FRG). Displacements are detected via an inductive sensor (W1E and MC2A from HBM – FRG). The obtained resolution and reproducibility are, in force, 1 mN for a maximum load of 20 N, which corresponds to one step of the motor. In displacement, resolution is 0.1 μm and reproducibility is better than 0.2 μm at constant temperature. It decays to 0.4 micrometer when temperature is also changed.

As the sample itself does not touch the temperature controlled plates some time is needed to achieve the final temperature after the control in the plates has reached it. For temperature changes of 2.5 deg, in 500 s the temperature of the sample is within 0.005 deg of the final value. To smooth the room temperature fluctuations the whole system is inside a metal sheath with an additional layer made of rubber foam. Inside, it has a circulating liquid controlled by an exterior thermostat LAUDA RM6.

The digitalization of the analogical outputs of the different sensors is done through Hewlett-Packard voltmeters HP 3478A that allow a resolution of 0.001 Ω in the measurements for the resistance and for the tension associated to the other parameters there is a resolution of 100 nV (DC). When using them as amperometers the maximum current measurable available is ±3 A (full scale), sufficient for the control of the Peltier effect.

The computer (PC-XT or AT-286 or similar) has a board (bus IEEE-488) to control the voltmeters HP. The DC current control is done through an interface ADDA-14 (14 bits digital analogic converter) that activates a power source (DC current) PREMIUM SR-120 with the help of a tension divider. The switching of the electrical current (to achieve heating or cooling) is done with the help of the switches activated from a board PC Industrial I/O card FPC-046. In the stress-strain system, the stepper motor (Charly Robot France) is activated through RS-232 interface. The programs for measuring and analysing data are written in Microsoft ASSEMBLER and QUICK-BASIC languages.

Results

The observation of the growing and shrinking of a plate of martensite has established the existence of an intrinsic thermoelasticity [9, 10]. It has visualised the effects of the processes of nucleation, of the "secular" evolutions of the

transformation temperatures in the bulk sample and the locally deviating effects linked to the movement of the interfaces. This observation is essential to reach a successful pattern of the behaviour of the alloy.

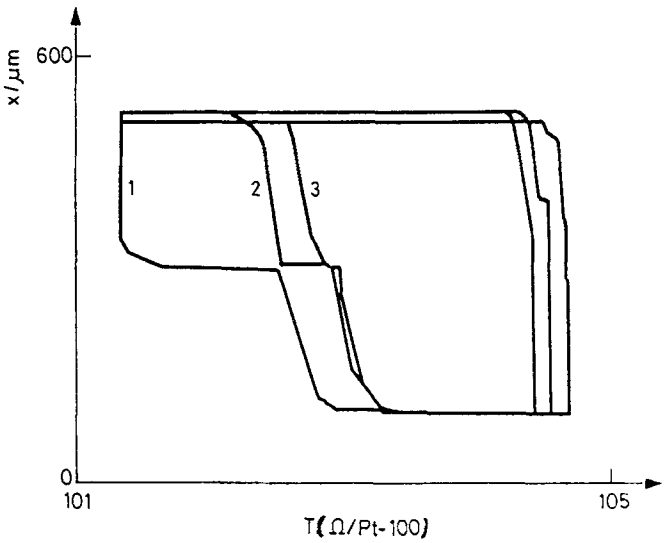

Fig. 4 Change of hysteresis width with cycle number (sample: Cu-Zn-Al with γ precipitates). Single plate width (x) growing-shrinking temperature induced process: 1) first transformation; 2) second cycle; 3) third cycle

The HRTA linked to described experimental systems allows for a great resolution, in general, superior to the direct possibilities of the crystallographic techniques. For example, in Fig. 4 a radical change of the hysteresis loop from the first interface-pass to the following cycles can be observed. In this case we are looking at the growing-shrinking of a martensite plate under the action of a temperature evolution. The material (Cu–Zn–Al) has γ precipitates with a diameter close to 100 Å. The interface position, done with an Olympus BH2-UMA microscope and a Sony EVC-X10 video camera are digitalised from the videomagnetic tape. The direct observation of the related minor changes in the precipitates through Transmission Electron Microscopy (TEM) is extremely difficult.

In Fig. 5 we can see a serie of calorimetric cycles for an air-quenched sample. The signal processing of the thermograms produces the hysteresis loops and analyses their evolution depending on the number of cycles. The thermograms

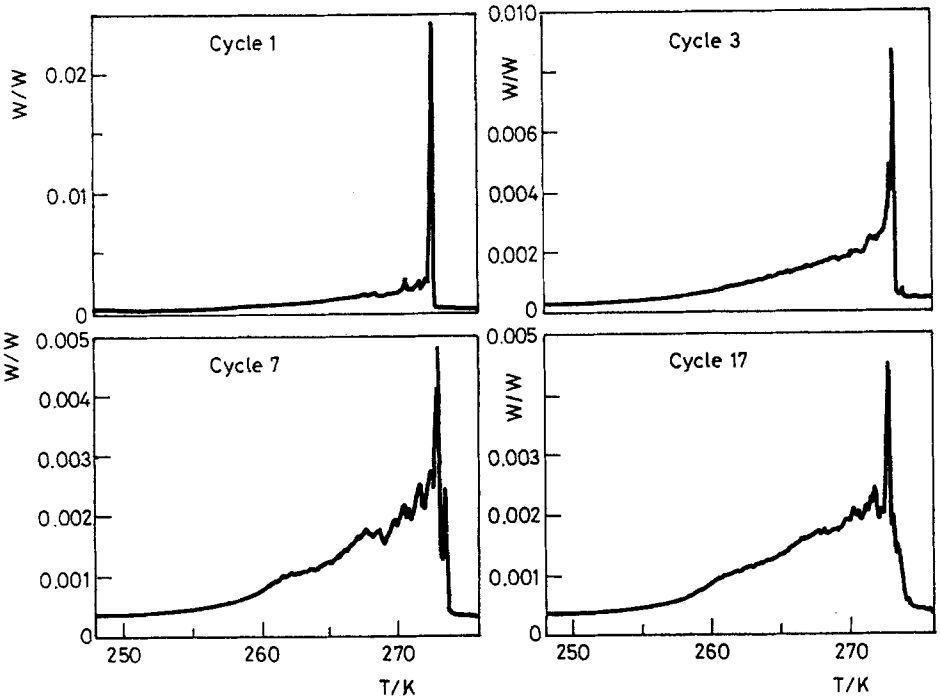

Fig. 5 Calorimetric cycles for an air-quenched sample; heat rate in Watt *vs.* temperature

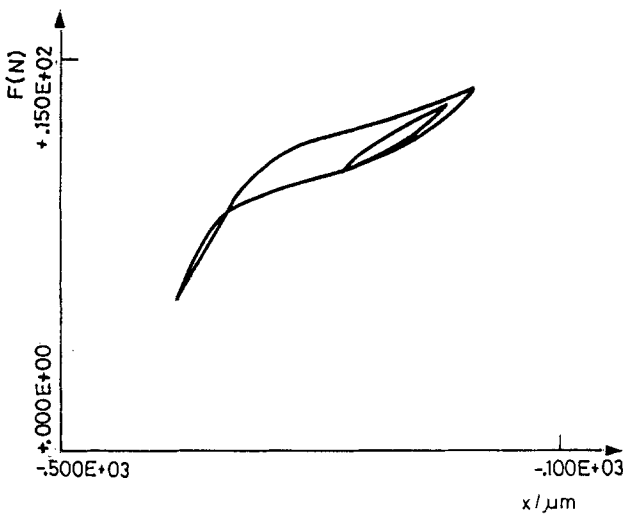

Fig. 6 Partial cycles: force (in N) *vs.* displacement (in µm) for a water-quenched sample

show progressive changes in the cycling that are coherent with the appearance of dislocations.

In Fig. 6 we can see a consecutive series of partial cycles of stress-strain with constant temperature in the area of coexistence of the two phases. Consecutive curves have a ± 1 mN and ± 0.2 μm reproducibility. In this case the alloy was water-quenched, left to age at room temperature for 3 months, and it has been repeatedly – but gently – cycled (near of 500 cycles).

The Figs 4, 5 and 6 show some remarkable changes in the behaviour of the material, and as a result of that, structural changes. In Fig. 4 the interaction of the interface with the precipitates changes the width of the hysteresis loop. Figure 5 shows a progressive evolution of the material with the cycling that brings about dislocations. In Fig. 6 we can see a repetitive cycling of the alloy that consequently is probably predictable.

Conclusions

The introduction of automatised equipment of thermal analysis of high resolution (HRTA) allows an accurate treatment of the behaviour of the alloys with memory (Cu-Zn-Al) and visualises the process of transformation with a high performance.

The basis system allows to develop a group of instruments of high resolution, in particular an automatised heat flux or conduction calorimeter and a set-up for analysis of stress-strain-temperature behaviour. The results show that high resolution allows to separate the different effects that take place in alloys. The instrumental technique allows to detect minor changes in the structure of the material. For example the changes in the hysteretic loop caused by dislocations or the ones associated with the interaction of the precipitates with the interfaces are easily detected, and the same happens with the conditions that allow a reproducible behaviour.

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Zusammenfassung — Es wird ein Versuchsaufbau unter Ausnutzung des Peltier-Effektes und eines Computers für die hochauflösende Thermoanalyse (HRTA) beschrieben. Die Signalverarbeitung erlaubt eine hochauflösende Programmierung der Temperatur und eine Reproduzierbarkeit besser als ± 0.01 K.

Das Grundgerät eignet sich zur Untersuchung des Verhaltens von Legierungen mit Formerin-nerungsvermögen (z.B. Legierungen auf Kupferbasis). Auch die Anwendungen des Systemes werden beschrieben, was den Aufbau einer kalorimetrischen Anlage (Wärmefluß- oder Leitfähigkeitskalorimetrie mit einer Auflösung von 1.5 μW) oder einer Zug-Dehnungstemperatur-Anlage mit 20 N Höchstlast (Auflösung bei 1 mN und 0.1 μm) ermöglicht.