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# Study of reorientation of martensite variants under stress in Ti-Ni-Cu by resistivity and by thermoelectric power techniques

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**Abstract:** It is well known that the martensitic phase of shape memory alloys presents a self-accommodation of variants when it is obtained by simple cooling. Theses variants can be reoriented in a new configuration by applying a stress on the material. Macroscopic properties like, electrical and mechanical ones, are very sensitive to this phenomenon. Moreover, it has been proved that thermoelectric power (TEP) is a powerful technique to characterize isotropic properties. In this work, thermoelectric power under stress has been used to study the evolution of the reorientation of variants in a shape memory alloy. The obtained results are compared with those of mechanical and electrical tests.

## 1. INTRODUCTION

Shape Memory Alloys (SMA) presents a memory effect (ME) which is due to the martensitic transformation. This transformation takes place when the alloy is cooled from a higher temperature phase called parent phase or austenite (β). The transformation occurs without diffusion and corresponds principally to an homogenous shear strain. During cooling of a single austenite crystal, there are several possibilities of martensite orientation, called variants. Without stressing the sample, all the variants have the same possibility to grow and self-accommodation occurs. Their shape strain compensate each other and thus, the macroscopic shape change is nearly zero. But, if some stress is applied under the sample in the martensitic phase, there will be a variant growth towards the most favorable configuration in the stress direction namely, variant reorientation, causing an important macroscopic shape change (strain ε) [1-3].

One-Way Shape-Memory effects (OWME) happens when the reoriented martensite is heated towards the parent phase. During the inverse martensitic transformation, the sample is regenerated to the initial crystal and shape. If the sample is thermally cycled with stress, some variants grow preferentially to others : a deformation occurs during the martensitic transformation. This transformation is called Assisted Two Way Memory Effect (ATWME). During thermal cycles under stress (called training), internal stresses appear inside the material. These internal stresses can be sufficient to orient the variants during the cooling, even without applied external stress. This effect is called a Two Way Memory Effect (TWME). In a polycrystal, the same phenomena occurs in each single crystal, however the strain is limited by the strain compatibility at the grain boundaries and the TWME is smaller [4]. In this paper, the reorientation of the martensitic variants under stress has been studied by comparing thermomechanical results with electrical resistance and thermoelectric power measurements.

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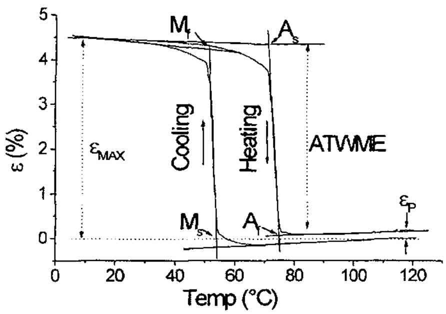
## 2. EXPERIMENTATION

### 2.1 The sample

The nominal composition (%at) is 50Ti-45Ni-5Cu. The sample has been received in form of wire with 0.5 mm of diameter. Initial treatment made by the manufacturer is : 35 % strain by cold drawing and 600 K during 1 hour. Transformation temperatures are : $M_s = 312$, $M_f = 301$, $A_s = 319$ and $A_f = 330$ K.

### 2.2 Thermomechanical and electrical resistivity measurements

For thermomechanical tests, a constant strength was applied on the shape memory wires. Strain measurements were realized with a LVDT captor and the sample was immersed in a temperature regulated oil bath. Electrical resistance was measured by the four wires method. This equipment has been already described in [5]. Figure (1) describes the evolution of $\varepsilon$ and $\Delta\rho/\rho_0$ vs. temperature obtained by this equipment. In (a) ATWME corresponds to the difference between the high temperature and martensitic shapes. $\varepsilon_p$ corresponds to the variation of the high temperature shape. In (b) $\Delta\rho/\rho_0 = (\rho-\rho_0)/\rho_0$ where $\rho_0$ is the resistivity of the initial high temperature phase and $\rho$ the resistivity of martensitic phase. Resistivity variations are calculated from resistance and strain measurements supposing insignificant the volume change due to the martensitic transformation : $\Delta\rho/\rho_0 = \Delta R/R_0 - 2\varepsilon$ [6].



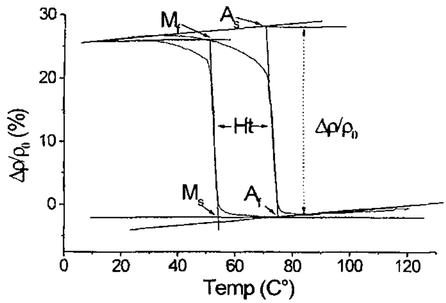




Figure [1] (a) and (b) show $\varepsilon$ (%) and $\Delta\rho/\rho_0$ vs. temperature respectively, $\sigma = 200$ MPa.

### 2.3 Thermoelectrical power

When a closed circuit is made of two dissimilar metals in which the two junctions are maintained at different temperatures a current is generated and the thermoelectricity phenomenon is created, called also the Seebeck effect. Today the Seebeck effect is usually envisaged like an open circuit, such as that shown in Figure 2. The voltage $\Delta V=V_b-V_a$ is the thermoelectric voltage developed by this couple, $\Delta T=T_2-T_1$ (about 10K) is the difference of temperatures of the two TEP block surfaces in contact with the wire. The thermoelectric power of the couple is defined by the equation 1 [11-12]. ThermoElectric Power (TEP) is a transport technique simple to use, and it have proved to be sensitive to isotropic properties. In addition, TEP values are directly obtained independently of sample shape and dimensions. TEP has been used in martensitic alloys to measure martensite stabilization, cold work and alloy concentration [12-14].

$$S_{WA} = \lim_{\Delta T \to 0} \left( \frac{\Delta V}{\Delta T} \right) \qquad (1)$$

A mechanical apparatus has been constructed to apply the stress in the TEP machine. The wire is tied in both ends by screws, so this one remains straight. A spring with a K= 9 N/mm is used to exert the strength on the wire. One end of the wire has to be electrically and thermally isolated to avoid heat lost and bad electrical contact in the TEP machine. The apparatus is placed in the TEP blocks and measurements can be taken at different stresses when the spring is compressed, as in Figure 2.

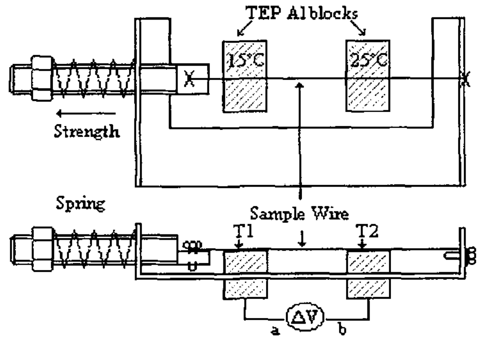



Figure 2. Apparatus to measure the TEP with in-situ stressing the sample.

### 2.4 Strain Test

$\varepsilon$, $\Delta\rho/\rho_0$ and TEP measurements were done on another sample at room temperature (< $A_s$), loading and unloading the sample, at different stresses, as shows figure 3 (a). The former test was done to estimate the strain behavior of the alloy at martensitic state.

### 2.5 TEP thermomechanical cycling

The TEP measurements were done at room temperature between thermomechanical cycles at constant stress $\sigma$ (from 0 to 225 MPa) as shown in Figure 3 (b).

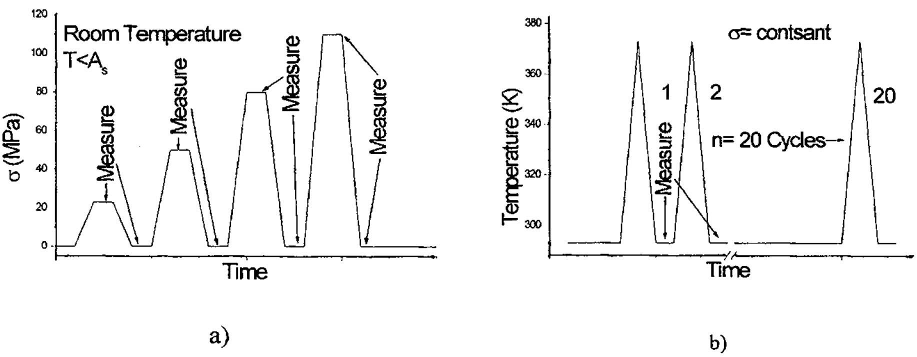
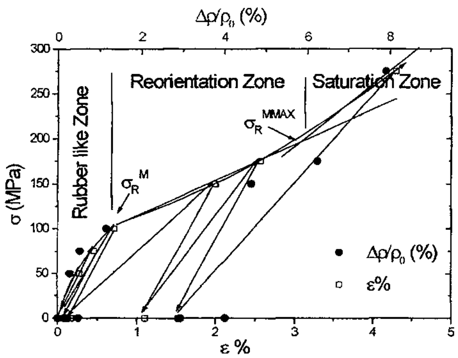



Figure 3. (a) Strain Test. (b) Way to measure TEP during thermomechanical cycling

## 3. RESULTS AND DISCCUSION

### 3.1 Strain Test

The strain test is represented by figure 4, which shows the evolution of $\varepsilon$, $\Delta\rho/\rho_0$ and TEP vs. $\sigma$. In (a) for values smaller than 100 MPa, $\varepsilon$ and $\Delta\rho/\rho_0$ increase slowly and when stress is taken off, $\varepsilon$ gets back to the initial state, this is known as rubber like effect [16]. Once $\sigma$ is higher than 100 MPa, $\varepsilon$ and $\Delta\rho/\rho_0$ increase more rapidly and the initial state is no more recoverable when $\sigma$ is taken off, this is due to the variant reorientation. The variant reorientation is a limited phenomenon so, once all the variants are reoriented a Saturation Zone is expected, for the present case it is reached approximately at 200 MPa ($\sigma_R^{MMax}$). In this Zone, $\varepsilon$ and $\Delta\rho/\rho_0$ growth is due to plastic strain. So three Zone are observed in figure 4 (a), a Rubber like, Reorientation and Saturation Zone respectively. In 4 (b) TEP measurements decreases with the applied stress but it follows a similar behavior as $\varepsilon$ and $\Delta\rho/\rho_0$. The Saturation Zone is not reached because of equipment limitation. As a first observation of these results, TEP has followed the stress-strain behavior of an AMF.



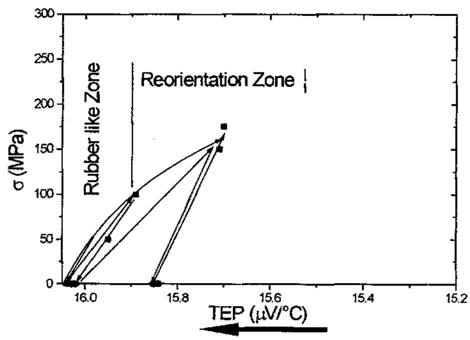




Fig 4. (a) Strain test, $\sigma$ vs. $\varepsilon$ and $\Delta\rho/\rho_0$ loading and unloading the sample. (b) the same for TEP.

### 3.2 Thermomechanical cycling

Figure 5 shows the evolution of ATWME, $\varepsilon_P$, $\Delta\rho/\rho_0$ and TEP at different stresses and cycle numbers. In 5 (a), ATWME for cycle 1 and 20 grows with $\sigma$ in a linearly way from 0 to 100 MPa approximately. Above 100 MPa ATWME increases but no more linearly is observed and it stops growing at 200 MPa (Saturation is reached). This result is the same obtained by the Strain Test (figure 4 (a)). With training from cycle 1 to 20, a little ATWME increase is observed from 0 to 200 MPa and above 200 MPa ATWME decreases. The 1 % of ATWME at 0 MPa is due to a wire education done by the processes of drawing, i.e., drawing is enough to orient variants during cooling. The curve of $\Delta\rho/\rho_0$ and TEP vs. $\sigma$ are given by figure 5 (b) and (c) respectively. $\Delta\rho/\rho_0$ presents the same evolution than ATWME for cycle 1 and 20. TEP measurements have the same behavior with stressing the sample but seem also to be affected by the number of cycle.

Figure 5 (a) shows also the evolution of plastic strain ($\varepsilon_p$) vs. $\sigma$ and cycle number. Above 125 MPa, $\varepsilon_P$ increases with cycling and $\sigma$. Below 125 MPa, $\varepsilon_P$ increases only with cycling. The $\varepsilon_P$ is a plastic strain of the sample due to the formation of dislocations during thermomechanical cycling. Whereas the ATWME, corresponds to the variant reorientation during thermomechanical cycling. In this work, we have tried to find a correlation between $\Delta\rho/\rho_0$ and TEP measurements with those of reorientation variants (ATWME) and $\varepsilon_P$. On figure 5 (d), $\Delta\rho/\rho_0$ vs. ATWME measurements for cycle 1 and 20 are reported. It can be seen that all these measurements are in a straight line, so $\Delta\rho/\rho_0$ is directly function of ATWME, then of reorientation variants. Figure 5 (e) and (f) show TEP measurements vs. ATWME and $\varepsilon_P$ respectively. In both figures, several linear relationships are founded :

- When TEP is plotted vs. ATWME for cycle 1 and 20, a linear relationship is founded for each cycle number : which means that for a given thermal cycle, changes of TEP values due to stress are proportional to the amount of reoriented variants (ATWME).
- When TEP is plot vs. $\varepsilon_P$ at different stresses, three linear relationship or state are founded. An upper line at 0 MPa, a middle line at 50 MPa and a lower for 150 MPa and higher values. These three states are obtained because in the upper state at 0 MPa the reoriented variants which exist in the sample are only those reoriented by the wire drawing. In the middle state at 50 MPa there is an increase of reoriented variants but it is not so high because the applied stress is in the rubber like Zone. And after 150 MPa almost all the variant reorientation has taken place, so this is the lower state. But fort each of the three states, changes of TEP due to the number of cycles are proportional to $\varepsilon_P$ or to the amount of dislocations. From these results, it can be concluded that TEP depends of ATWME and $\varepsilon_P$. As a first approximation, TEP can be written :

$$TEP = \kappa \times ATWME + \phi \times \varepsilon_p$$

Where $\kappa$ and $\phi$ are the coefficient for each property.

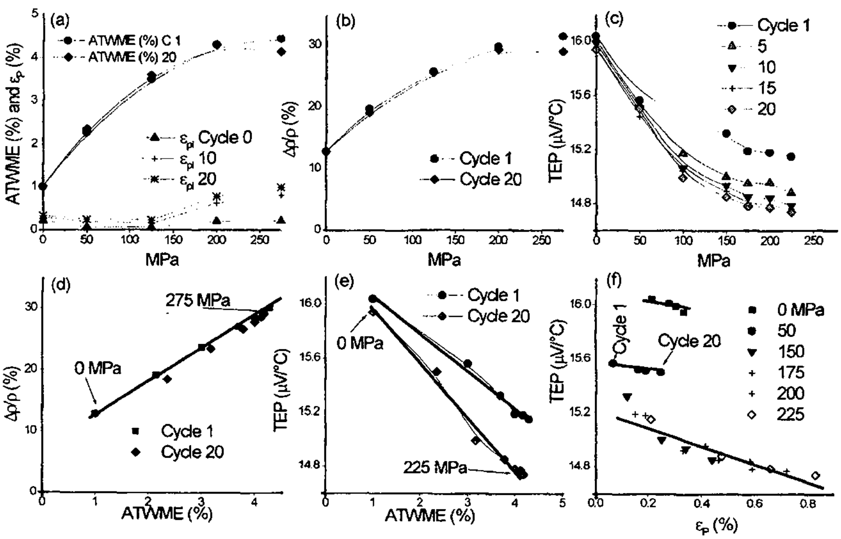



Figure 5. TWME, $\varepsilon_P$, $\Delta\rho/\rho_0$ and TEP measurements of TiNiCu alloy. (a) TWME, $\varepsilon_P$ vs. $\sigma$ at different number of cycles. (b) $\Delta\rho/\rho_0$ vs. $\sigma$. (c) TEP vs. $\sigma$. (d) $\Delta\rho/\rho_0$ vs. ATWME. (e) and (f) Relationship of TEP vs. ATWME and $\varepsilon_P$ respectively.

In addition, a sample had been recrystallised and its TEP in the martensitic phase is 18.2μV/°C. TEP of a cold-drawing sample is around 16 μV/°C. This difference shows that TEP has detected the reoriented variants induced by drawing, because a decrease in TEP by increasing the stress for this alloy means variant reorientation. This could be confirmed by the 1% of EMDSA at 0 MPa reported in figure 4 (a). For a recrystallised sample 0% of EMDSA and the augmentation of TEP are expected because a self accommodation of variants has take place and no more reoriented variants induced by drawing exist in the sample after recrystallisation.

## 4. CONCLUSIONS AND PERSPECTIVES

- Three different zones of the martensitic behavior are obtained from the stress-strain test, the Rubber like, Reorientation and Saturation Zone.
- Resistivity difference between the austenite and martensitic phase are only function of ATWME, then of the variant reorientation.
- Evolution of TEP seems to depend on variant reorientation (ATWME) and on the amount of dislocations (related to $\varepsilon_P$) created by thermomechanical cycling.
- New tests will be done with a recrystallised Ti-Ni-Cu alloy to know the effect of cold drawing on the sample and also with another SMA (Cu-Zn-Al).

**References**

[1] T Saburi and S Nenno, *The Shape Memory Effect and Related Phenomena*, Osaka University, Suita, Osaka, Japan. 1455-1479

[2] C M Wayman and T W Duerig, *An Introduction to Martensite and Shape Memory*, University of Illinois at Urbana-Champaign ,1990, 3-20

[3] AL Roytburd , Journal De Physique IV, V 5, Dec. 1995, C8-21

[4] G Guenin, Phase Transitions, 1989, Vol.14, 165-275

[5] C J De Araujo, M Morin, G Guénin, Materials Science and Engineering, A273-275 (1999), 305-309

[6] G Airoldi, T Ranucci, G Riva and A Sciacca, J Phys. : Condens. Matter 7, (1995), 3709-3720

[7] M Pozzi, G Airoldi, Materials Science and Engineering, A273-275 (1999) 300-304

[8] J Pons, M Masse, R Portier, Materials Sciences and Engineering, A273-275 (1999) 610-615

[9] Y Liu and P G McCormick, Acta metall. mater., Vol. 38, No. 7 , 1321-1326, 1990

[10] J Blatt, P A Schroeder, C L Foiles and D Greig, *Thermoelectric Power of Metals*, 1976 Plenum Press, NY, USA

[11] R D Barnard, *Thermoelectricity in Metals and Alloys*, 1972, Taylor & Francis LTD, London

[12] J M Pelletier, G Vigier and R Borrelly, Scripta Metallurgica, Vol. 16, 1343-1346, 1982

[13] L Cooreman, J Van Humbeeck and L Delaye, Acta metall. mater., Vol. 38, No. 12, 2663-2666, 1990

[14] J E Hanlon, S R Butler and R J Wasilewski, Transactions of the Metallurgical Society of AIME, Vol. 239, Sept. 1967, 1323-1327

[15] C. J de Araujo, *Thesis, Comportement cyclique de fils en alliage à mémoire de forme TiNiCu : analyse electro-thermomécanique, dégradation et fatigue par cyclage thermique sous contrainte, INSA de Lyon, France*, 1999

[16] Etienne Patoor and Marcel Berveiller, *Techologie des alliages à memoire de forme, Hermès, Paris*, 1994, 54-55.