

**EFFECTS OF COLD-ROLLING AND POST-DEFORMATION ANNEALING ON THE MARTENSITIC TRANSFORMATION OF A TiNi SHAPE MEMORY ALLOY**J.M. LEGRESY, B. PRANDI\*<sup>(1)</sup> and G.M. RAYNAUD*Centre de Recherches de Voreppe S.A., BP 27, F-38340 Voreppe, France**\*CEZUS, Centre de Recherches d'Ugine, BP 33, F-73400 Ugine, France***ABSTRACT**

The thermoelastic transformation of shape-memory titanium -nickel alloys is highly influenced by the microstructural state of the alloy and particularly by the plastic deformation of the metal.

In this study, the influence of cold-work and annealing on martensitic and austenitic transformations is performed with "in situ" thermoelectric power measurements during thermal cycling.

In the recrystallized state the transformations are very well defined, and the thermal hysteresis is generally less than 30 degrees. After work hardening the transformation becomes "diffuse" and is no longer observed if the deformation is greater than a critical value of approximately 25%.

The effects of post-deformation heat treatments were also characterized using a heavily cold-worked metal within a temperature range of 300-600°C.

Thermoelectric power measurements applied to the characterization of shape-memory alloy transformation proves to be a high performance tool displaying a great sensitivity to martensitic transformation.

**INTRODUCTION**

The characteristics of the thermoelastic transformations of shape memory alloys are highly influenced by cold work [1] [2] [3]. It usually shifts temperatures of the transformation and reduces the extent of phase transformation [4]. The shift, of  $M_s$  for example, is due to such defects as dislocations generated during cold working. These defects act in two ways : they promote the nucleation of martensite (raising  $M_s$ ), and they reduce the transformation rate acting as barriers for interphase boundaries motion [3]. The thermal hysteresis is consequently increased.

The purpose of this study is to measure the effect of cold rolling and post-deformation annealing treatments on the austenite (A) and martensite (M) transformations of an industrial TiNi alloy.

The temperatures at which the A and M transformations occur i.e.  $A_s$ ,  $A_f$  and  $M_s$ ,  $M_f$  were determined using thermoelectric power (T.E.P.) measurements performed during thermal cycling of the samples. The validity of this method was verified by comparison with more usual techniques such as differential calorimetry or direct measurements of shape memory deformation temperatures.

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## I. MATERIALS AND METHODS

A near equiatomic TiNi alloy of the composition listed in Table I was prepared by vacuum melting techniques and hot forged to  $5.3 \text{ mm}^2$  section recrystallised wire. Samples were then cold rolled to reductions listed in Table II.

The reduction is here defined as  $R = 1 - S/S_0$  where  $S$  and  $S_0$  represent the final and initial sections of the wire. The post deformation heat treatments were performed on the heavily cold rolled sample ( $R = 52\%$ ) for 15 mn at temperatures of 300°, 400, 500 and 600°C.

The principle of T.E.P measurements [6], [7] consists in generating a temperature difference ( $\Delta T$ ) between the two ends of a sample thus creating a voltage difference ( $\Delta V$ ) [6]. The T.E.P.,  $\Delta S$ , is defined as  $\Delta S = \Delta V/\Delta T$  (in V/K). It is a relative measure by reference to the material constituting of the connections between the sample and the voltage measurement device, in our case pure Al.

The T.E.P. is independant of the shape of the sample. For wires a few millimeters in diameter the measurements are possible without any preparation except for the contact areas. The experimental set-up is shown in Figure I. Electric heaters are placed at each end of the sample to ensure a constant  $\Delta T$  of about 13°C. The heaters are computer controlled to allow thermal cycling (heating and cooling) at 3°C/min.

The temperatures of the austenitic and martensitic transformations and the extent of reversible transformations are determined exactly as for resistivity measurements [1] [3]. The characteristic temperatures are defined by the first detectable deviations from the linear part of the curves (figure II). The extent of the transformation ( $H$  in Table III is measured by the difference in T.E.P. due to the transition, (i.e.  $\Delta S$  at  $A_s - \Delta S$  at  $A_f$ , Figure II).

The capability of the method to follow the reversible thermoelastic transformation has previously been mentioned [8]. A comparison with differential calorimetry and direct measurements of deformation due to shape memory effects [9] shows that the T.E.P. measurements yield equivalent results (within 5 to 6°C) but with much better accuracy and consistency.

Table I : Chemical composition of the TiNi alloy used in this study

Ti (wt %)	Ni (wt %)	O (ppm)	C (ppm)	N (ppm)	H (ppm)
44.8	55.1	1500	97	47	7

## II. RESULTS AND DISCUSSION

### II.1 Cold worked samples

Figure II shows the TEP vs temperature curves for the annealed sample and for four deformed states (7, 9, 13, 18 % reduction). In the annealed state the transformations are sharp with a thermal hysteresis of 30°C. On cooling, a small peak located at a temperature of about 40°C may indicate a premartensitic effect [10].

Samples rolled at reductions up to 18 % undergo more and more diffuse transformations with increasing deformation and above 18 % no transformation is detectable. The  $M_f$  and  $A_f$  temperatures are respectively decreased and increased by the reduction (Figure III, Table III), thereby increasing the thermal hysteresis. The  $A_s$  and  $M_s$  temperatures are also decreased by deformation

but in much smaller proportions. There are no detectable premartensitic effects with deformed samples as noted by [11] in NiTiCu alloys. The relative amount of reversible martensite (Table III, Figure IV) decreases with deformation as shown by the relative decrease of the TEP variations during the transformations. Figures III and IV show drastic modifications of the reversible transformation in a narrow domain of deformations ranging from 7 to 9 % of reduction.

We attribute the drop in the transformation extent to the formation of irreversible austenite as previously observed [4]. This conclusion is supported by the behaviour of a cold worked sample maintained at low temperature ie 77 K. When reheated, this sample exhibits a martensite to austenite transformation (Figure V). This indicates the formation of martensite during the low temperature treatment. If the temperature is not lowered enough during the following thermal cycles (during TEP measurements) the formation of martensite is again not observed.

This narrow deformation range for which the formation of irreversible (or reversible with difficulty) austenite takes place is of practical importance for controlling final properties of shape memory alloy, since they are highly dependent upon the cold working of the transformation characteristics.

## II.2 Annealed samples

The heavily cold-rolled sample (reduction of 52 %) was annealed at 300, 400, 500 and 600°C for 15 minutes.

A gradual recovery of the characteristics of the annealed state is observed with increasing heat treatment temperature (Figure VI). Below 400°C, annealing does not affect the TEP vs temperature curves relative to the cold-worked state. Residual defects are not sufficiently removed to allow any reversible transformation while thermally cycling between - 60 to + 80°C. After annealing at 500°C, a low magnitude hysteresis is detectable. The  $A_f$  and  $M_f$  temperatures are respectively - 40 and + 80°C. After annealing at 600°C, the TEP curves exhibit sharp transitions indicating that recrystallization took place in accordance with previous observations [4], [11]. On heating, the transformation occurs at the same temperature as for the annealed sample, whereas it occurs at lower temperatures during cooling :  $M_s = - 26^\circ\text{C}$  and  $M_f = - 46^\circ\text{C}$ . These lower transformation temperatures may either be due to residual defects of cold- work or to modifications of the phase equilibrium (precipitation - redissolution) [12] [13].

**Table II** : Reductions and deformation of the cold-rolled samples. The initial state was a recrystallized wire (see text)

Sample	Reduction R (%)
A	7.2 ± 0.1
B	9.2 ± 0.2
C	13.0 ± 0.3
D	18.5 ± 0.4
E	52 ± 1

**Table III** : Transformation temperatures based on TEP measurements for various deformations.  
H/Ho indicates the extent of the transformation relative to the recrystallized sample

Deformation $\epsilon$ $\times 10^2$	Annealing Temperature $^{\circ}\text{C}$	Temperature ( $^{\circ}\text{C}$ )				H/Ho
		$M_f$	$M_s$	$A_s$	$A_f$	
0	-	-21	13	12	40	1
7.4	-	-26	10	3	45	0.90
9.4	-	-48	8	5	55	0.36
13.9	-	-50	-	5	58	0.17
$\geq 20.4$	-	-	-	-	-	-

## CONCLUSION

TEP measurements during thermal cycling of TiNi industrial alloys were used to determine the deformation and post-deformation annealing effects on the characteristics of the reversible thermoelastic transformations. The reversible transformations are particularly sensitive to deformation in a narrow range corresponding to reductions of 7 to 9 %.

The increase in thermal hysteresis and the drop of the transformation extent are associated with the formation of irreversible austenite during cold rolling.

For reductions above 18.5 % no transformations are detectable when cycling from - 60 to + 80 $^{\circ}\text{C}$ . During low temperature treatments (77 K), martensite may be formed.

Thermal treatments at 450 $^{\circ}\text{C}$  or more gradually restore the initial capability to undergo a reversible transformation. After a 600 $^{\circ}\text{C}$  treatment of 15 mn, sharp transformations are observed. However, the material is not strain-free. The thermal hysteresis is still larger than in the undeformed state and the extent of the transformation is less than 81 % of its maximum.

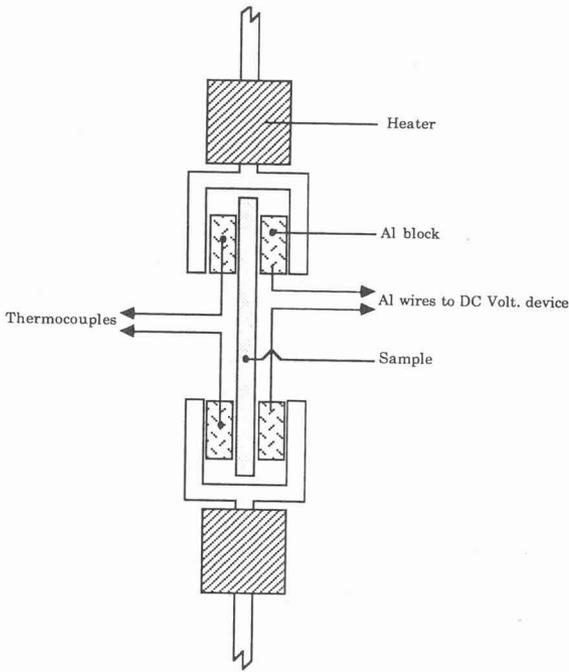
From an engineering point of view, the high sensitivity of the transformations to deformation for reductions of 7 to 9 % is of great importance for controlling final properties.

## ACKNOWLEDGMENTS

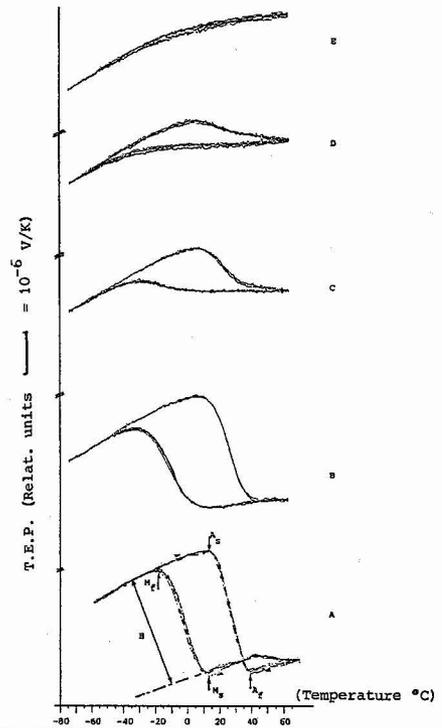
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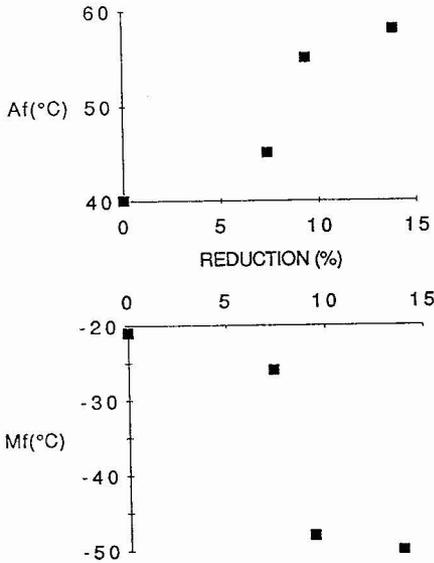
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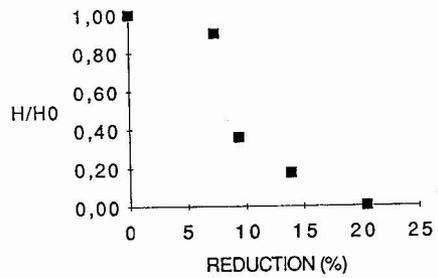
**Figure I :** Schematic representation of the experimental set-up for T.E.P measurements



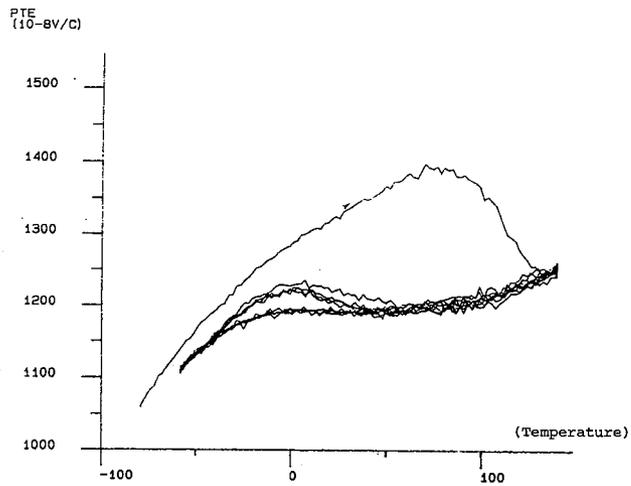
**Figure II :** TEP versus temperature curves for A: the recrystallized state and cold worked sample at reductions of B: 7.2, C: 9.2, D:13.0 and E: 18.5 %



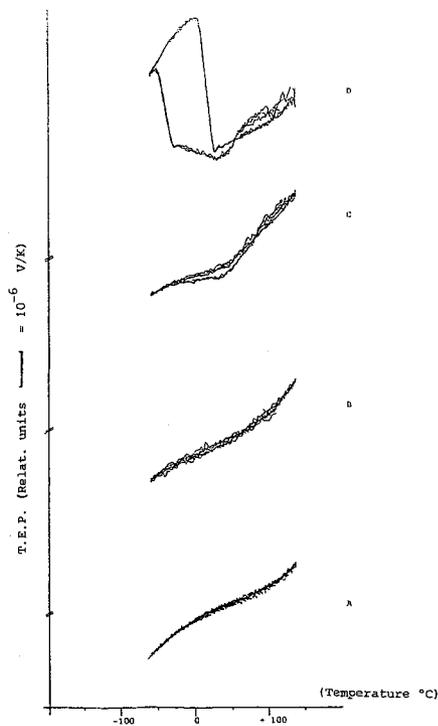
**Figure III :** A<sub>f</sub> and M<sub>f</sub> temperatures for different reductions



**Figure IV :** Relative height of the T.E.P curves vs reduction curves



**Figure V** : T.E.P vs temperature curve of a sample deformed (Reduction of 13 %) and treated at low temperature (77 K). During the first heating, a martensitic to austenitic transformation is detected



**Figure VI** : T.E.P. vs temperature curves for 15 mn anneals at A: 300°C, B: 400°C, C: 500°C, D: 600°C