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A New Hysteretic Behavior in the Electrical Resistivity of Flexinol Shape Memory Alloys Versus Temperature

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The electrical resistivity (ER) of Flexinol nickel-titanium shape memory alloys (SMA) has been measured in the range from −15 to 105°C. The investigated Flexinol wires have two diameters, 150 and 375 μm. The experimental results show new temperatures of phase transformation (TTR) evidencing the unexpected presence of the R-phase. The transformations from austenite to martensite, from austenite to R-phase, and *vice versa* are simultaneous. In the range [20 to 110°C] the hysteresis is almost negligible, whereas in the range [−15 to 105°C] the accommodation process of the hysteresis is observed.

KEY WORDS: electrical resistivity; Flexinol; hysteresis; phase transformation; shape memory alloy (SMA); temperature.

1. INTRODUCTION

Shape memory alloys (SMAs) have the property to recover their previous shape when deformed and heated. This phenomenon is due to the thermo-elastic transformation of the crystalline lattice of the alloy, which has two main crystalline phases: martensite and austenite. In the martensitic phase, at lower temperatures, the specimen can be easily deformed plastically. When the temperature is increased, the crystalline phase is changed to the austenitic phase and the specimen returns to the previous non-deformed shape. The property to recover the shape is due to the dislocations present in the austenitic phase, which are induced by the

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memorization process, consisting of the annealing process of the specimen in a desired shape for a given time and temperature. High recovery forces are generated during the phase transformation from martensite to austenite. The macroscopic characteristics of the alloy, such as stress-strain or electrical resistivity, depend on the microscopic crystalline structure.

The phase transformation of a nickel-titanium (Ni-Ti) alloy is characterized by the hysteretic behavior, as shown in Fig. 1. The temperatures of transformation from martensite to austenite are indicated as *As* and *Af*, respectively, at the beginning and end of the transformation, while the temperatures for the austenite to martensite transformation are indicated as *Ms* and *Mf*, respectively, at the beginning and end of the transformation. The temperatures of phase transformation are generally designated as TTR.

Ni-Ti alloys, in coiled or straight shapes, are employed in several fields such as biomedical, space, civil, robotics, and sensor-actuator devices. The most important Ni-Ti characteristic is the double sensor-actuator property, useful in a number of applications. Moreover, the excellent biocompatibility and resistance to corrosion makes the Ni-Ti alloy one of the most interesting among SMAs. The most popular Ni-Ti alloy, called NiTiNol, was discovered by Buehler [1] at the Naval Ordinance Laboratory. Starting from the Ni-Ti alloy, the company Dynalloy developed a specific Ni-Ti alloy, named Flexinol, with optimized characteristics of an actuator, such as long work life, high repeatability, and strength for shape recovery.

The temperatures of the phase transformation, TTR, of Flexinol are investigated in the present work with measurements of the electrical

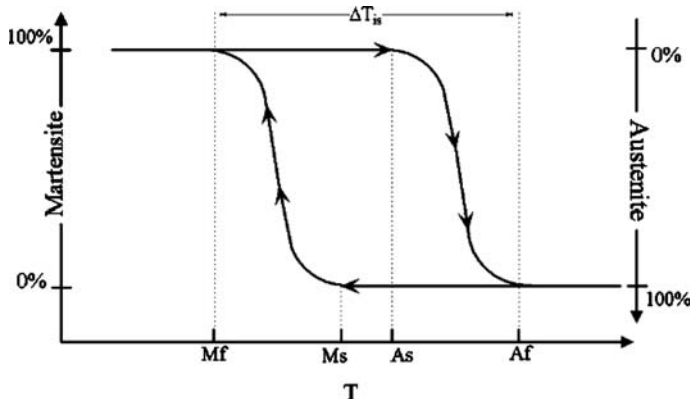

Fig. 1. Hysteretic behavior of Ni-Ti alloy.

Table I. Transition Temperatures from Ref. 2

MARTENSITE	AUSTENITE
$Ms = 52°C$	$As = 68°C$
$Mf = 42°C$	$Af = 78°C$
$\rho = 0.76\,\mu\Omega \cdot m$	$\rho = 0.82\,\mu\Omega \cdot m$

resistivity (ER) because the ER depends directly on the internal crystalline phase structure. Some technical data, released by a Dynalloy Flexinol producer, [2] are reported in Table I. A knowledge of TTR is necessary when the alloy is used for actuator or sensor purposes. The phase transformation crystalline lattice in shape memory alloys has been investigated [3–5]. The temperatures of phase transformation (TTR) have been studied through ER and differential scanning calorimeter (DSC) experiments [6,7], and with a high resolution diffraction study [8]. The experiments are important in the application of several smart devices [9–11].

2. EXPERIMENTAL APPARATUS

The variation of temperature is obtained in a thermostat with a mixture of ethylene glycol and water as the bath liquid. The sketch of the apparatus, with the thermostat, the Dewar flask, and the acquisition data system, DAQ, is shown in Fig. 2.

The liquid thermostatic mixture is brought into a container, shown in Fig. 3, where the Flexinol specimen and the platinum resistance thermometer (PRT) are present. The Flexinol specimen wire has a length of 22 cm. The container, with the Flexinol specimen and PRT, is located into a Dewar flask. The ER measurement is carried out with the

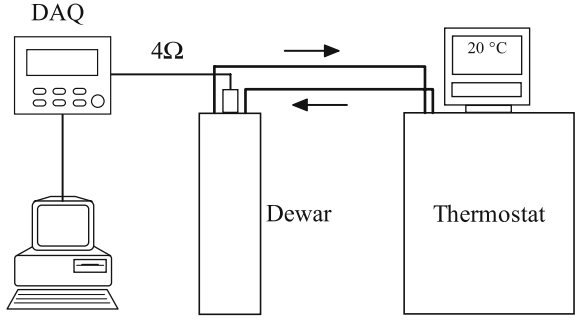

Fig. 2. Experimental apparatus.

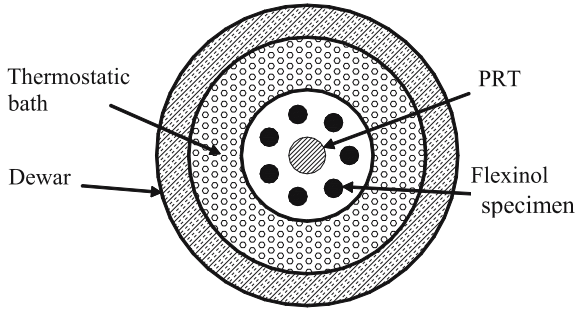

Fig. 3. Dewar flask and Flexinol specimen container.

four-terminal resistance method. A six-digit multimeter is used to record the measurements.

The tested wire specimens have the following characteristics and are designated as follows:

- "Flexinol 375 new" with a diameter of 375 μm
- "Flexinol 375 old" with a diameter of 375 μm, subjected to a moderate aging process
- "Flexinol 150 new" with a diameter of 150 μm

"Flexinol 375 old" is plastically deformed 40 times by wrapping it around a cylinder with a diameter of 38 mm at 22°C, inducing a plastic deformation of about 5%. After each deformation the sample is heated in a furnace at 100°C for 20 s to recover completely the initial straight shape, and then is air-cooled at room temperature (22°C). The aim of the repetitive deformations and heating of "Flexinol 375 old" is to test how the ER depends on a moderate aging process.

All the specimens are tested simultaneously in the same thermostatic bath. The temperature variation rate, measured by the PRT at the specimens' site, is in the range from -0.26 to $-0.76°C \cdot min^{-1}$ for cooling, and from 0.33 to $1.14°C \cdot min^{-1}$ for heating.

2.1. Error Analysis

The temperature of the specimen is measured with a platinum resistance thermometer with a resistance of 100 Ω, i.e., PRT 100, which has a standard uncertainty of 0.05°C, and the temperature is maintained stable in the thermostat with a maximum variation of 0.1°C.

The error analysis of the ER measurements is performed for the first kind of experiment with all the samples. In this experiment, the samples are heated from 20 to 110°C and then cooled to 20°C, completing a cycle. The measurements are performed at steps of about 5°C, and evaluation of the ER is carried out during heating and cooling. The first kind of experiment has been repeated five times.

The measurements of the ER provide an average value of the ER, with a standard deviation σ and a maximum error, Δ, from the mean value. For "Flexinol 375 new" the standard deviation is $\sigma = 0.00327 \times 10^{-7}$ with a maximum error, $\Delta = 0.0137 \times 10^{-7}$. For "Flexinol 375 old" the standard deviation is $\sigma = 0.00301 \times 10^{-7}$ with a maximum error $\Delta = 0.0011 \times 10^{-7}$. For "Flexinol 150 new" the standard deviation is $\sigma = 0.00401 \times 10^{-7}$ and the maximum error $\Delta = 0.018 \times 10^{-7}$.

Table II summarizes the above results.

3. EXPERIMENTAL ANALYSIS AND RESULTS

The ER of Flexinol, also designated as ρ, depends on the parameters (T, D, P, t), where T is the temperature, D is the deformation induced by an applied load P, and t is the time. In this work the following steady-state relation is investigated:

$$\rho(T, D = 0, P = 0, t \geqslant t_e) \tag{1}$$

i.e., when the deformation D and the applied load P are zero at a given temperature T for each $t \geqslant t_e$.

The time t_e is the minimum time for which the PRT and the samples, during a time interval of $\tau = 10$ min at the temperature T, have fluctuations smaller than $1\mu\Omega$ with respect to the local mean at time t of PRT and samples, respectively. Local means have been evaluated by the PRT and sample data measured in the time interval $[t - \tau, t]$. The apparatus is said to reach the steady state at the temperature T when t_e is achieved and the data collected during the interval time $[t_e - \tau, t_e]$ are used for the analysis.

Table II. Error Analysis

SMA alloy	Standard deviation, σ	Maximum error, Δ
Flexinol 375 new	0.00327×10^{-7}	0.0137×10^{-7}
Flexinol 375 old	0.00301×10^{-7}	0.011×10^{-7}
Flexinol 150	0.00401×10^{-7}	0.018×10^{-7}

Two kinds of experiments are performed to measure the ER in different temperature ranges. Before each experiment, all the specimens in the container are heated to 100°C for one hour to recover all the possible previous deformations (due to the hard work industrial process or any accidental stress). After one hour at 100°, the container was cooled to the initial temperature specified in each kind of experiment.

3.1. First Kind of Experiment

The first kind of experiment is done measuring the ER at each temperature step during a thermal cycle characterized by heating from 20 to 110°C, and cooling from 110 to 20°C. The temperature is increased and decreased monotonically during heating and cooling with an average step of 5°C, evaluating t_e at each step and storing the data measured in the time interval $[t_e - \tau, t_e]$. To guarantee repeatability and to perform the error analysis for the ER results, the complete thermal cycle has been repeated five times.

The ERs of "Flexinol 375 new" and "Flexinol 375 old" have the same values at each temperature, and their experimental results during heating and cooling almost coincide, as shown in Fig. 4. The temperature range in the heating and cooling processes is from 20 to 110°C. Hysteresis in this range of temperatures is stable and negligible over five repeated thermal cycles.

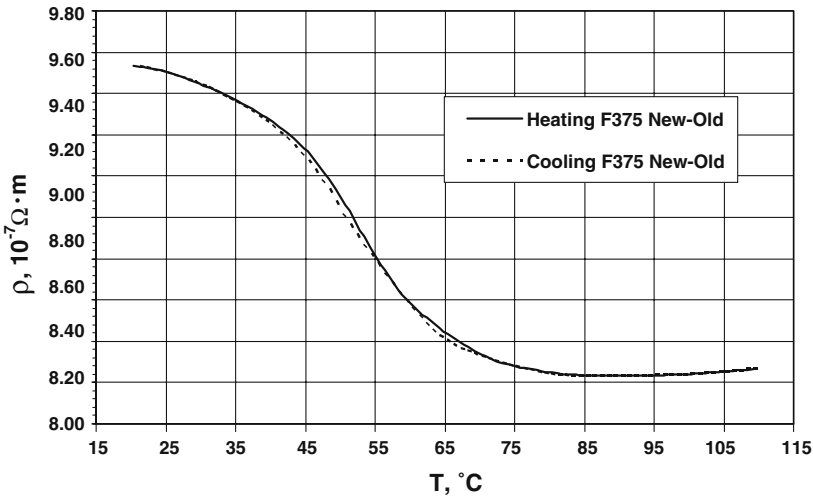

Fig. 4. Electrical resistivity of "Flexinol 375 new" and "Flexinol 375 old" in the first kind of experiment.

A similar behavior is observed in "Flexinol 150 new," as shown in Fig. 5, where hysteresis is a little more evident.

3.2. Second Kind of Experiment

The second kind of experiment is performed in the temperature range from -15 to 105°C. Figure 6 shows the measurements of the ER for "Flexinol 375 new" and "Flexinol 375 old" during the first thermal cycle. The starting point of the experiment is at -15°C where the ER is equal to $\rho_s(8.76 \times 10^{-7}\,\Omega \cdot \mathrm{m})$. Increasing the temperature, the ER increases linearly up to 42°C ($9.06 \times 10^{-7}\,\Omega \cdot \mathrm{m}$), where the ER shows a relative maximum, then the ER decreases to a minimum at 85°C (about $8.04 \times 10^{-7}\,\Omega \cdot \mathrm{m}$), and finally the ER remains almost constant up to 105°C with a resistivity ρ_r ($8.07 \times 10^{-7}\,\Omega \cdot \mathrm{m}$).

In the cooling process, from 105°C (ρ_r) to 80°C, the ER practically coincides with the values measured during heating above 80°C, where the austenitic phase is present. From 80 to 45°C a little hysteresis in the ER is observed. From 45 to 18°C, the ER is higher for the cooling process than for heating. At 18°C the ER has a maximum value ($9.53 \times 10^{-7}\,\Omega \cdot \mathrm{m}$) during the cooling process. Below 18°C the ER decreases sharply to $8.64 \times 10^{-7}\,\Omega \cdot \mathrm{m}$ at -15°C (ρ_f). The difference between "Flexinol 375 new" and "Flexinol 375 old" can be considered negligible. After the first thermal cycle the final ER is lower than at the beginning. Further measurements are carried out

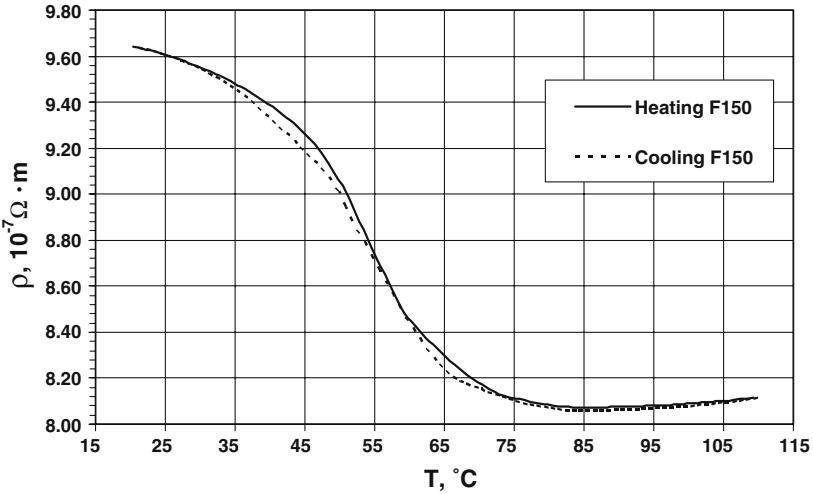

Fig. 5. Electrical resistivity of "Flexinol 150 new" in the first kind of experiment.

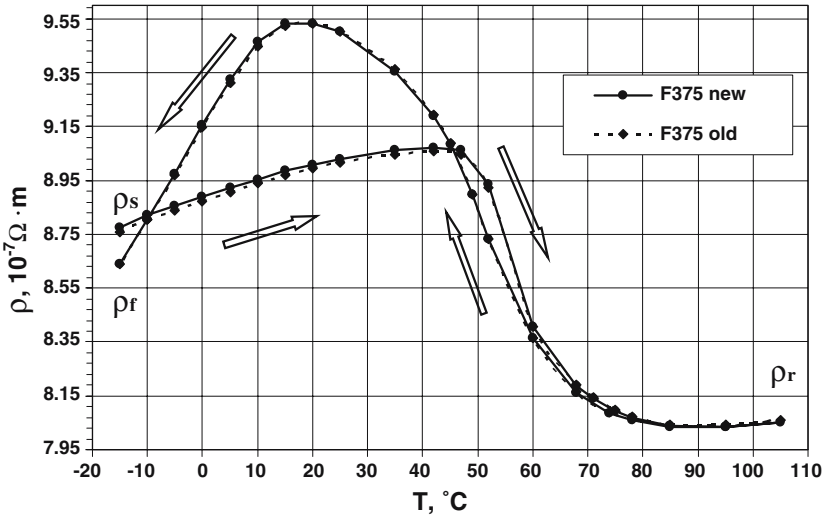

Fig. 6. Electrical resistivity of "Flexinol 375 new" and "Flexinol 375 old" during the first thermal cycle in the second kind of experiment.

for the ER of "Flexinol 375 new" in the second cycle, which is compared to the first cycle in Fig. 7. The ER in the martensitic state, from -15 to 80°C, shows some differences with the first cycle. On the contrary, in the austenitic state, from 80 to 105°C, the measurements almost coincide. The hysteresis shown in the second cycle (Fig. 7) has a twist, between 45 and 60°C, which is smaller than the one presented in the first cycle. The experiments in the third and fourth cycles on "Flexinol 375 new" are also presented in Fig. 7. The fourth cycle is carried out only for heating. The difference between the ER in successive cycles decreases and seems to disappear with succeeding cycles. The cooling curves in the three cycles are very similar, and they differ only at temperatures lower than 0°C.

The ER measured in "Flexinol 150 new" are shown in Fig. 8 which shows the ER measurements in the first and second thermal cycles, and their difference is small. Further cycles are practically the same as the second cycle and are not shown.

4. DISCUSSION

4.1. First Kind of Experiment

The experimental results of "Flexinol 375" between 20 and 110°C (Fig. 4) are similar to the data released by the Dynalloy information

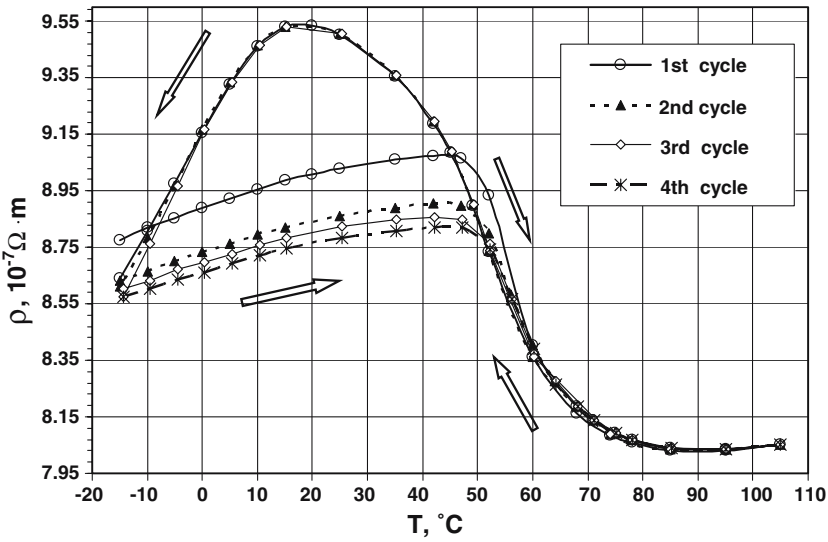

Fig. 7. Electrical resistivity of "Flexinol 375 new" during four thermal cycles in the second kind of experiment.

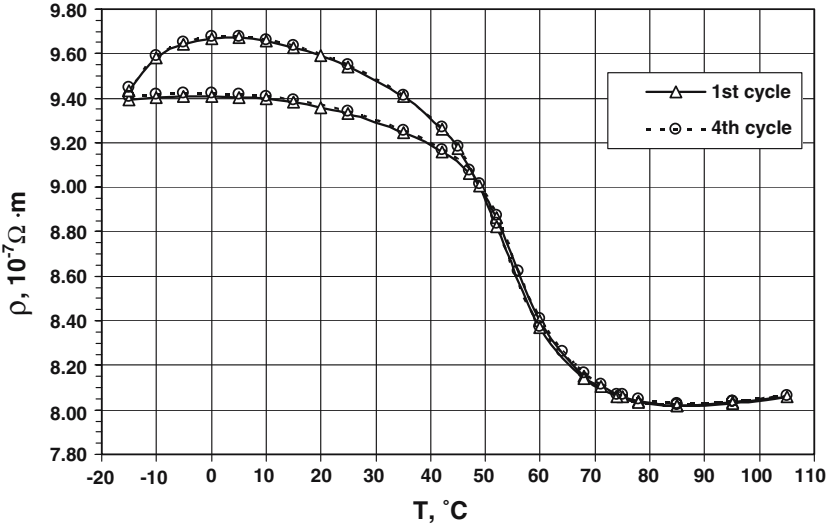

Fig. 8. Electrical resistivity of "Flexinol 150 new" in the second kind of experiment.

sheet, as far as the austenitic phase is concerned, while the martensite data differ from the Dynalloy results. In Ref. 6 it has been shown that the R-phase crystalline lattice has the maximum ER between the Ni-Ti crystalline phases of austenite and martensite; then it is possible to conclude that the R-phase, not reported by the industry data, is present in the specimen.

The thermostat induces a temperature rate that changes within the range [0.115 to $1.14°C \cdot min^{-1}$] depending on the set temperature for the measurements, between 20 and 110°C. For some materials their ER can depend on the temperature rate. To establish the rate independence of Flexinol, the thermal step and settling times of the thermostat have been changed in order that all the previous temperatures, for which the ER has been measured, are reached with temperature rates of 0.11 and $1.15°C \cdot min^{-1}$. With these new ER measurements the standard deviation has always been approximately $\sigma = 0.004 \times 10^{-7}$, i.e., comparable to the standard deviation used to evaluate the reproducibility of the hysteresis.

In conclusion, the Flexinol SMA, between 20 and 110°C, is independent of the temperature rate within the range [0.11 to $1.15°C \cdot min^{-1}$].

4.2. Second Kind of Experiment

The second kind of experiments is discussed separately for the two Flexinol wires with different diameters.

4.2.1. Flexinol 375 μm

The experiments on "Flexinol 375 new" in the temperature range from −15 to 105°C (Figs 6 and 7) show a new behavior for different cycles. The descending branch of the ER curve decreases after each cycle, for temperatures below 0°C, originating different ascending branches. In magnetic materials such an instability of the hysteresis curve is called an "accommodation process," and the hysteresis tends, cycle after cycle, towards a steady-state situation. In this case, the stable ascending branch seems to stand close to the forth ascending branch. Along all the cycles, a maximum is observed at about 42°C and a minimum at about 85°C during heating. During cooling, the minimum is found at about 85°C and the maximum at about 18°C.

These points are candidates to be the transition phase temperatures (TTR), but, because of the unexpected ER hysteresis and in contrast to the industry data, the well known experiment, named Active (*As, Af*), is carried out in order to confirm the TTR determined by the ER measurements.

The Active (*As, Af*) experiment consists of bending the specimen at room temperature until the wire strain is of about[1] 4%. The temperatures corresponding to the recovery of the straight shape are recorded during heating in a furnace. This experiment gives the austenite transformation temperatures, *As* and *Af*, with a lower precision than for the ER method. By the Active (*As, Af*) experiment, *As* is found in the range of 40 to 45°C, when the shape recovery starts, whereas *Af* is about 85°C, when the shape recovery is complete. Then, the maximum at 42°C and the minimum at 85°C from the ER measurements, during heating, have a clear meaning, they are *As* and *Af*, respectively.

The ER maximum at 18°C during cooling suggests the presence of the R-phase, a rhombohedral crystal structure, which is intermediate between the austenite and martensite phases and is present if the Ni-Ti alloy is annealed in the temperature range of 200 to 460°C, as discussed in Ref. 6. Moreover, the R-phase has higher resistivity than the austenite and martensite phases and a smaller capacity to recover the deformation (maximum of 1%), with negligible and stable hysteresis. Thus, we can infer that during cooling below 85°C, the transformation from austenite to martensite and the R-phase takes place simultaneously[2] and below 18°C, the R-phase starts to transform into martensite. Note that also by a differential scanning calorimeter (DSC) [6,7], the exact transformation temperatures from austenite into martensite, $A \Rightarrow R$, and from austenite into R-phase, $A \Rightarrow M$, cannot be determined because they are overlapping transformations. Moreover, for temperatures lower than *As*, it is clear from the ER hysteresis curve (Figs. 6 and 7) that during heating a lower quantity of the R-phase coexists with martensite than during cooling. This is sufficient to deduce that, also during heating, martensite and R-phase transform into austenite simultaneously.

The accommodation process has not been observed previously in Flexinol wires. A possible explanation is that cycle after cycle the R-phase grains expand, favoring the transformation from the R-phase to the martensite phase, $R \Rightarrow M$ (where the grains are larger than in the R-phase). This is a possible explanation for the lower values of the ER at the end of the cycle, as compared to the starting point. After each cycle, the internal crystalline lattice structure passes throughout an energetic minimum decreasing the complexity of hysteresis. During cooling the grain expands its borders, where a higher number of dislocations are present that remain in the same location during heating, favoring the new expansion of the

[1] Tables of bending radius, wire diameter, and fiber strain can be found in classical books of mechanical engineering.

[2] Note that the plastic deformation at room temperature, about 22°C, completely recovered after heating (Active (*As, Af*) experiment), implies that martensite is already present at about 22°C.

grain and then the $R \Rightarrow M$ transformation. This process continues until the system reaches the energetic minimum of the internal structure.

Summarizing the results of ER measurements for Flexinol 375, the evaluated TTRs are as follows:
During heating:

- $A's = 42°C$, martensite and R-phase begin to transform into austenite.
- $Af = 85°C$, the crystalline structure is fully austenitic.

During cooling:

- $RMs = 85°C$, austenite begins to transform into R-phase and martensite.
- $M's = 18°C$, R-phase begins to transform into martensite.
- $Mf < -15°C$, the temperature corresponding to a fully martensite phase is not reached.

The hysteresis of Flexinol in this temperature range can be modeled by the differential model presented in Ref. 12 and not by the Preisach type mathematical models for the hysteresis [13,14], because of slope inversion of the branches during heating or cooling.

4.2.2. Flexinol $150\,\mu m$

"Flexinol 150 new" shows a stable hysteresis in the temperature range from -15 to $110°C$. The hysteresis is present at higher values of the ER because the transformation from austenite to the R-phase, $A \Rightarrow R$, is facilitated and the transformation from the R-phase to martensite, $R \Rightarrow M$, is hindered by the different geometry of the specimen. The small size of the wire seems to inhibit the growth of R-phase grains and its transformation into martensite grains. Moreover, if the grains have smaller dimensions, a greater resistivity is measured because of the greater anisotropy introduced by grain borders.

The presence of the R-phase does not allow determination of TTRs through ER measurements, because it is contemporary to the other transformation. The Active (*As, Af*) experiment revealed that the temperature *As* is around 42 to 45°C and the temperature *Af* is around 80 to 83°C, i.e., very close to the results for "Flexinol 375 μm new."

5. CONCLUSIONS

The unload transformation temperatures *As, Af, RMs, M's* of Flexinol wires with diameters of 375 and $150\,\mu m$, are detected through electric

resistivity (ER) measurements. A moderate aging process does not affect the ER hysteresis. The presence of the R-phase has been found, although its existence is not reported by the Flexinol producer. The transformations from austenite to martensite, from austenite to R-phase, and *vice versa* are simultaneous. The instability of the R-phase and austenite transformation in the Flexinol wire with a diameter of 375 μm is observed. The transformation of R-phase into martensite, $R \Rightarrow M$, is a non-diffusive process, characterized by an accommodation process and a dependence on the annealing process as well as on the geometry and the volume of the sample is assumed. In the temperature range from 20 to 110°C the hysteresis is stable, and negligible for the two diameters investigated and is independent by the temperature rate in the range [0.11 to 1.15°C·min^{-1}]. It is then possible to propose these Flexinol wires for use as temperature sensors in several applications.

NOMENCLATURE

Symbols

Af	Temperature at which austenite begins to form
As	Temperature at which structure is fully austenitic
A's	Temperature at which martensite and R-phase begins to transform into austenite
D	Deformation
Ms	Temperature at which martensite begins to form
M's	Temperature at which R-phase begins to transform into martensite
Mf	Temperature at which structure is fully martensite.
RMs	Temperature at which austenite begins to transform into martensite and R-phase
P	Applied load
SMA	Shape memory alloy
T	Temperature, °C
t	Time, s
TTR	Temperatures of phase transformation
DSC	Differential scanning calorimeter

Greek Symbols

ρ	Electrical resistivity
σ	Standard deviation
Δ	Maximum error
η	Discrepancy

Subscripts

e Equilibrium
f End of transformation
r Final value
s Beginning of transformation

REFERENCES

1. W. J. Buehler and R. C. Whiley, *Techn. Report* (1965); U. S. Patent 3174851
2. Dynalloy Inc., 1070 Commercial Street, Suite No. 110, San Jose, California 95112. Web site: www.dynalloy.com
3. X. Huang X. and Y. Liu, *Surf. Coat. Technol*. **190**:400 (2005)
4. P. Sittner, P. Lukas, V. Novak, D. Neov, and M. Ceretti, *J. Neutron Res*. **9**:143 (2001)
5. F. Auricchio, *Ph. D. Thesis* (University of California at Berkeley, 1955)
6. J. Uchil, *PRAMANA – J. Phys*. **58**:1131 (2002)
7. M. Brugnara, *Laurea Thesis* (Università degli Studi di Trento, 1998/1999)
8. R. Eisenhower and T. Wroblewski, *Mater. Sci. Forum* **216**:278 (1998)
9. K. Otsuka and T. Kakeshita, *MRS Bull*. **27**:91 (February 2002)
10. A. E. Bergles, *Exp. Therm. Fluid Sci*. **26**:335 (2002)
11. John J. Gill, Ken Ho, and Greg P. Carman, *J. Microelectromech Syst*. **11**:1057 (2002)
12. D. Carnevale, S. Nicosia, and L. Zaccarian, *16th IFAC Congress*, to be published (2005)
13. G. Bertotti, *Hysteresis in Magnetism* (Academic Press, San Diego, 1998)
14. I. D. Mayergoyz, *Mathematical Models of Hysteresis and Their Applications* (Academic Press, Boston, 2003)