J. Phys. IV France **11** (2001)

Anomalies in the pseudoelastic effect of a $Ni_{45}Ti_{50}Cu_5$ shape memory alloy

S. Besseghini, T. Ranucci[1] and G. Airoldi[2]

CNR-TeMPE, Corso Promessi Sposi 29, 23900 Lecco, Italy
[1] CNR-TeMPE, Via R. Cozzi 53, 20125 Milano, Italy
[2] Università di Milano Bicocca, Dipartimento di Scienza dei Materiali, Via R. Cozzi 53, 20125 Milano, Italy, and INFM, Unità di Milano Bicocca, Via R. Cozzi 53, 20125 Milano, Italy

Abstract: An extended investigation of the pseudoelastic properties of Ni45Ti50Cu5 alloy suggested the presence of a two-stage transformation behavior. This behavior was brought to evidence performing stress strain measurement on ternary alloy specimens submitted to different thermal treatments and pulled slightly overbehind the maximum pseudoelastic transformation strain. The concurrent measurement of Electric Resistance(ER) and of the temperature of the specimen proved clear modifications of these physical properties at the end of the pseudoelastic plateau both during the loading and unloading process. Investigation of the stress strain curve at different temperatures above the Af (austenite finish) values together with a systematic comparison of ER measurements on differently thermally treated specimens suggest the presence of an another transformation in competition with the usually accepted cubic to monoclinic. Results obtained are here presented and discussed at the light of this working hypothesis. Analysis of the ER(ε) curves allows to relate directly this physical property to the transformation strain of the pseudoelastic curve. Both at the end of the loading and unloading plateau there is evidence of a marked change of the ER(ε) , only slightly modified by the thermal treatment procedure. In more detail measurements were performed at different temperatures taking into account the modification in Af temperature induced by the thermal treatment.

1. INTRODUCTION

Although the substitution of copper maintains the thermoelastic martensitic transformation (TMT) in the $Ni_{(50-x)}Ti_{50}Cu_x$ alloys the martensite phase is different depending on Cu content. Up to about 7at% of Cu the transformation scheme is very similar to the binary system with a B2 austenitic phase transforming to a monoclinic B19' martensite. Controversial is the presence in these alloys of the R-phase with different experimental findings [1]. For Copper content in the range 7-15at% a different transformation scheme is found with the B2 austenitic phase transforming to an orthorhombic B19 martensite closely followed, on the temperature scale, by the transformation to the monoclinic B19' structure.. Further increase of the Cu content stabilizes the orthorhombic transformation and for Cu content higher than about 15at% there is no evidence of the transformation to the monoclinic phase.

However the concentration limit for the existence of the cubic-orthorhombic transformation is controversial [2] and has never been precisely settled. Recent work [3] performed on the characterization of $Ni_{45}Ti_{50}Cu_5$at% pointed out the possibility that, as a function of the external pressure, the state diagram of the ternary alloy could take in account different transformation sequences.

In a previous paper [4] present authors have advanced the idea of a new phase transformation occurring during tensile tests performed in the pseudoelastic window ($A_f<T_{test}<M_d$) of $Ni_{45}Ti_{50}Cu_5$ alloy. This working hypothesis was put forward at the light of the results summarized in Figure 1. The Electric Resistance measurement as a function of strain [ER(ε)] during a tensile test exhibits a sudden increase once the maximum transformation strain has been overcome. (Figure 1b).

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jp4:2001865

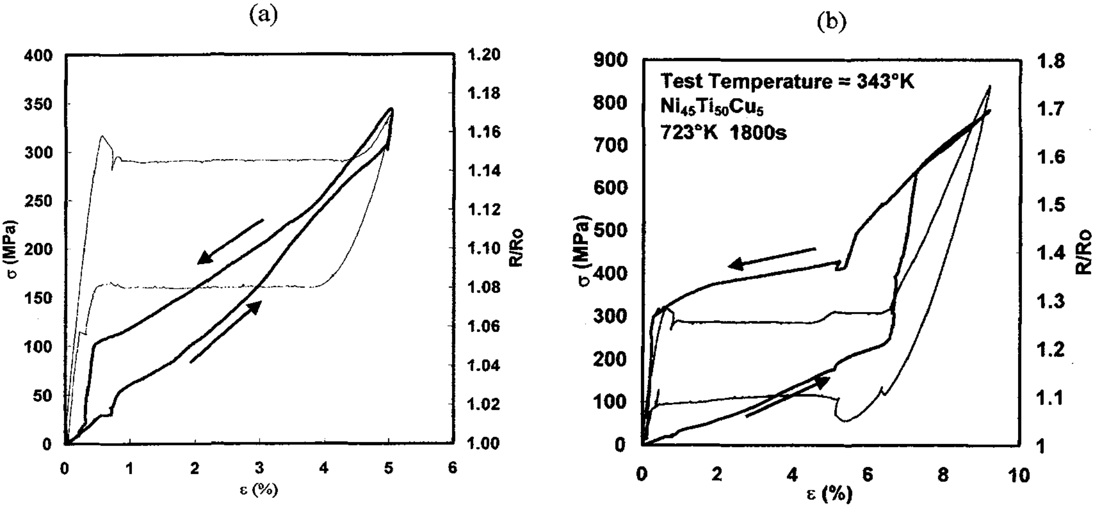


Figure 1: comparison of the ER(ε) curves in the case in which the maximum strain imposed overcomes the maximum transformation strain (b) or not (a) for a $Ni_{45}Ti_{50}Cu_5$ alloy in the pseudoelastic regime. The σ(ε) curve is plotted on the curves for clarity.

Aim of the present work was to extend the experimental evidence of these results through a complete characterization of the effect in a wide range of thermal treatments and experimental conditions.

2. EXPERIMENTAL

Experimental work was performed on a $Ni_{45}Ti_{50}Cu_5$ alloy produced at TeMPE laboratories starting from pure elements by induction melting in a graphite crucible under vacuum. The ingot obtained was Plasma remelted, canned in steel and hot extruded. The extruded bar, removed from the steel can, was subsequently hot rolled and cold rolled to $0.95x0.95mm^2$ square wires. The whole set of specimens used was taken from the same batch of material.

Different thermal treatments (573, 673, 723, 773 K for 1.8 Ks or 3.6 Ks) were performed in an evacuated quartz tube under dynamic vacuum (less than 10^{-5} mbar) followed by quench in cold water. Thermal treatments (TT) were performed on specimens in the as-rolled condition with a residual cold work (CW) of about 20%.

Stress-Strain (S-S) tests were performed with a Zwick 1455 material testing machine equipped with a 20 kN load cell and a miniature extensometer (range ±20%) at a constant strain rate of $10^{-4}s^{-1}$. On each sample three T-type thermocouples (TC) were attached. One TC was placed in the middle of extensometer's harms and the other two outside. If not differently specified data here reported refers to the average value of the three thermocouples.

Simultaneous electric resistance (ER) measurements were performed with the conventional four probes methodology with an ESI 1701B microohmmeter whose resolution is 0.01 mΩ. Temperature control during the tests was obtained through a thermostatic chamber using liquid nitrogen as a coolant and allowing temperature control within ±0.5°C of the temperature set point.

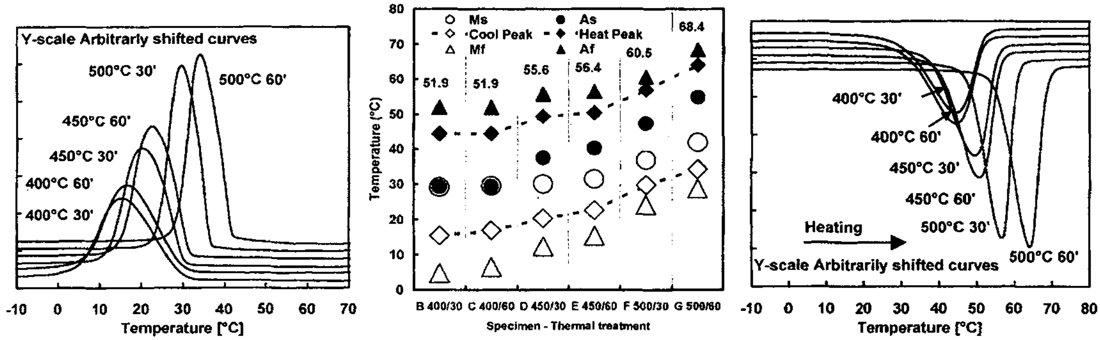
For a correct comparison of the different σ(ε) curves, taking care of the shift in transformation temperatures related to different thermal treatments, the specimens were characterized by means of a common protocol.

1) A small sample cut from the end of the tensile test specimen was examined by DSC to identify the transformation temperatures
2) A specimen was tested up to rupture at a temperature correspondig to Af+30°C to evaluate the maximum transformation strain and the general mechanical features

3) Three different specimens were tested in their pseudoelastic state at three different temperatures above Af namely : Af+10°C, Af+20°C and Af+30°C. In each case the maximum strain was chosen slightly higher than the maximum transformation strain

3. RESULTS AND DISCUSSION

The preliminary calorimetric investigation gave the expected results typical of the progressive recovery towards the full-annealed state of the specimens. The single peak related to the B2⇔B19' transformation is progressively better defined and shifted to higher temperatures on the temperature scale.
Figure 2 summarizes the whole set of calorimetric curves for the different thermal treatments.



(a) (b) (c)

Figure 2. Calorimetric curves respectively on cooling (a) and on heating (c) and transformation temperatures (b) obtained by thermograms analysis. The A_F temperatures are explicitly reported.

As previously explained the different specimens underwent a common testing protocol for a correct comparison of results. . In Figure 3 together with the σ(ε) curves the main mechanical parameter are reported. For subsequent analysis, attention is focussed on the maximum transformation strain (ε^T_{MAX})evaluated as the maximum strain value at the constant critical stress to induce martensite (σ_{SIM}). Its value increases with thermal treatment ranging from a minimum of 6.6% up to 7.1%.

(a) (b) (c)

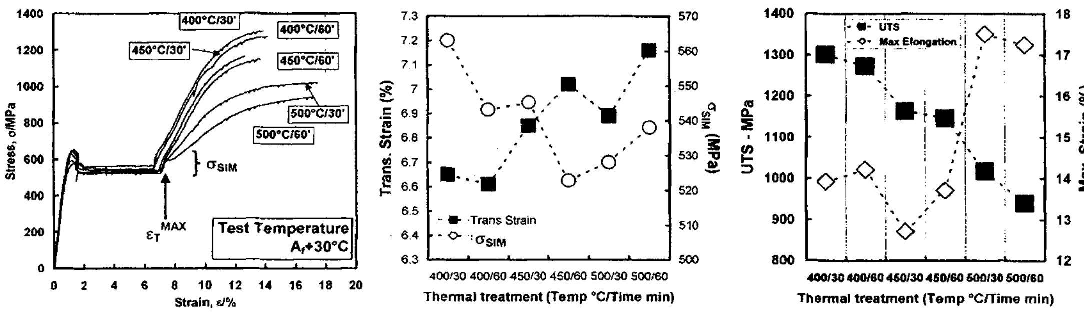


Figure 3: summary of the preliminary tensile tests performed on the specimens after the various thermal treatments. In (a) the whole set of S-S curves is reported. In (b) and (c) the main data obtained from the analysis of the curves in (a) are reported.

To an increasing TT temperatures correspond an increase both of the elongation to failure and of the transformation strain and a decrease (about 10%) of σ_{SIM} as outlined in Figure 3(b). The elongation to failure is only slightly increased changing from 400°C to 450°C whilst the thermal treatment at 500°C induces an increase in ε_F of about 4%. The ultimate tensile strength (UTS) generally decreases with the

TT temperature increase. On the other hand aging time at the same temperature induces only a small change in this parameter, except for the TT at 500°C.

After this extensive preliminary characterization, specimens were tested in their pseudoelastic state by measuring a complete loading, unloading cycle at the three temperature chosen, i.e. Af+10°C; Af+20°C and Af+30°C. The whole set of data on these pseudoelastic characterization will be published elsewhere [5]; here attention will be paid on the effects induced on the Electric Resistance as a function of strain [ER(ε)]by overcoming the maximum transformation strain..ER(ε)is reported in Figure 4: in each graph the four curves normalized to the initial value (ER(0)) refer to four specimens. The curves related to increasing test temperatures have been arbitrarily shifted on the ordinate scale for clarity. Note that in each graph two curves recorded at Af+30°C are reported. One is the result obtained during the test up to rupture, the other one has been recorded during the standard loading/unloading pseudoelastic cycle.

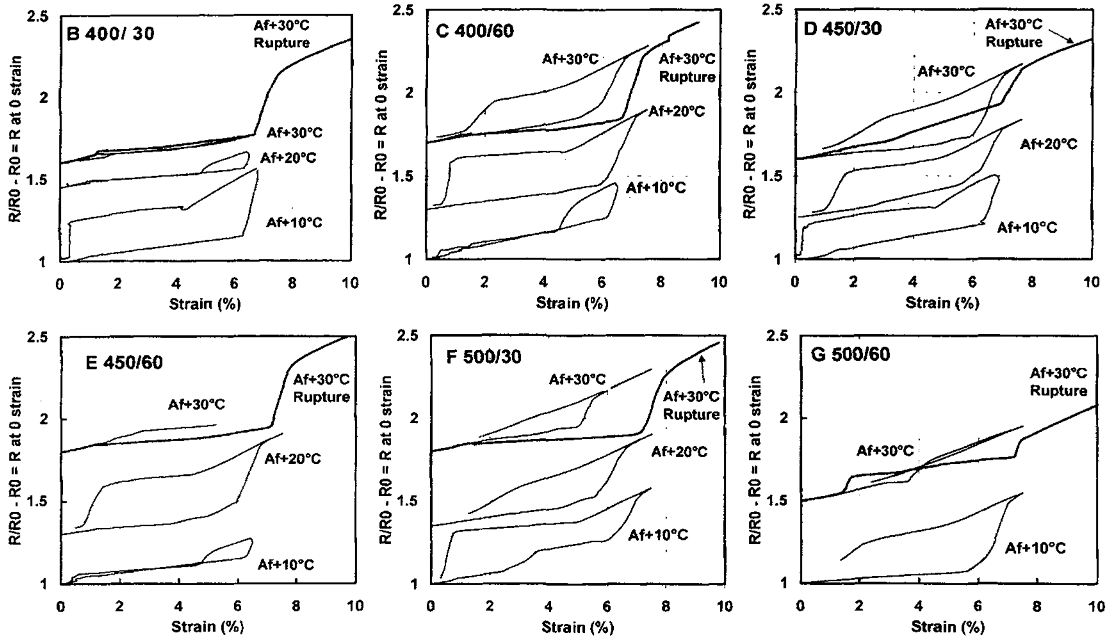


Figure 4: the whole set of experimental curves obtained at various temperatures on the specimens submitted to the indicated thermal treatments. See text for details.

It is worthwhile to remember that each loop in the ER(ε) curves in Figure 4 must be examined at the light of the general result reported in Figure 1(b) i.e. the lower part of the loop is related to the loading branch of the σ(ε) curve. The steep increase in the ER(ε) corresponds to the overcoming of the maximum transformation strain whilst the upper part of the curve is related to the unloading of the σ(ε) curve. Often the ER(ε) curve doesn't recover the initial value due to some permanent plastic or pseudo-plastic deformation accumulated in the specimens. As a rule each specimen was heated up well above Af at the end of each tensile test and in the case of pseudo-plastic deformation one can observe that ER actually recovers its initial value.

It can be noticed that despite the different thermal treatments and the different test temperatures some common features can be outlined. On increasing the test temperature there is a progressive smoothing of the upper part of the loop related to unloading.. This is quite evident in specimens C and D.

Another feature that deserves attention is that the transformation strain changes with temperature. As a consequence in the presented curves three different situations occur (he curves in Figure 4 of the specimen B 400/30 are a good reference):

1) The maximum tested strain is lower than the transformation strain (curve Af+30°C) and no loop is observed: thus the unloading branch is superimposed to the loading one.
2) The maximum tested strain is slightly higher than the transformation strain (curve Af+20°C): just a small loop appears.
3) The maximum tested strain is definitely higher than the transformation strain(curve Af+10°C): the loop is completely defined and the previously observed features are present. [4].

The "small loop" behavior is clearly present also in curves Af+10°C of specimens C and E and deserves some comment. In the hypothesis the steep increase in ER(ε) for $\varepsilon > \varepsilon_T$ is related to another transformation all these curves can be viewed as the results of partial cycling. If the maximum imposed strain of the test was not enough to complete the "transition", at the start of the unloading step, ER(ε) quickly recovers the loading behavior. This behaviour is characteristic of a partial cycling procedure that involves only the beginning of a transition process.

ER(ε) curves related to TT higher than 450°C (specimens F and G) clearly show that new features can be recognized in the loading branch too: one must however remind that the high temperature TT can deeply affect the pseudoelastic behavior of the specimens. The curves are here reported just for reference as they show a similar general trend but the details will not be discussed.

Another interesting feature is related to the TC signals acquired all along the S-S tests: all the TCs gave evidence of an exotermic peak both at the start of the pseudoelastic plateau and more strongly (even a 7-8°C increase) when the conventional transformation strain was overcome

In Figure 5 a comparison of the results presented in Figure 4 is given to better appreciate the effect of the three test temperatures after the different thermal treatments.

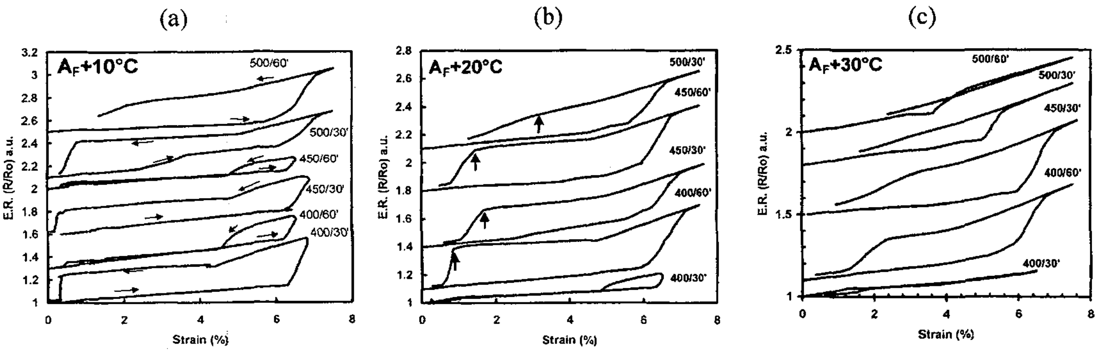


Figure 5: ER(ε) curves for the different specimens tested at three different temperatures above the Af value.(a) Af+ 10°C; (b) Af + 20°C and (c) Af + 30°C. For the sake of clarity the curves have been arbitrarily shifted on the (Y) scale.

Again the ER(ε) curves show a common behavior. During loading the ER value increases linearly in quite a regular way in spite of different thermal treatments and temperature conditions. The rate of ER variation as a function of strain [dER/dε] is roughly constant at an average value of 0.79 mΩ/%. When ER(ε) steeply increases the new rate has an average value of 14.5 mΩ/%. These values are quite constant in the entire set of ER(ε) curves. In many curves it can be appreciated that after the linear part with the higher rate (confined in a deformation range from 6 to 7%) ER(ε) rate lowers again (see for example all the curves at Af+20°C except the one of the specimen treated at 400°C for 30 minutes). It should be noted that whilst the first ER(ε) rate change is in good coincidence with the end of the pseudoelastic plateau, the subsequent rate change has no correspondence on the σ(ε) curve. On unloading the ER(ε) curve maintains this new rate value down to the onset of the unloading plateau in the σ(ε) curvewhere it recovers the same rate value as in the loading plateau. This effect is more clear cut when the σ(ε) curve has a neat pseudoelastic plateau otherwise it smears out: in fact in the highest test temperatures and TT it can be only hardly detected. Only in correspondence of the end of the unloading plateau, as indicated by the arrows in the curves related to Af+20°C, ER(ε) rate changes again, and finally restore the initial value.Conclusions

The experimental data here presented refer to an extensive investigation of the pseudoelastic properties of a NiTiCu5at% alloy submitted to different thermal treatments. Great care has been taken in testing procedures to allow a direct comparison of the results. Attention was focussed on the behavior of the ER curves as a function of strain [ER(ε)] both in the pseudoelastic regime and above the generally accepted transformation strain value.

The experiments performed give a global overview of the influence of thermal treatments and test temperatures on the ER(ε) behavior. Specifically it can be concluded that the working hypothesis put forward in previous work [4] related to the presence of a transition activated at the end of the pseudoelastic plateau appears confirmed.

The general behavior of the ER(ε) can be summarized as follows:

- ✓ During loading, on occurrence of the stress induced martensite formation process, the ER(ε) increases linearly with a quite constant rate. This rate is symmetrically found during the unloading process in the reverse transformation;
- ✓ At the end of the pseudoelastic plateau and in a small deformation range around 6-7% ER(ε) rapidly modifies to a new linear trend. The start of this change sets in at the start of what is generally considered the macroscopic elastic deformation of the transformed martensite. The end of this range, however, has no evidence on the σ(ε) curve.
- ✓ If unloading is performed below the end of this new transition range a small loop is activated and ER(ε) quickly resumes the loading behavior;
- ✓ After a loading process above the end of this new transition range (ε>7%), on unloading, ER(ε) decreases in a linear way with the same rate value attained at the end of the loading process. In correspondence of the unloading plateau the rate changes resuming a value almost the same as the one of the loading step: only at the end of the reverse transformation the rate changes again to close the cycle.

Several features of the ER(ε) curves detected during σ(ε) curves on a Ni45Ti50Cu5 alloys, submitted to different thermal treatments, strongly support the hypothesis of another transition when the maximum transformation strain related to the conventional SIM plateau is overcome.

Unfortunately none of the performed treatments allowed to separate clearly the two transitions and both the mechanical tests and the physical probes used don't allow to get insight in the nature of the transition itself. Perspective work will be required to gain deeper understanding of this "transition"

Acknowledgments
Thanks are due to Mr. G. Carcano for specimen preparation and to Dr. E. Villa for DSC measurements.

References

[1] Y.C. Lo, S.K. Wu, Journ. of Mat. Sc. 30, 1995, 1577-1583
[2] T.H. Nam, T. Saburi, K. Shimizu,Mat. Trans. JIM 31,(1990), 959-967
[3] T. Fukuda, T. Kakeshita. N. Tamura, T. Saburi, S. Endo, Materials Science Forum, Vols 327-328, (2000), 115-118
[4] Ranucci T., Besseghini S., Airoldi G., Materials Science Forum, Vols 327-328, (2000), 143-146
[5] Besseghini, Ranucci, Airoldi – to be published