Journal of Alloys and Compounds 356–357 (2003) 669–672

www.elsevier.com/locate/jallcom

Mechanical spectroscopy of the H-free and H-doped $Ni_{30}Ti_{50}Cu_{20}$ shape memory alloy

A. Biscarini[a,*], B. Coluzzi[a], G. Mazzolai[a], F.M. Mazzolai[a], A. Tuissi[b]

[a] *INFM-UDR of Perugia, Physics Department, University of Perugia, Perugia, Italy*

[b] *CNR-Tempe, Lecco, Italy*

Received 1 August 2002; accepted 25 October 2002

Abstract

The temperature dependence of the dynamic Young's modulus E, the elastic energy dissipation coefficient Q^{-1} and the heat flow (DSC) has been studied between 20 and 370 K in a H-free and H-doped ($n_H = H/Me = 0.006$ and 0.01 at.) $Ni_{30}Ti_{50}Cu_{20}$ alloy. The Young's modulus exhibits softening when the start temperature M_s of the B2→B19 martensitic transition is approached on cooling and a steep modulus decrease between M_s and M_f. This steep decrease is associated with stress-induced motions of twin boundaries within the B19 martensite. Hydrogen reduces background damping of the martensite and dramatically enhances the dissipation in the temperature region of the transformation. These observations suggest that hydrogen (a) forms fixed pinning points for twin boundaries at low temperature and (b) gives rise to an anelastic relaxation P_H associated with H dipoles and to a peak P_{AM} due to H-twin boundary interactions.

Keywords: NiTiCu alloys; Martensitic transition; Hydrogen in metals; Internal friction

1. Introduction

NiTiCu alloys are of great technological interest as they exhibit small hysteresis in their physical properties during cooling/heating cycles carried out at around the B2–B19 martensitic transition [1,2]. For Cu contents higher than 15 at.%, on cooling, only the B2–B19 transformation is expected to occur between about 330 and 300 K, while for copper contents included between 7 and 15 at.% the orthorhombic phase B19 is expected to transform into the B19′ monoclinic structure at lower temperatures [2]. At smaller Cu contents only the B2–B19′ transition should occur.

Recently, it has been found that hydrogen markedly affects the elastic properties and the damping capacity of NiTi binary alloys [3] and of the $Ni_{40}Ti_{50}Cu_{10}$ ternary alloy [4,5]. In particular, an enhancement has been observed of the internal friction (IF) peak P_{AM} occurring at the transitions B2–B19′ and B2–B19 while an anelastic relaxation process P_H is introduced by H at around 260 K for vibration frequencies f in the kHz range. Furthermore, an increase is induced by H impurities in the Young's modulus (E) of the martensite (M). This increase has been interpreted as being due to pinning processes of twin boundaries by hydrogen atoms.

Although the mentioned effects associated with hydrogen doping are large and well established by now their structural mechanisms are, nevertheless, not clear as yet. To improve our understanding of these effects it is of crucial importance to better characterise them in relation to different types of transitions and of martensites. Thus, it has appeared of interest to further investigate the B2–B19 transition, which is the only one expected to occur in the 20% Cu alloy.

2. Experimental

An ingot of NiTiCu with nominal composition of 30 at.% Ni, 50 at.% Ti and 20 at.% Cu was prepared at CNR-TEMPE by vacuum induction melting. The material was solution treated at 1173 K for 1 h then water quenched. For the measurements of the Young's modulus

---

*Corresponding author. Fax: +390-75-44-666.
E-mail address: biscarini@fisica.unipg.it (A. Biscarini).

0925-8388/02/$ – see front matter © 2002 Elsevier B.V. All rights reserved.
doi:10.1016/S0925-8388(02)01289-6

and of the internal friction two samples (U, V), in the shape of bars of dimensions $43 \times 5 \times 0.5$ mm^3 (U) and $47 \times 5 \times 1$ mm^3 (V), were used. The DSC specimens were cut from samples U and V, thus, they had the same microstructure as the IF specimens. Hydrogen was introduced by gas phase–solid surface reaction and its content n_H (n_H = H/Me atomic) was determined gravimetrically.

The Young's modulus was deduced from the resonant frequency of free–free or cantilever flexural resonant modes of the bars and the energy dissipation coefficient Q^{-1} either from the decay of free oscillations or from the bandwidth of the resonance curve. The measurements were carried out as a function of temperature at 0.48 and 1.5 kHz. During the actual measurements under vacuum the rate of temperature change $\dot{T}$ was about 1 K/min, while the measuring strain was of the order of 10^{-7}. A DSC 7 Perkin-Elmer apparatus was used for heat flow measurements, which were carried out at a cooling/heating rate of 10 K/min.

3. Results

3.1. DSC data

The heat flow measurements led to the following characteristic temperatures and enthalpies for the direct (B2→B19) and reverse (B19 →B2) transition, respectively, $M_s = 318$ K, $M_f = 298$ K, $\Delta H_D = -12.7$ kJ/kg and $A_s = 303$ K, $A_f = 320$ K, $\Delta H_R = 12.9$ kJ/kg. All the above temperatures are about 15 °C smaller than the ones reported by Nam et al. [2] and indicate a thermal hysteresis of 17–20 K, which is about two degrees higher than the one (15–18 K) deducible from the data of Nam et al. [2].

3.2. IF and E data

As can be seen in Fig. 1 the IF for the undoped material is very small in the austenite (*A*) ($T > M_s$ (318 K)) while it shows an approximately linear increase with decreasing temperature between M_s and M_f (298 K). At temperatures lower than M_f, in the martensitic state of the sample, the IF is almost temperature independent and shows a hardly noticeable bump at around 100 K. No well-developed peak P_{AM} is seen in the B2–B19 transition region. The IF background of the martensite is relatively high (about 100×10^{-4}), similar to that previously found with the binary alloy $Ni_{50.8}Ti_{49.2}$ [6] and with the ternary alloy $Ni_{40}Ti_{50}Cu_{10}$ both permanently deformed at room temperature and subsequently aged at 673 K for 30 min [4,5]. The Young's modulus of the austenitic phase ($T > M_s$) decreases (softens) with decreasing temperature at a rate much smaller than the one in the two-phase region. This behaviour clearly shows that the physical sources of the softening processes in the two cases are different. Thermal hysteresis of the Young's modulus and of the IF during cooling/heating cycles amounts to about 5–7 K.

Hydrogen impurities introduce a wide tall peak whose temperature is about 290 K (Fig. 2). The peak is steeper on the high temperature side and exhibits a bump (P_H) on its low temperature side at around 260 K. Hydrogen does not significantly affect the Young's modulus of the austenitic phase above A_f while it causes an increase in the Young's modulus of the martensite below M_f. These effects are better seen in Fig. 3, where the reported cooling/heating

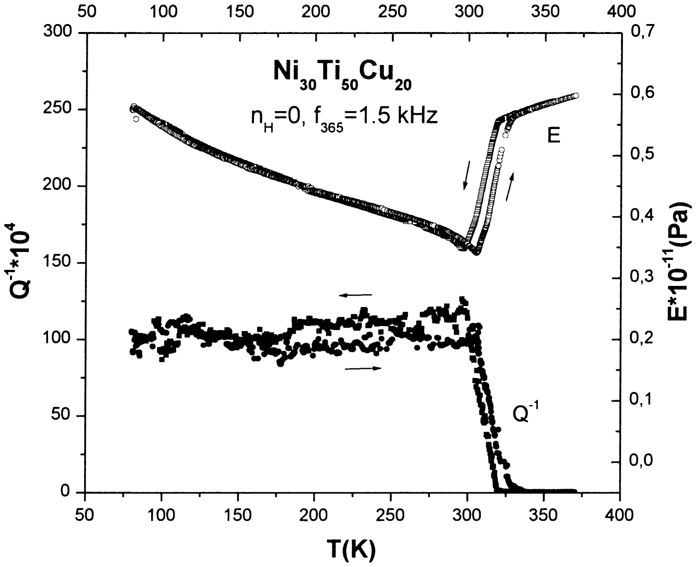

Fig. 1. Temperature dependence of the dissipation coefficient Q^{-1} and of the Young's modulus E as measured during cooling/heating in undoped sample U.

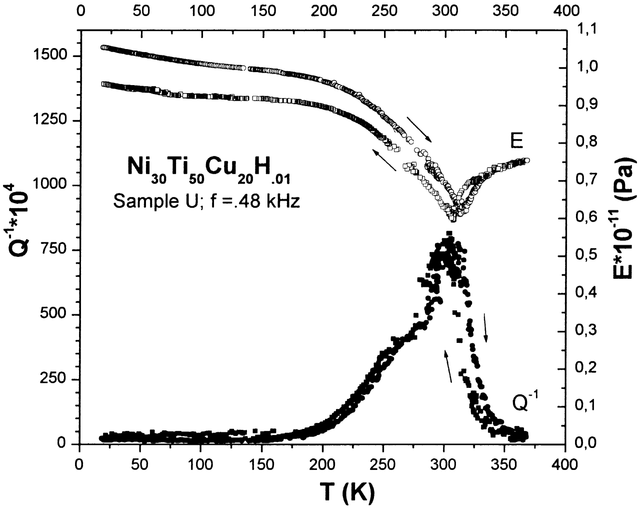

Fig. 2. As in Fig. 1 but for H doped sample U ($n_H = 0.01$).

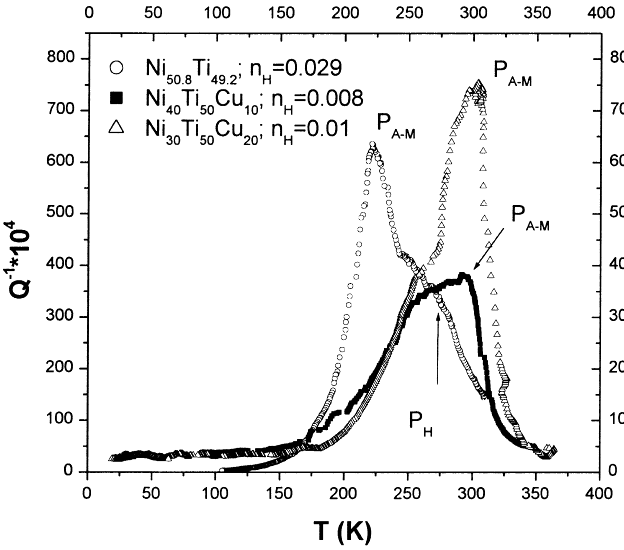

Fig. 4. Comparison of Q^{-1} (T) curves for hydrogen doped sample of $Ni_{50.8}Ti_{49.2}$, $Ni_{40}Ti_{50}Cu_{10}$ and $Ni_{49}Ti_{51}$ alloys.

data refer to both samples used in the present experiments. As can be seen in this figure the depth of the minimum in the Young's modulus, as estimated with respect to the values of E in the austenitic phase, is reduced by hydrogen loading. The thermal hysteresis between cooling and heating curves observed below about 100 K in the H-free and slightly H-doped ($n_H = 0.006$) specimen is due to the B19–B19′ transition, which is seen to occur also in the 20% Cu alloy, contrary to the expectations [2].

In Fig. 4 are shown the IF results obtained at frequencies included between 1.14 and 1.4 kHz, on cooling, with three different alloys charged with H. As can be seen, in all these alloys, besides the transformation peak P_{AM}, a bump P_H occurs. In the case of the binary $Ni_{50.8}Ti_{49.2}$ alloy, which transforms at a lower temperature ($M_s = 228$ K, $M_f = 214$ K), the bump is on the high temperature side of the main peak P_{AM} ($T_{AM} = 224$ K); the reverse is true for the two ternary alloys, which transform at higher temperatures. While the temperature of the main peak P_{AM} is in all cases slightly smaller than M_f, the one of P_H increases with increasing f as it is shown by the plot of Fig. 5, where the logarithm of the vibration frequency is plotted against $1/T_H$ for three different alloys (T_H is the temperature at the peak maximum). The activation enthalpy W and the limiting relaxation time τ_0 derived from the least-square fit

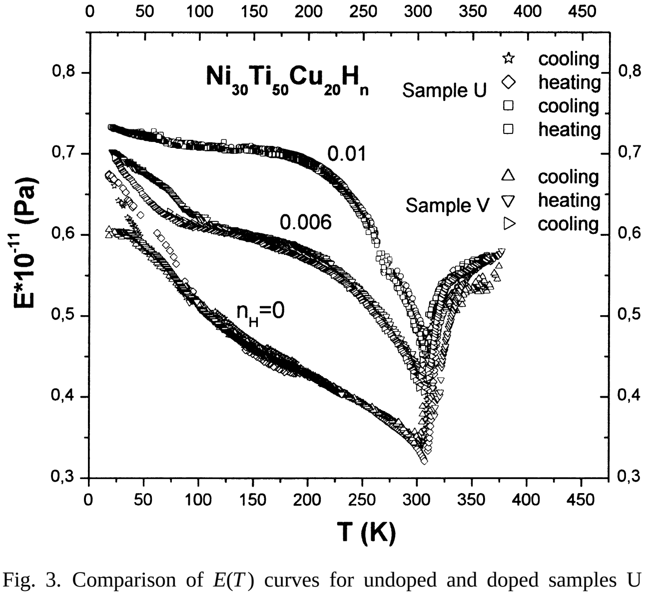

Fig. 3. Comparison of $E(T)$ curves for undoped and doped samples U and V.

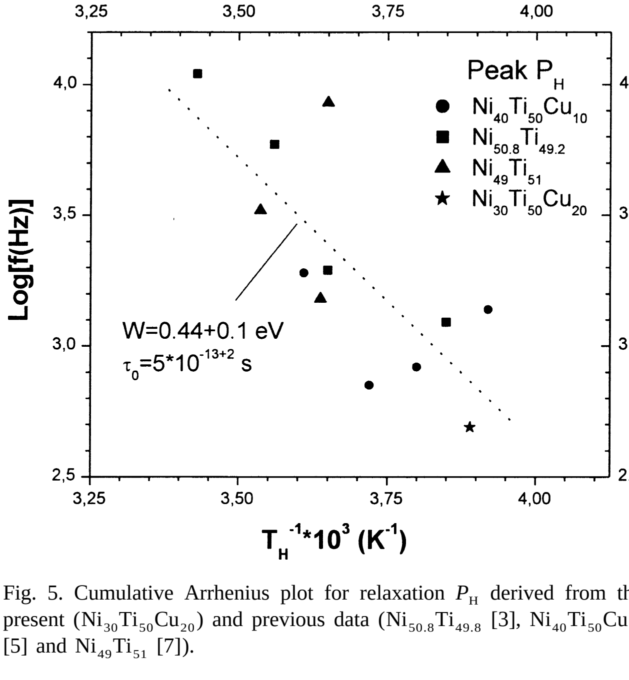

Fig. 5. Cumulative Arrhenius plot for relaxation P_H derived from the present ($Ni_{30}Ti_{50}Cu_{20}$) and previous data ($Ni_{50.8}Ti_{49.8}$ [3], $Ni_{40}Ti_{50}Cu_{10}$ [5] and $Ni_{49}Ti_{51}$ [7]).

to all the data in this figure are 0.44±0.1 eV and $5\times 10^{-13\pm 2}$ s, respectively. These figures differ only slightly from the ones ($W=0.5$ eV; $\tau_0=(1\text{–}4)\times 10^{-12}$ s) deduced from a fit to the only data points relative to the binary alloy $Ni_{50.8}Ti_{49.2}$ [3].

4. Discussion and conclusions

The main questions to be addressed now are about the nature of (a) the main peak P_{AM} occurring at the transition temperatures in the presence of H impurities, (b) the increase induced by H in the Young's modulus of the martensite, (c) the damping of the H-free martensite and, finally, (d) the peak P_H. Some of these issues have already been discussed with reference to the binary alloys $Ni_{50.8}Ti_{49.2}$ and $Ni_{49}Ti_{51}$ [7] as well as with the ternary alloy $Ni_{40}Ti_{50}Cu_{10}$ [4,5]. The present data shed new light on stress-induced motions of H and on H-twin boundary interactions substantially confirming our earlier views. In particular, the increase of E and the decrease of Q^{-1} induced by H in the martensitic state, now also found in the $Ni_{30}Ti_{50}Cu_{20}$ alloy, clearly appears to be due to pinning by H of twin boundaries.

The P_H peak is now proved to be a thermally activated relaxation process whose temperature is not related to the transition temperatures but, rather, to the vibration frequency as evidenced by the comparisons made in Fig. 4. The relaxation parameters, although still affected by high uncertainty, due to the large scatter of data points in Fig. 5, are, nevertheless, now more accurately determined.

The dramatic effect of H on peak P_{AM} is now well documented also for the B2–B19 transition. This finding shows that the peak, although intimately related to the transition, as indicated by its occurrence at all times just below M_s, is nevertheless, extremely sensitive to H impurities. Therefore, P_{AM} is not to be regarded as an intrinsic effect of the transition but, rather, as an extrinsic one, most probably associated with complexes formed by H atoms and twin boundaries and/or phase interfaces. Actually, the peak is much wider than the transition temperature region as it lies to a large extent over temperatures ranges where the only martensitic phase B19 is present. This means that the structural mechanism of the peak is operative also in the fully martensitic state. This suggests that the peak involves twin boundaries and cannot be due only to stress-assisted motions of phase interfaces. For the same reason, stress-induced collective motions of strongly interacting twin boundaries located within isolated martensite plates, embedded in the austenite matrix, cannot be the only operating mechanism, as it would require the presence of both phases simultaneously.

As shown by Fig. 4, peak P_{AM} occurs all the time at a temperature slightly smaller than M_f, independently of the vibration frequency, this is probably indicative of the fact that only in the proximity of the martensitic transitions the mobility of twin boundaries and phase-interfaces rapidly changes with temperature. Wang and co-workers [8–11] have studied the viscous motion of domain walls under an alternating stress and have reached the conclusion that an anelastic relaxation may occur just below the temperature T_c of second-order phase transitions. The relaxation time was found to depend on temperature according to the relation

$$\tau = \tau_0 \exp[-B/(T_c - T)] \tag{1}$$

where B and τ_0 are constants independent of T. It is possible that a mechanism similar to the one elaborated by these authors also applies for peak P_{AM}, in spite of the fact that the martensitic transition is first order. In the present case the viscosity for the twin boundaries motions would be provided by H atoms rather than by phonons.

Acknowledgements

The authors gratefully acknowledge financial support from Progetto Strategico Materiali Speciali per Tecnologie Avanzate of CNR.

References

[1] T. Saburi, in: K. Otsuka, M. Wayman (Eds.), Shape Memory Materials, Cambridge University Press, London, 1998.

[2] T.H. Nam, T. Saburi, K. Shimizu, Mater. Trans. JIM 31 (1990) 950.

[3] A. Biscarini, B. Coluzzi, R. Campanella, G. Mazzolai, L. Trotta, A. Tuissi, F.M. Mazzolai, Acta Mater. 47 (1999) 4525.

[4] A. Rotini, A. Biscarini, R. Campanella, B. Coluzzi, G. Mazzolai, F.M. Mazzolai, Scripta Mater. 44 (2001) 719.

[5] F.M. Mazzolai, A. Biscarini, R. Campanella, B. Coluzzi, G. Mazzolai, A. Rotini, A. Tuissi, Acta Mater. (2002) (in press).

[6] B. Coluzzi, A. Biscarini, R. Campanella, L. Trotta, G. Mazzolai, A. Tuissi, F.M. Mazzolai, Acta Mater. 47 (1999) 1965.

[7] A. Biscarini, R. Campanella, B. Coluzzi, L. Di Masso, G. Mazzolai, F.M. Mazzolai, in: M. Koiwa, K. Otsuka, T. Miyazaki (Eds.), Proc. Internat. Conf. on Solid–Solid Phase Transformations '99 (JIMC-3), JIM, 1999.

[8] Y.N. Huang, Y.N. Wang, H.M. Shen, Phys. Rev. B 46 (1992) 3290.

[9] Y.N. Wang, Y.N. Huang, H.M. Shen, Z.F. Zhang, J. Phys. III 6 (1996) C8–505.

[10] Y.N. Wang, Y.N. Huang, J. Alloys Comp. 211–212 (1994) 356.

[11] Y.N. Huang, X. Li, Y. Ding, H.M. Shen, Z.F. Zhang, Y.N. Wang, C.F. Fang, H.S. Zhuo, J. Phys. III 6 (1996) C8–815.