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Diffusion of hydrogen in the shape memory alloy $Ni_{47}Ti_{40}Hf_{10}Cu_3$

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Abstract

The H chemical diffusion coefficient D_c has been determined in the $Ni_{47}Ti_{40}Hf_{10}Cu_3$ alloy from the kinetics of the gas/solid-surface reaction in the temperature range 350–1000 K. The mobility of H was also investigated by mechanical spectroscopy at temperatures included between 240 and 260 K, where a Snoek internal friction peak occurs for frequencies in the kHz range. The results on the Einstein diffusion coefficient D_E obtained from the relaxation time of the Snoek effect were correlated to the high temperature absorption results. Combined Arrhenius plots of D_E and D_c data allow to determine the H diffusion parameters to: $W = 0.47 \pm 0.01$ eV, $D_0 = 2 \times 10^{-3.0\pm0.2}$ cm^2/s.

Keywords: Internal friction; H diffusion; NiTiHfCu shape memory alloys; Martensitic transition

1. Introduction

NiTi-based alloys are the most important shape memory materials as they exhibit a remarkable shape effect, good stability of their properties with respect to thermal cycling and very good mechanical and corrosion resistance. As it is well known the shape memory effect is due to martensitic transitions that lead these alloys from a high temperature cubic (CsCl) austenite to structures of lower symmetry, which, according to the system and to the history of the material, may be monoclinic B19' (NiTi, NiTiHf(Cu)), orthorhombic B19 (NiTiCu), or trigonal R (NiTi). Within this class of materials, the ternary NiTiHf and quaternary NiTiHfCu alloys have attracted much attention as high temperature shape memory alloys [1–9].

H impurities affect the martensitic transitions of NiTi-based alloys as well as the twin boundary mobility, which is responsible for the high damping capacity of these materials [10–16]. Thus, it is of importance to fully characterise the H behaviour in these alloy systems, where only few investigations have been carried out so far dealing with the diffusion and solubility of H as well as hydride formation [17–19].

2. Experimental

An ingot of NiTiHfCu with nominal composition of 47 at.% Ni, 40 at.% Ti, 10 at.% Hf and 3 at.% Cu was prepared at CNR-IENI by vacuum induction melting. Two bars, S and T, of initial dimensions 44.9 mm×5.2 mm×0.89 mm (S) and 44.9 × 5.2 × 1.05 mm^3 (T) were machined from the ingot and solution treated at 1173 K for 1 h and, finally, water quenched. Two kinds of experiments were carried out. One involves measurements at low temperatures ($20\,K < T < 400\,K$) of internal friction (IF), Young's modulus (E) and heat flow (DSC), the other consists in measurements at high temperatures ($323\,K < T < 1000\,K$) of the H-gas pressure during isothermal absorption. H loading was performed through the gas/solid-surface reaction and n_H determined by monitoring changes in the sample weight or in the gas pressure.

The Young's modulus E was deduced from the resonant frequency f of free–free or cantilever flexural modes of the bars and the IF from the free decay of the sample vibrations or from the bandwidth of its resonance curve. A DSC

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7 Perkin-Elmer apparatus was used for the 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 have been made both in the H-free and -doped material. The martensitic transition was found to be hardly affected by H impurities for $n_H \leq 0.03$ and almost fully suppressed for $n_H = 0.10$ as seen in the heat flow data of Fig. 1.

3.2. IF and E data

The IF of sample S as measured by using free–free or cantilever flexural modes is reported in Fig. 2 for various H contents n_H and various frequencies f. As can be seen, peak P_H occurs at all times, regardless of the H content, while peak $P_{H'}$ only appears for $n_H \leq 0.01$. It is worth noting that P_H takes place in the martensitic state for $n_H \leq 0.01$ and in the austenitic state for $n_H \geq 0.05$. In both cases the peak temperatures are about the same for comparable frequencies indicating that the relaxation time does not appreciably differ in the two lattice structures. As already reported [15], both peaks correspond to thermally activated relaxation processes, whose parameters are: $W_H = 0.6 \pm 0.1\,\text{eV}$, $\tau_{0H} = 2 \times 10^{-(16\pm1)}\,\text{s}$ and $W_{H'} = 0.010 \pm 0.003\,\text{eV}$, $\tau_{0H'} = 3 \times 10^{-(5.0\pm0.3)}\,\text{s}$. As expected [20] a relaxation in the Young's modulus accompanies each IF peak as shown by the S-shaped $E(T)$ curves in the temperature regions of the two peaks.

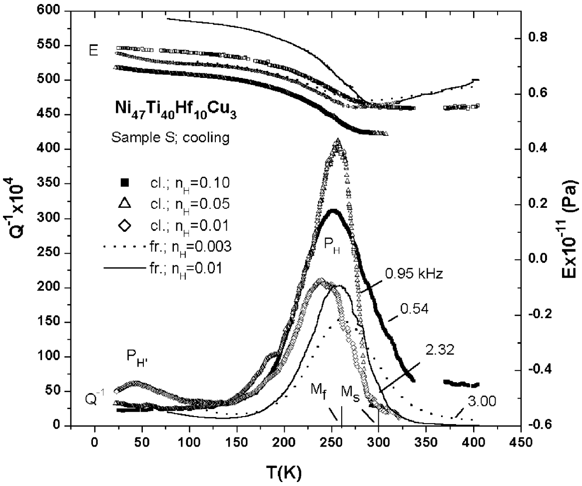

Fig. 2. Temperature dependence of the dissipation coefficient Q^{-1} and of the Young's modulus E of sample S containing various amounts of H.

Differently from peak P_H, which is also found in NiTi [10,13–15] and NiTiCu alloys [11,12], peak $P_{H'}$ only appears in the alloy NiTiHfCu containing Hf, which has a stronger affinity for H than Ti. In this alloy substitution of Hf for Ti and Cu for Ni occurs and H atoms are expected to occupy octahedral interstitial sites of type (Ni, Cu)$_2$(Ti, Hf)$_4$ [17,18], that is, sites having two Ni(Cu) atoms as nearest neighbours and four Ti(Hf) atoms as next nearest neighbours. P_H is believed to be due to the stress-induced reorientation of H elastic dipoles taking place through classical over-barrier jumps between adjacent (Ni, Cu)$_2$(Ti, Hf)$_4$ sites. In view of its extremely low activation energy and of its appearance only in the alloy containing Hf, $P_{H'}$ is attributable to quantum-mechanical transitions of H bound to Hf atoms. These transitions are expected to take place between closely spaced adjacent tetrahedral sites [15]. As can be seen in Fig. 3 the height Q_M^{-1} of peak P_H linearly increases with increasing n_H from 0 to 0.03, in agreement with previous data established on a Ni$_{50.8}$Ti$_{49.2}$ binary alloy [10] also included in Fig. 3. For higher values of n_H, Q_M^{-1} behaviour deviates from linearity

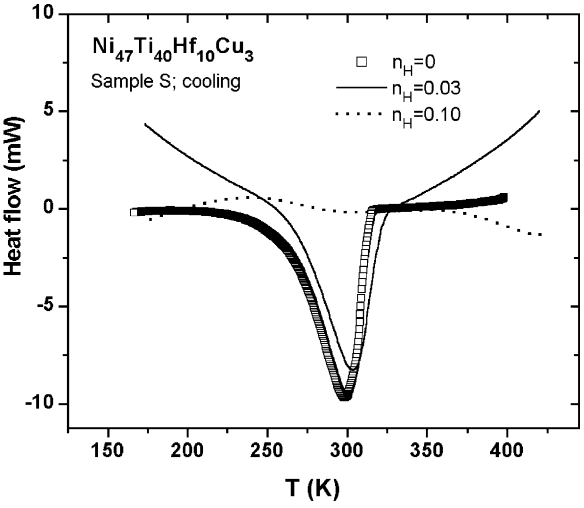

Fig. 1. Temperature dependence of heat flow as measured for different H contents n_H.

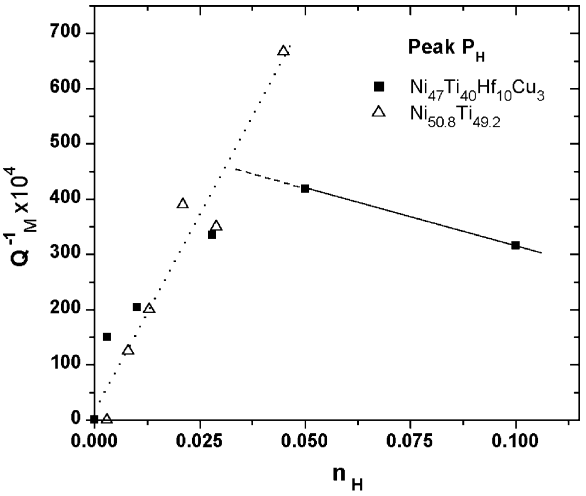

Fig. 3. Dependence of the height of peak P_H on the H content n_H (n_H = H/Me at.).

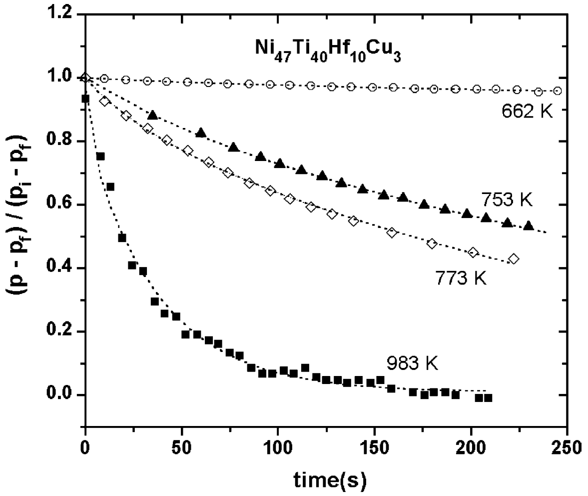

Fig. 4. Normalised pressure data taken during H absorption at the indicated temperatures. The dotted lines represent fits to the experimental data of relation (2) in the text.

and for the highest value of n_H it even exhibits a slight decrease.

3.3. *Absorption/desorption data*

In Fig. 4 normalised isothermal pressure data obtained during H absorption at several different temperatures are reported as a function of time. In this figure the dotted lines are fits to the experimental data according to relation (2). The fits are good, indicating that the absorption rate is controlled by H diffusion in the bulk.

As shown in Fig. 5 thermal desorption of H during heating occurs at rather high temperature. As can be seen in Fig. 6 the derivative dP/dT of the desorption curves exhibits a single wide peak likely due to the hydride dissociation.

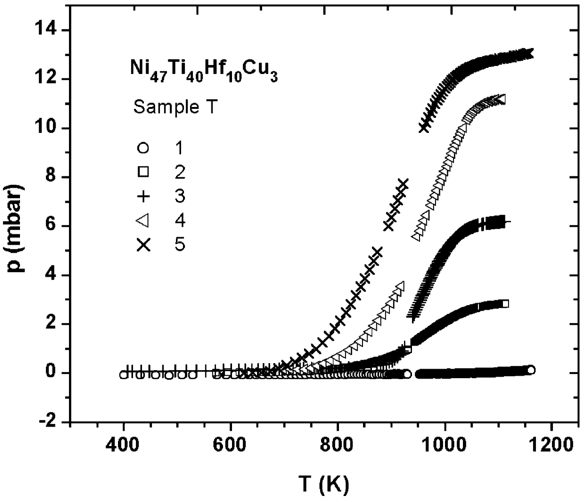

Fig. 5. Desorption data during heating of sample T pre-loaded with different amounts of H.

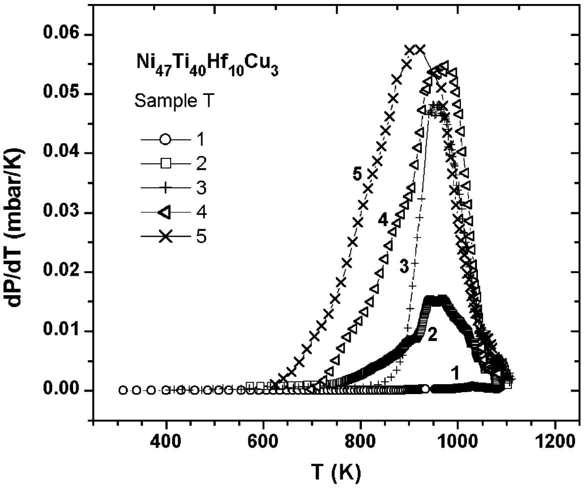

Fig. 6. Time derivative of the pressure curves as represented in Fig. 5.

4. Discussion

Peak P_H occurring in NiTi and NiTiCu alloys has previously been interpreted as an H-Snoek (or H-Zener) effect [10] based on the fact that its height Q_M^{-1} linearly increased with increasing n_H (see Fig. 3). The present data confirm this view and also help to discriminate between the two proposed alternatives (Snoek or Zener). As a matter of fact, according to a Snoek-type of mechanism an increase should take place in the peak height for n_H varying from zero to the H solubility limit, α_{max}, in the α phase. However, for larger values of n_H a slight decrease should occur, due to an increase in the volume fraction of the hydride with respect to the α phase. In the case of the Zener effect the relaxation mechanism is expected to be operative within the hydride, thus, P_H should appear for $n_H = \alpha_{max}$ and beyond this limit it should increase with n_H. From the present data of Fig. 3 the conclusion can be drawn that P_H is a Snoek-type of relaxation.

For H jumps between two adjacent interstitial sites of the type (Ni, Cu)$_2$(Ti, Hf)$_4$ the following relationship holds between D_E and the relaxation time of the Snoek effect in the cubic austenite:

$$D_E = \frac{1}{6}\left(\frac{a_0^2}{2}\right)\left(\frac{2}{3\tau_R}\right) \tag{1}$$

where a_0 is the lattice parameter. Within the monoclinic B19' lattice structure of the martensite a variety of non-equivalent jumps of H atoms could take place between adjacent (Ni, Cu)$_2$(Ti, Hf)$_4$ sites and separate IF peaks could appear in the Q^{-1}(T) curves. Actually, this does not happen indicating that the jump frequencies are very similar. Furthermore, because P_H occurs at about the same temperature both in the austenite ($n_H \geq 0.05$) and in the martensite ($n_H \leq 0.03$) relation (1) also applies for the martensite. The results of D_E calculation are reported in Fig. 7.

The solution of the second Fick's equation, under boundary and initial conditions appropriate for the present

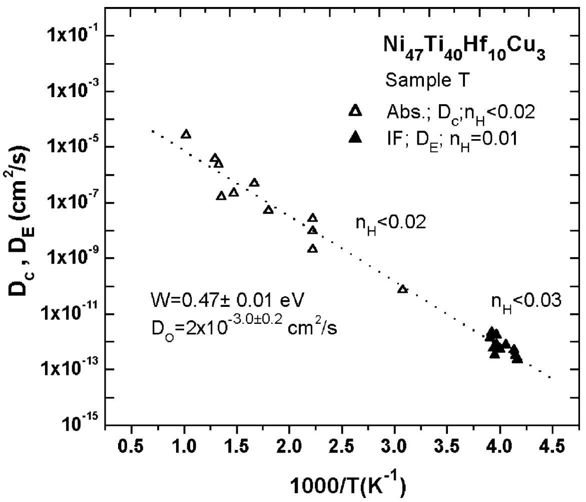

Fig. 7. Chemical (D_c) and Einstein (D_E) diffusion coefficients as deduced from absorption (D_c) and internal friction (D_E) data at low H contents.

absorption experiments [21] gives the following time dependence for the H-gas pressure P:

$$P(t) = P(\infty) + [P(0) - P(\infty)]\frac{8}{\pi^2}\sum_{j=0}^{\infty}\frac{1}{(2j+1)^2}\exp \times \left\{-\left[\frac{(2j+1)\pi}{h}\right]^2\frac{t}{\tau}\right\} \qquad (2)$$

where $\tau = h^2/\pi^2 D_c$ is the time constant of the absorption process, D_c the chemical diffusion coefficient and h the sample thickness. As it is well known $D_c = (\rho/RT)(\partial\mu/\partial\rho)D_E$ [22] (μ is the chemical potential of H within the sample, ρ the number of H atoms per unit volume within the sample and R the gas constant). At low H densities $\partial\mu/\partial\rho \cong RT/\rho$ and, consequently, $D_c \cong D_E$. Hence, the low H content data obtained from absorption and IF experiments can be compared to one another as reported in Fig. 7. As seen all the data dots are aligned along the same straight line indicating that D_c and D_E well coincide. The diffusion parameters deduced from Fig. 6, which cover about eight orders of magnitude, are $W = 0.47 \pm 0.01$ eV; $D_0 = 2 \times 10^{-(3.0\pm0.2)}$ cm^2/s.

5. Conclusions

From the previous discussion the following conclusions can be drawn.

(a) Hydrogen loading at H contents $n_H \geq 0.05$ suppresses the martensitic transition in the $Ni_{47}Ti_{40}Hf_{10}Cu_3$ alloy; (b) the peak P_H is a Snoek effect; (c) the diffusion coefficients in both the austenitic and martensitic structures, as measured for the first time in a NiTiHfCu alloy, are very similar.

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