

Solubility and diffusion of hydrogen in $\text{TiNi}_{1-x}\text{Cu}_x$ ($x = 0.2$ and 0.4) shape memory alloys

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Abstract

The solubility of hydrogen has been determined between about 700 and 1250 K in the austenitic phase of the $\text{TiNi}_{0.8}\text{Cu}_{0.2}$ and $\text{TiNi}_{0.6}\text{Cu}_{0.4}$ shape memory alloys for hydrogen contents n_{H} ($n_{\text{H}} = \text{H/f.u.}$) ≤ 0.048 . The solubility was found to obey the Sieverts law and decrease with increasing the copper content; the values of the partial molar enthalpy and partial molar non-configurational entropy of solution per mole of hydrogen are:

$$\Delta H_{\text{H}}^0 = -28 \pm 2 \text{ (kJ/mol)}; \quad \Delta S_{\text{H}}^{\text{nc}} = -80 \pm 2 \text{ (J/mol K)} \quad (\text{TiNi}_{0.8}\text{Cu}_{0.2})$$

$$\Delta H_{\text{H}}^0 = -31 \pm 3 \text{ (kJ/mol)}; \quad \Delta S_{\text{H}}^{\text{nc}} = -88 \pm 4 \text{ (J/mol K)} \quad (\text{TiNi}_{0.6}\text{Cu}_{0.4})$$

The chemical diffusion coefficient D_{c} of H was determined for the $\text{TiNi}_{0.8}\text{Cu}_{0.2}$ alloy by fitting the isothermal pressure versus time absorption curves to a relationship derived from the second Fick's equation for diffusion. The data for D_{c} are in good agreement with those of the Einstein diffusion coefficient D_{E} prior determined by the Snoek anelastic relaxation peak due to hydrogen. The activation energy W and the pre-exponential factor D_0 deduced from the composite Arrhenius plot of the absorption and Snoek relaxation data for the $\text{TiNi}_{0.8}\text{Cu}_{0.2}$ alloy are: $W = 0.53 \pm 0.02$ eV, $D_0 = (3 \pm 2) \times 10^{-7} \text{ m}^2/\text{s}$. A comparison of the present results with those available for other NiTiCu alloy compositions shows a gradual decrease of D_{c} with increasing the copper content x from 0 to 0.4.

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1. Introduction

As it is well known NiTi-based alloys are a very important class of functional materials as they exhibit shape memory effect and super-elasticity [1]. These alloys are of some interest also for the ability, in their martensitic state and at sufficiently high stresses, to convert mechanical energy into heat through stress-assisted motions of twin boundaries [2]. Recently, it has been shown that small additions of H make these alloys really high damping materials even at low stress amplitudes [3], due to anelastic processes, which for appropriate compositions and thermo-mechanical treatments of the alloys, may occur at around room temperature [4–6]. Of particular interest, under this

respect, is the NiTiCu alloy system which is found to exhibit very high damping levels at around 293 K [7,8].

Hydrogen behaviour in the binary alloy NiTi has been studied by several groups [9–11], including ours [12], and to date the diffusivity [9,12] and solubility [9] of H as well as hydride structures [10] are rather well known, at high temperatures. Instead not much is known about H behaviour in the NiTiCu alloy system. The diffusion coefficient has only been measured in a 20% Cu alloy [13], while no information is apparently available regarding the H solubility for any alloy composition. Thus, the main aim of this work was to characterise the general trends of diffusivity and solubility in this alloy system.

2. Experimental

Two ingots of NiTiCu with nominal atomic compositions $\text{TiNi}_{0.8}\text{Cu}_{0.2}$ and $\text{TiNi}_{0.6}\text{Cu}_{0.4}$ were prepared at IENI-CNR by vacuum induction melting. Two samples in the shape of plates of dimensions $5 \text{ mm} \times 45 \text{ mm} \times 0.515 \text{ mm}$ ($\text{TiNi}_{0.8}\text{Cu}_{0.2}$) and $5 \text{ mm} \times 45 \text{ mm} \times 1.02 \text{ mm}$ ($\text{TiNi}_{0.6}\text{Cu}_{0.4}$) were cut from the

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ingots by spark erosion. The samples were annealed under vacuum at 1173 K for 2 h and then rapidly cooled (200 K/min) in the furnace. Hydrogen was introduced into the material by the gas-phase/solid-surface reaction method and its content n_H ($n_H = H/f.u.$) was determined both gravimetrically and volumetrically to an accuracy of 0.006. The calibrated experimental chamber of about 200 cm³ volume, sealed with all metal gaskets, was evacuated by a pumping system composed of a rotary and a turbo-molecular pump. The absorption of hydrogen at constant temperature was monitored through the measurement of the gas pressure by a sensitive Datametrix capacitance manometer.

The chemical diffusion coefficient (D_c) of hydrogen was determined by using the following relation between the H-gas pressure P and time t ,

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

which was deduced from the second Fick's equation solved under boundary and initial conditions appropriate for the present absorption experiments [12–14]. Here $\tau = h^2/\pi^2 D_c$ is the time constant of the absorption process, h the sample thickness, P_i and P_f are the initial and final pressure, respectively.

3. Results

Two sets of normalised absorption isotherms are represented in Figs. 1 and 2 with the associated best fit curves (dotted lines) to relation (1), obtained using the diffusion coefficient D_c as the fitting parameter. The fits are reasonably good for temperatures higher than about 850 K, indicating that the absorption process at high temperatures is surely controlled by bulk diffusion. Below 850 K deviations from relation (1) were observed, which suggested some effect of surface energy barriers on the rate of H absorption. Thus, only data for $T > 850$ K were used to deduce the H chemical diffusion coefficient D_c , while for the H solubility determination, which is not affected by the pressure versus time relationship, also data taken at lower temperatures were used. The best fit values of D_c for the TiNi_{0.8}Cu_{0.2} alloy are plotted versus T^{-1} in the semi-logarithmic plot of Fig. 3. These data represent average values of several absorption processes carried out at each temperature for different H contents ($n_H = H/f.u. \leq 0.010$). In the same figure are also

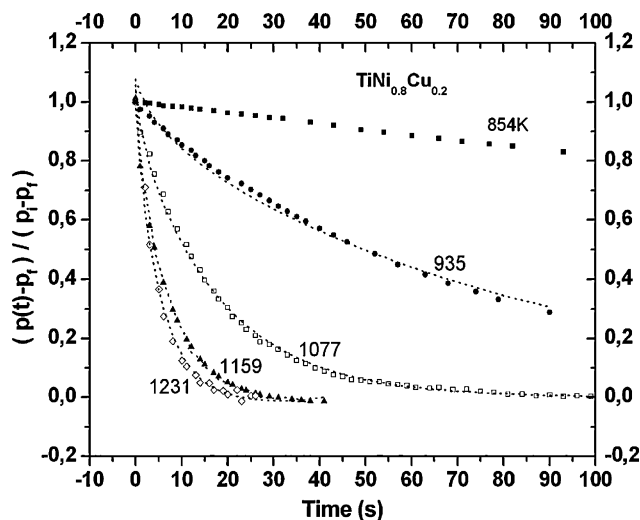


Fig. 1. Normalised pressure data taken during H absorption at the indicated temperatures with the TiNi_{0.8}Cu_{0.2} alloy. The dotted lines represent fits to the experimental data of relation (1) in the text.

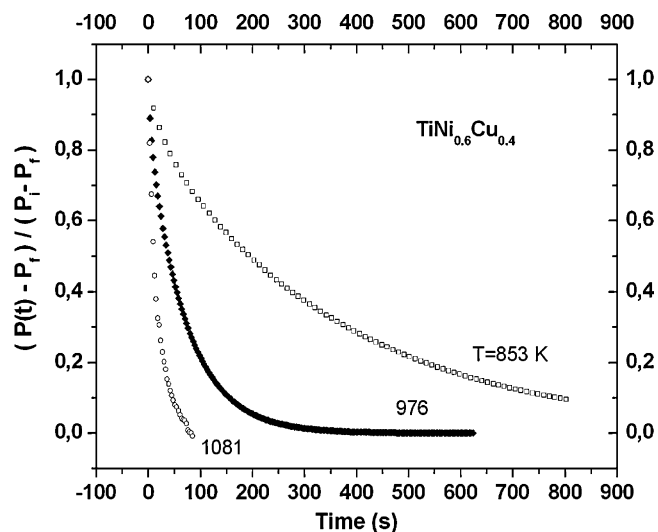


Fig. 2. As in Fig. 1 but for the TiNi_{0.6}Cu_{0.4} alloy.

reported the regression lines to data points for the Ni_{50.8}Ti_{49.2} [12] and TiNi_{0.60}Cu_{0.40} [13] alloys. It is useful to recall at this point that the alloys are in their cubic B2 (CsCl-type structure) austenitic states at the temperatures of the present absorption experiments ($T \geq 725$ K). As a matter of fact, the martensite start-temperatures M_s for the investigated alloys are only slightly higher than room temperature (315 K for TiNi_{0.8}Cu_{0.2} and 325 K for TiNi_{0.6}Cu_{0.4}). The low temperature data points of Fig. 3 taken from Refs. [8,13] were deduced from the anelastic Snoek relaxation due to stress-induced local motions of H atoms within the orthorhombic B19 structure of the martensite. They, actually, represent a measure of the Einstein (tracer) diffusion coefficient (D_E) rather than of D_c . Thus, in principle, the absorption and Snoek data would not be comparable one with the other. However, at the low H contents of the present experiments D_E

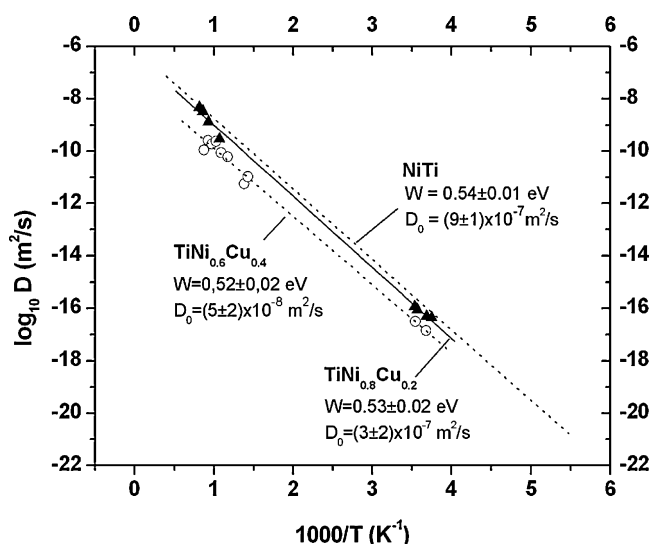


Fig. 3. The high temperature data points represent the chemical diffusion coefficient (D_c) deduced from absorption experiments; the low temperature data represent the Einstein (tracer) diffusion coefficient (D_E) obtained from the Snoek effect of H (Ref. [7] for TiNi_{0.8}Cu_{0.2} and [13] for TiNi_{0.6}Cu_{0.4}). The line for the binary alloy NiTi is from previous absorption/Snoek data [12].

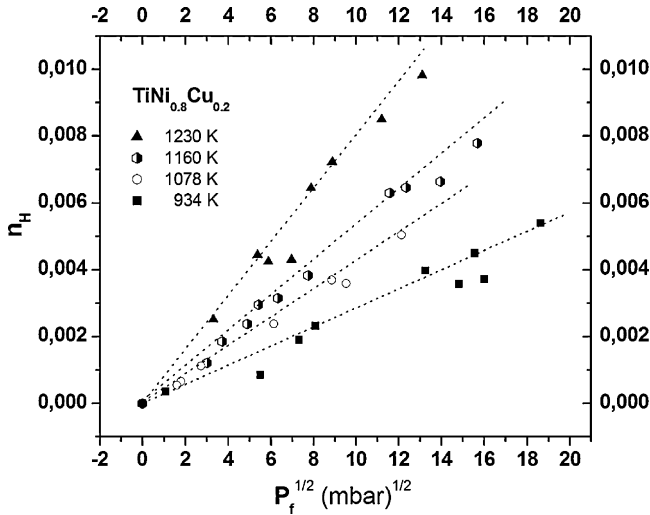


Fig. 4. Pressure-composition isotherms for H in the $\text{TiNi}_{0.8}\text{Cu}_{0.2}$ alloy. In the figure n_{H} ($n_{\text{H}} = \text{H/f.u.}$) is plotted against the square root of p in order to test the Sieverts law (relation (2) in the text).

and D_{C} are expected to approximately coincide [15]. Furthermore, no appreciable differences have been observed between the values of D_{E} as measured in the austenite B2 and in the martensite B19' (or trigonal R) in the case of the $\text{Ni}_{50.8}\text{Ti}_{49.2}$ alloy. This finding suggests a substantial insensitivity of D_{E} to the lattice structure. Therefore, the comparison made in Fig. 3 between the absorption/austenite and anelastic/martensite data seems to be essentially correct. The linear regression through all the experimental points (absorption and Snoek-effect) gives the diffusion parameters reported in the same figure. As seen, the diffusion coefficient at all temperatures gradually decreases with increasing the copper content x from 0 to 0.4.

Figs. 4 and 5 show that n_{H} linearly varies with the square root of pressure as predicted by the Sieverts law, which implies ideal behaviour of the H gas,

$$n_{\text{H}} = K_{\text{s}} \sqrt{p} \quad (2)$$

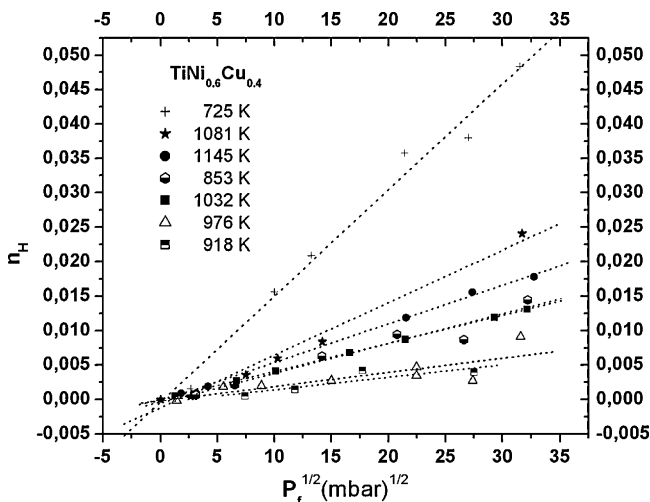


Fig. 5. As in Fig. 4 but for the $\text{TiNi}_{0.6}\text{Cu}_{0.4}$ alloy.

K_{s} has the following expression [16]

$$K_{\text{s}} = \beta \exp \left(\frac{\Delta S_{\text{H}}^{\text{nc}}}{R} - \frac{\Delta H_{\text{H}}^0}{RT} \right). \quad (3)$$

where R is the gas constant, β the number of interstitial sites per formula unit, ΔH_{H}^0 and $\Delta S_{\text{H}}^{\text{nc}}$ are the partial molar enthalpy and partial molar non-configurational entropy of H solution, respectively. The quantities $\Delta H_{\text{H}}^0 = H_{\text{H}} - (1/2)H_{\text{H}_2}^0$ and $\Delta S_{\text{H}}^{\text{nc}} = S_{\text{H}}^{\text{nc}} - (1/2)S_{\text{H}_2}^0$ represent the differences between the partial molar enthalpies and entropies of H atoms in solid solution and in the standard gaseous state, respectively. Following [9], we assume occupancy of octahedral interstitial sites by H in the NiTiCu alloys and, consequently, $\beta = 3$. In Fig. 6, the natural logarithm of K_{s} is plotted against T^{-1} . As seen, the data points are approximately aligned along straight lines in agreement with relation (3). This result, combined with the linear behaviour of n_{H} versus \sqrt{p} observed in Figs. 4 and 5, indicates that under the present investigation conditions ($p < 1.2$ bar; $725 \text{ K} < T < 1250 \text{ K}$) H–H interactions are negligible. As deduced from inspection of Fig. 6 and relation (2) the H solubility for a given pressure increases with decreasing temperature; this means that the H absorption process is exothermic.

The slope and y-intercept of the straight lines in Fig. 6 represent $-\Delta H_{\text{H}}^0/1000R$ and $\Delta S_{\text{H}}^{\text{nc}}/R + \ln \beta$, respectively, and give

$$\Delta H_{\text{H}}^0 = -28 \pm 2 \text{ (kJ/mol)};$$

$$\Delta S_{\text{H}}^{\text{nc}} = -80 \pm 2 \text{ (J/mol K)} \quad (\text{TiNi}_{0.8}\text{Cu}_{0.2})$$

$$\Delta H_{\text{H}}^0 = -31 \pm 3 \text{ (kJ/mol)};$$

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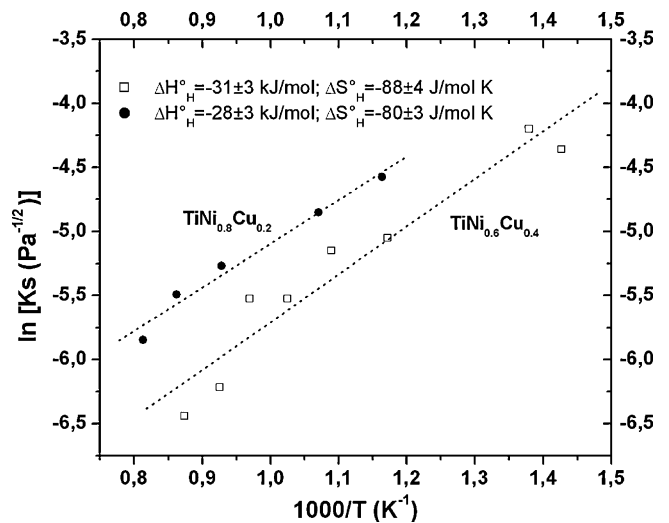


Fig. 6. Logarithmic plot of the solubility constant K_{s} against T^{-1} . The slope and the y-intercept of the fitting straight lines allow the calculation of the partial molar enthalpy and of the partial molar non-configurational entropy of H solution, respectively.

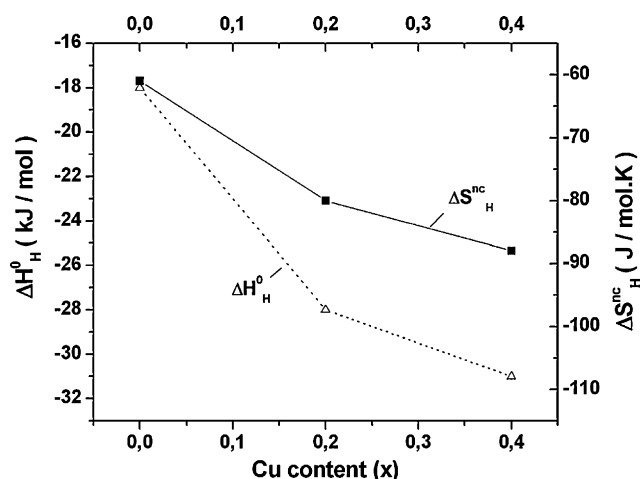


Fig. 7. Dependence on the copper content of the partial molar enthalpy and entropy. Data for the binary NiTi alloy are from Ref. [9].

As seen in Fig. 7, where data for the binary NiTi alloy [9] are also plotted, both the enthalpy and entropy decrease with increasing copper content.

4. Discussion and conclusions

The results in Fig. 3 show that for NiTiCu alloys the values of the H diffusion coefficient is much smaller (one order of magnitude at 1000 K) and those of the associated activation energy W much higher than the ones encountered with the bcc refractory metals Nb, Ta and V [15]. The values of these two quantities, actually, more closely resemble the ones found for fcc metal alloys, where H atoms usually sit in octahedral interstitial sites. This fact supports the assumption of octahedral site occupancy advanced by Wipf and co-workers [9] and suggests that in NiTi-based alloys quantum effects do not play any role for temperatures higher than about 250 K. The values of the solution enthalpy and entropy reported here are in agreement with those by Wipf and co-workers for the binary equi-atomic NiTi alloy: $\Delta H_H^0 = -18 \pm 4$ kJ/mol; $\Delta S_H^{nc} = -61 \pm 4$ J/mol K [9]. The overall data show that the H absorption process becomes gradually more exothermic with increasing copper content. This is most likely due to the lattice dilation caused by copper [17].

From the present and previous sections, it has become apparent that H diffusivity and solubility in NiTiCu alloys exhibit

similar trends as they both decrease with increasing copper content. Furthermore, the present data suggest a substantial insensitivity of the H mobility to the lattice structure of these alloys, namely, in an Arrhenius plot of D , the data points for the cubic B2 austenite and orthorhombic B19 martensite fall on the same straight line.

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