

Transport properties of some hydrogenated nickel-based alloys

A.W. Szafrński*

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

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Abstract

Nickel-based alloys – $\text{Ni}_{0.98}\text{Ti}_{0.02}$, $\text{Ni}_{0.4}\text{Cu}_{0.6}$ (constantan) and $\text{Ni}_{0.9}\text{Cr}_{0.1}$ (chromel) have been saturated with hydrogen at ca. 1 GPa at room temperature. The electrical resistance and thermoelectric power of the hydrogenated samples have been simultaneously measured in the temperature range between 80 and 300 K. The electrical resistance of Ni–Ti/H and Ni–Cu/H alloys exhibits an anomalous behavior. The temperature dependent component of the resistance of the $\text{Ni}_{0.98}\text{Ti}_{0.02}$ alloy increases upon hydrogenation and *continues* its increase when hydrogen is desorbed in a stepwise manner. The hydrogenation of $\text{Ni}_{0.4}\text{Cu}_{0.6}$ results in a *decrease* of electrical resistance while the opposite effect is usually observed in other hydrogenated Pd- and Ni-based alloys.

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1. Introduction

The nickel–copper ($\text{Ni}_{1-x}\text{Cu}_x$) alloys form a series of solid solutions in the whole range of the alloy compositions. The hydrogen-free nickel-rich alloys are ferromagnetic. The increase of the copper content is accompanied by a decrease of the Curie temperature, and finally, for a Cu content exceeding ca. 60%, the alloys are non-magnetic. Because of its large thermoelectric power, the $\text{Ni}_{0.4}\text{Cu}_{0.6}$ alloy together with copper forms a copper-constantan thermocouple commonly used in the 50–700 K range.

The Ni/Me/H alloys exist either as solid solution of hydrogen in the metal (α -phase) or hydride (β -phase). In the case of the Ni-rich alloys, at room temperature, the α -phase contains very small amount of hydrogen. On the other hand, the hydrogen content in the hydride is not far from the stoichiometric value, $\text{H/Me} = 1$.

At room temperature, a miscibility gap exists in the $\text{Ni}_{1-x}\text{Cu}_x\text{–H}$ alloy system for $x < 0.6$ [1], but the hydrogenated constantan ($x = 0.6$) is a mono-phase alloy. The

maximal solubility of hydrogen ($\text{H/Ni} \sim 1$ for pure nickel) decreases with increasing copper content [1,2] in a nearly linear manner up to $x \sim 0.6$. Above this x -value the hydrogen solubility is low. Both effects are related to a gradual filling of the empty states at the top of the nickel 3d band as copper and hydrogen act as electron donors (see [3]).

The nickel-rich Ni–Cu alloys, if saturated with hydrogen, lose their long-range magnetic order but nickel clusters with their non-magnetic surrounding give rise to a Kondo-like effect. In the resistance versus temperature relationship it leads to a low-temperature resistance minimum [3].

The nickel–titanium alloys form a series of solid solutions up to ca. 10 at% Ti. The intermetallic compounds Ni–Ti exhibit shape-memory phenomena related to martensitic transformation (see e.g. [4]).

The nickel alloyed with chromium forms a series of solid solutions up to ca 30 at.% Cr. In a recent paper [5] the results of measurements of electrical resistance and thermoelectric power of $\text{Ni}_{0.95}\text{Cr}_{0.05}\text{H}_c$ have been presented. They support a model [6] according to which the negative temperature coefficient of resistance over a wide temperature range and the non-monotonic course of the thermoelectric power can be attributed to a Kondo-like effect, i.e. spin-flip

* Tel.: +48 22 3433262; fax: +48 22 6325276.

E-mail address: aws@ichf.edu.pl (A.W. Szafrński).

scattering of electrons on magnetic moments localized at the chromium atoms. In this paper the analogous measurements have been performed on the $\text{Ni}_{0.90}\text{Cr}_{0.10}$ alloy (*chromel*), which is widely used as a thermocouple material, especially designated for measurements of higher temperatures (e.g. chromel–alumel thermocouple).

Recently, the composition dependence of thermoelectric power of Ni–Cu alloys (at 323 K) has been successfully calculated in terms of APW-VCA theory [7], but no attempts have been made so far to do this for the hydrogenated alloys based on neither nickel nor palladium.

In the recent papers [5,8,9], it was shown that the values of electrical resistance and thermoelectric power of some hydrogenated Pd alloys, measured as a function of temperature, often fulfill the modified Nordheim–Gorter rule, i.e. the $S(T)/T$ quantity for a given alloy is a linear function of its electrical conductivity. Therefrom the partial thermopowers could be derived. This procedure also succeeded in the case of the $\text{Ni}_{0.95}\text{Cr}_{0.05}\text{H}_{0.9}$ hydride [5].

The dissolved hydrogen affects qualitatively the electronic structure of the Ni-based alloys and their phonon spectrum (generation of optical phonons). The aim of this work was check how this affects the transport properties of the nickel alloys, chromel and constantan, commonly used as thermoelements.

2. Experimental

The insulating coating of constantan and chromel wires (Oxford Instruments, 0.2 mm i.d.) has been removed and the wires have been cold rolled to a thickness of 20 μm . This value is much less than the penetration depth of hydrogen in nickel [10].

The alloys in the form of small foil samples (10 mm \times 1 mm \times 20 μm) mounted onto a teflon/copper support have been exposed at room temperature to gaseous hydrogen compressed to ca. 1 GPa for at least 1 week. Several additional samples have been enclosed for further determinations of hydrogen content. Thereafter, the pressure chamber has been cooled down to 170 K, the pressure released and the samples taken off and placed in a cryostat. The hydrogenated alloys are not stable at normal conditions but the procedure mentioned greatly prevents hydrogen desorption. The nickel-rich hydrides are especially difficult for handling and for measurements of the electrical properties because of their extreme brittleness.

The electrical resistance (r) and the thermoelectric power (S) have been measured simultaneously starting at 80 K with temperature increasing up to a region where hydrogen desorption occurred. Thereafter, the samples were quickly cooled down to liquid nitrogen temperature. The $r(T)$ and $S(T)$ measurements have been repeated several times with the hydrogen content successively decreased. More experimental details can be found in [8]. The hydrogen contents corresponding to the first run (undesorbed samples), and,

in some cases, to subsequent runs, were determined mass-spectroscopically using the above mentioned additional samples.

3. Results and discussion

3.1. $\text{Ni}_{0.40}\text{Cu}_{0.60}$ (constantan)

3.1.1. Electrical resistance

In contrast to low-resistivity metals where the electrical resistance is roughly linearly dependent on temperature above ca. 100 K with its temperature coefficient, $\alpha = d\rho/(\rho dT)$, approximately equal to $3 \times 10^{-3} \text{ K}^{-1}$ at room temperature, the resistance versus temperature relationship of hydrogen-free $\text{Ni}_{0.40}\text{Cu}_{0.60}$ exhibits a strong deviation from linearity (see Fig. 1). The coefficient α decreases nearly one order of magnitude—from $0.20 \times 10^{-3} \text{ K}^{-1}$ at 100 K to $0.034 \times 10^{-3} \text{ K}^{-1}$ at 300 K. Such a behavior is in contrast with a simple theory of metals and semi-empirical Grüneisen formula.

In the α -phase Ni- and Pd-based alloys the hydrogen ions are randomly distributed among the available interstitial octahedral sites and this results in an increased number of scattering centers as compared to H-free alloys. Thus, an increase of electrical resistance is expected and it is really the case in most hydrogenated alloys including Ni- and Pd-based alloys. In some cases the situation was not so clear. The electrical resistance of $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{H}_{0.07}$ was observed (see [3]) to be 6% higher than that of the H-free alloy but further increase of hydrogen content lead to 22% resistance decrease (in fact, the measurements started from the hydrogenated state and lower H-contents have been obtained by partial desorptions). The electrical resistance of $\text{Pd}_{0.6}\text{Ag}_{0.4}\text{H}_c$ alloys decreased for c increasing up to 0.18 [11] where it was the lowest, and increased again for higher hydrogen contents. In the case

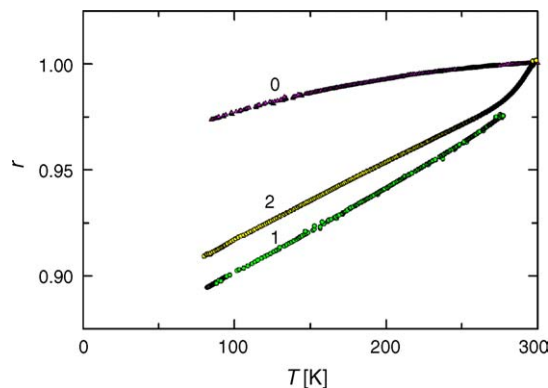


Fig. 1. Temperature dependence of the electrical resistance of constantan/hydrogen alloys: (0) hydrogen free alloy, (1) the hydrogenated alloy, $c = 0.15$, (2) the alloy after partial desorption, $c = 0.08$. The upward deviation of the curve 2 from linearity above 270 K results from hydrogen desorption. $r(T) = R(T)/R_0$, where R is the actual resistance of a hydrogenated sample and R_0 denotes the resistance of the sample prior to saturation with hydrogen, at 298 K.

of the latter alloys the initial decrease was attributed to the decreasing contribution from s to d scattering because additional electrons from hydrogen gradually filled the empty metal d-states.

The electrical resistance of $\text{Ni}_{0.4}\text{Cu}_{0.6}\text{H}_c$ alloy system is highest for $c = 0$ (see Fig. 1). So it appears that the resistance of the two mentioned $\text{Ni}_{1-x}\text{Cu}_x\text{H}_c$ alloys is highest for the alloy composition corresponding to the d-band filling i.e. $x + c \approx 0.6$. For hydrogen contents in the excess of $c \approx 0.6 - x$ the Fermi level is located in the region of flat s–p bands so it is not clear why the increase of hydrogen content in this region leads to resistance decrease. The opposite effect should be rather expected as the disorder of the hydrogen sublattice increases and, according to the Nordheim rule, its contribution to the total resistivity (for $0 < c < 0.5$) should increase as well.

It is interesting that the mentioned strong nonlinearity of the $r(T)$ dependence vanishes upon hydrogenation and the $r(T)$ relationship is linear between 80 and 270 K. Its temperature coefficient equals to $+0.4 \times 10^{-3} \text{ K}^{-1}$ at room temperature which is a typical value for medium-resistive ($\rho \approx 40 \mu\Omega \text{ cm}$) alloys. The phenomenon is very similar to that found in the mentioned Pd/Ag/H alloy where the strong non-linearity observed in the hydrogen-free alloy vanished upon hydrogenation as well [11].

3.1.2. Thermoelectric power

The thermoelectric power of constantan is large and negative. Its temperature dependence is almost linear in the temperature range between 80 and 300 K. The hydrogenation results in the marked decrease of the absolute TEP value (from -32 to $-13 \mu\text{V/K}$ at 200 K) but the character of the $S(T)$ dependence does not change (see Fig. 2).

3.1.3. Nordheim–Gorter plots

The thermoelectric power and electrical resistance of constantan/hydrogen alloys if plotted in the S/T and $1/r$ coordinates exhibit a linear dependence of the type $S/T = a + B/r$

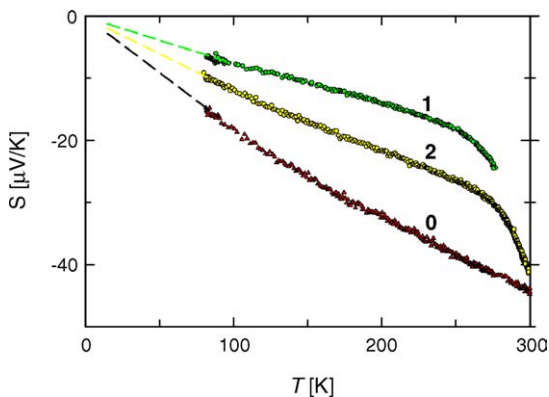


Fig. 2. Temperature dependence of the thermoelectric power of constantan/hydrogen alloys. The labels have the same meaning as in Fig. 1. The downward deviation of the curves 1 and 2 from linearity above 250 K results from hydrogen desorption.

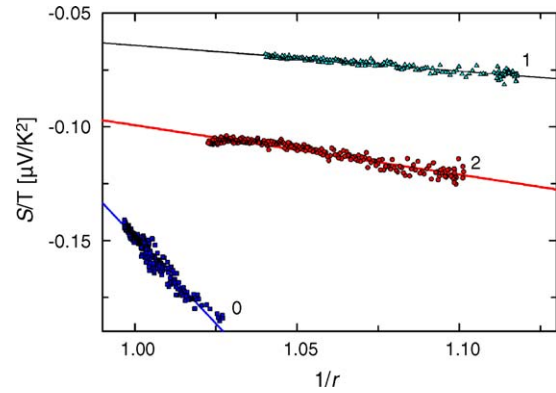


Fig. 3. Nordheim-Gorter plots for constantan/hydrogen alloys: (0) hydrogen free alloy, (1) the hydrogenated alloy ($c = 0.15$), (2) the alloy after partial desorption ($c = 0.08$).

(Fig. 3). From the a and B fit parameters the partial diffusion thermopowers, a_{ph} and a_{dis} , can be derived (Table 1). They are defined as

$$a_i = -\frac{\pi^2 k^2}{3|e|} \left[\frac{\partial \ln \rho_i}{\partial E} \right]_{E_F}, \quad i = \text{ph or dis} \quad (1)$$

where ρ_i is the electrical resistivity due to i th scattering mechanism (see [8] for details). The abbreviations ‘ph’ and ‘dis’ refer to two scattering mechanisms: scattering of electrons on phonons and scattering of electrons due to lattice disorder—random distribution of nickel and copper atoms in the fcc lattice of this substitutional alloy, and random distribution of hydrogens and vacancies in the sub-lattice formed by the octahedral interstitials. The total thermopower is given as a weighted sum of partial thermopowers:

$$S = \frac{\rho_{\text{ph}}}{\rho} a_{\text{ph}} T + \frac{\rho_{\text{dis}}}{\rho} a_{\text{dis}} T \quad (2)$$

Using Eq. (2) with resistance values from Fig. 1, and a_i values from Table 1, one can conclude that the large decrease of the absolute value of the partial thermoelectric power due to lattice disorder (a_{dis}) upon hydrogenation is the source of the observed decrease of the absolute value of the total thermopower.

3.2. Nickel–titanium

3.2.1. Electrical resistance

The electrical resistance of the $\text{Ni}_{0.98}\text{Ti}_{0.02}$ alloys increases upon hydrogenation, see Fig. 4, where its temperature dependence is shown for a sample in the initial (hydrogen-free) state, in the hydrogenated state (after remov-

Table 1
Total and partial diffusion thermopowers of $\text{Ni}_{0.4}\text{Cu}_{0.6}\text{H}_c$ alloys

Hydrogen content, c	S ($\mu\text{V/K}$), 200 K	a_{ph} ($\mu\text{V/K}^2$)	a_{dis} ($\mu\text{V/K}^2$)
0.15	–13	0.05	–0.08
0.08	–22	0.12	–0.13
0	–32	1.3	–0.21

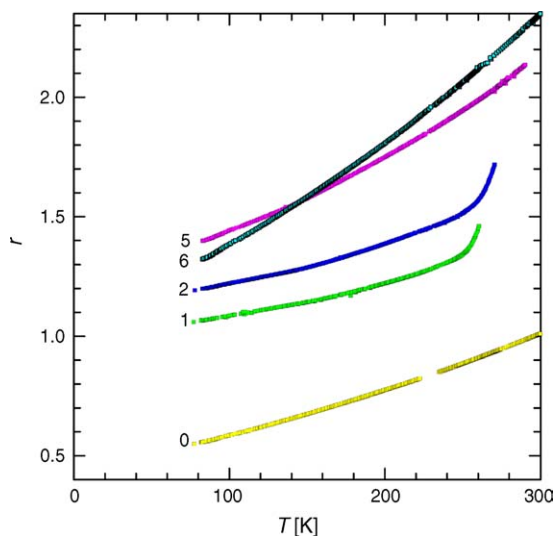


Fig. 4. Temperature dependence of the electrical resistance of $\text{Ni}_{0.98}\text{Ti}_{0.02}\text{H}_c$ alloys: (0) $c = 0$, (1) the hydrogenated alloy, $c = 0.9$, (2–6) the alloy after successive partial desorptions, (6) $c = 0$. The steep resistance increase above 250 K (curves 1 and 2) results from hydrogen desorption.

ing from the pressure chamber) and after several successive partial desorptions. The curve labeled “6” refers to the completely desorbed sample. The upward deviations of the curves 1 and 2 from linearity above ca. 250 K result from hydrogen desorption process. From the observed $r(T)$ -relationship for run “6” one can conclude that the residual resistance does not return to its initial value (see run “0”) if hydrogen is completely removed. It might suggest that some un-reversible changes (cracks) occurred in the crystal lattice. However, if it were so, the temperature-dependent part of the resistance corresponding to runs “6” and “0” should be equal. But, it is not the case—the temperature dependence of the desorbed sample is much stronger than that corresponding to the same sample prior to hydrogenation.

3.2.2. Thermoelectric power

The temperature dependence of the thermoelectric power of $\text{Ni}_{0.98}\text{Ti}_{0.02}/\text{H}$ alloys is shown in Fig. 5. It is seen that the $S(T)$ relationships – for the H-free alloy and the hydride – are quite different – the former, with its maximum close to 100 K, and the latter with a near proportionality between S and T . This behavior is similar to that previously found in hydrogenated nickel alloyed with vanadium [12] (the titanium neighbor in the table of elements) where it was interpreted in terms of virtual bound states model.

In contrast to electrical resistance, the behavior of the thermopower is reversible – if hydrogen is desorbed in a stepwise manner, a gradual change of the shape of the $S(T)$ -relationship is observed – from that corresponding to the hydride to that corresponding to the virgin sample.

3.2.3. Nordheim–Gorter plots

From the Nordheim–Gorter plot shown in the inset of Fig. 5 the partial thermoelectric power could be

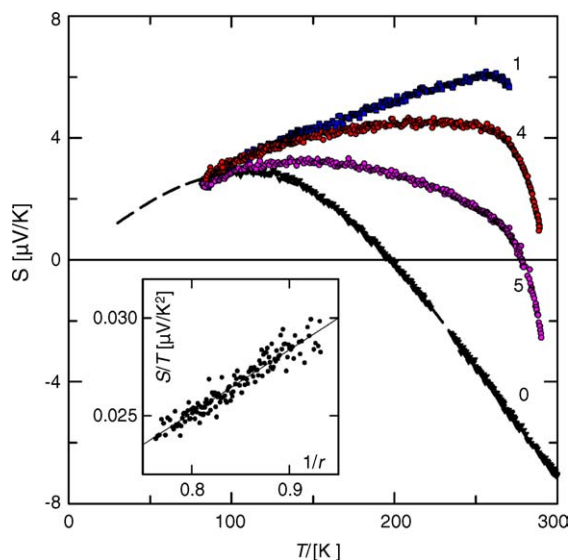


Fig. 5. Temperature dependence of the thermoelectric power of $\text{Ni}_{0.98}\text{Ti}_{0.02}/\text{H}$ alloys: (0) hydrogen free alloy, (1) the alloy hydrogenated at 0.9 GPa ($c = 0.9$), (4) and (5) ($c = 0.5$) the alloy after successive partial desorptions. The distinct downward deviations above 250 K result from hydrogen desorption. The dotted line indicates a hypothetical $S(T)$ course below 80 K. Inset: Nordheim–Gorter plot for the $\text{Ni}_{0.98}\text{Ti}_{0.02}\text{H}_{0.90}$ alloy.

derived for the hydrogenated alloy: $a_{\text{ph}} = -0.001 \mu\text{V}/\text{K}^2$ and $a_{\text{dis}} = +0.032 \mu\text{V}/\text{K}^2$. These values can be compared with those derived for $\text{Ni}_{0.95}\text{Cr}_{0.05}\text{H}_{0.96}$ (-0.13 and $-0.01 \mu\text{V}/\text{K}^2$, respectively [5]), and $\text{Pd}_{0.96}\text{Ti}_{0.04}\text{H}_{0.9}$ ($+0.02$ and $+0.03 \mu\text{V}/\text{K}^2$, respectively [8]). In the case of H-free alloy such a procedure cannot be performed because of its ferromagnetism.

3.3. Nickel–chromium ($\text{Ni}_{0.90}\text{Cr}_{0.10}$, chromel)

The effect of dissolved hydrogen on the electrical resistance and thermoelectric power of chromel (see Fig. 6) is similar to that observed previously in the $\text{Ni}_{0.95}\text{Cr}_{0.05}/\text{H}$ alloy system [5]. However, the hydrogenation pressure of 1 GPa was not high enough for full hydride formation because, in

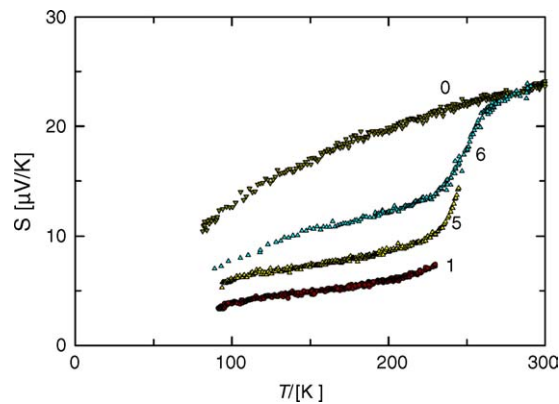


Fig. 6. Thermoelectric power of H-free chromel (0) and hydrogenated chromel ((1) $c = 0.7$, (5) $c = 0.5$). The abrupt change of the dS/dT derivative above 230 K (curves 5 and 6) results from hydrogen desorption.

contrast to Ni–Ti–H system, the hydride formation pressure of Ni–Cr alloys increases with increase of chromium content [13]. The achieved hydrogen content was as low as 0.7, what corresponds to two-phase region.

4. Summary

The electrical resistance of hydrogenated constantan appears to be lower than the H-free alloy in contrast to the expectation. The hydrogenation induces non-reversible changes in the residual resistance as well as in the temperature-dependent part of the electrical resistance of Ni-rich Ni–Ti alloy. More investigations are needed for an explanation of this anomalous behavior. The dissolved hydrogen affects much the thermoelectric power of commonly used thermoelements—constantan and chromel.

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