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The Magnetic Properties of Ni-Co-H Solid Solutions

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The behaviour of the Curie points at $P_{H_2} \leq 67$ kbar and of the magnetization at atmospheric pressure and $80 \leq T \leq 220$ K is investigated for hydrogen solutions on the base of the f.c.c. Ni-Co alloys with 30 and 60 at% Co. The samples for the magnetization measurement are hydrogenated at $P_{H_2} \leq 60$ kbar.

У растворов водорода на базе ГЦК сплавов Ni-Co, содержащих 30 и 60 ат% Co, исследовано поведение точек Кюри при $P_{H_2} \leq 67$ кбар и намагниченности при атмосферном давлении и $80 \leq T \leq 220$ К. Образцы для измерения намагниченности насыщали водородом при $P_{H_2} \leq 60$ кбар.

1. Introduction

The investigation of the Ni-Fe-H solid γ -solutions (with f.c.c. sublattice of the metal) has shown [1] that a change of spontaneous magnetization σ_0 at $T = 0$ K and of the Curie points T_C on hydrogenation is qualitatively analogous to that on substitution of Fe by Ni. In γ -alloys of the invar system $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ the effect of hydrogen on the magnetic properties turns out qualitatively analogous to that of Mn substitution by Ni. In either case, the effects on hydrogenation are analogous to those on substitution of atoms of the host metal by atoms with greater number of 3d + 4s electrons. The band structure calculations for the γ -hydrides of transition metals (for instance [3, 4]) show that at atomic ratio H-to-metal $n \leq 1$ no new hydrogen band is formed below the Fermi energy, but the presence of the protons in interstitial sites of the metal crystal lattice distorts strongly the band structure of the host metal. Now, the energy of states of sp-symmetry considerably decreases whereas the d-states (that predominantly determine the magnetic properties of transition metals) change insignificantly. The facts mentioned allow to expect that magnetic properties of hydrogen solid γ -solutions in many transition metals and their alloys can be qualitatively described considering hydrogen as a donor of a fractional quantity of electrons [2].

Indeed, to verify this suggestion one has to study a number of several Me-H systems since, for example, it cannot be excluded that the observed dependences $\sigma_0(n)$ and $T_C(n)$ of the Ni-Fe-H solution result from the specific properties of just this system. The present work is devoted to the investigation of hydrogen γ -solutions in the Ni-Co alloys containing 30 and 60 at% Co.

2. Experimental

The ingots were melted from electrolytical Ni and Co in an induction furnace in argon atmosphere. After a 10 h homogenization in vacuum at 1400 K and water-quenching these ingots were rolled into foils 0.2 mm thick. Then these foils were subjected to stress-relief annealing at 1400 K for 15 min in vacuum and again water-quenched.

The samples of ≈ 20 mg for the magnetic measurements were assemblies of 6×1 mm² bands cut from such foils. The magnetization of the samples was measured

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by the induction method [5] in a pulsed magnetic field up to 45 kOe in the temperature range 80 to 220 K, the pulse duration being ≈ 0.01 s (at normal pressure the Ni-Co-H solutions are kinetically unstable in regard to the desintegration into metal and molecular hydrogen at temperatures above ≈ 240 K). Hydrogenation of the Ni-Co specimens was conducted by several hours exposure to hydrogen pressures up to 60 kbar and $T = 520$ K with following quenching down to 240 K [1, 2]. The Curie points of the alloys at high hydrogen pressure were determined by the differential transformer technique [6]. The transformer core was a ring with an external diameter about 4 mm made from the foil of the investigated alloy. The temperature was measured by a chromel-alumel thermocouple insulated against the exposure to hydrogen. The pressure was measured with an accuracy of ± 3 kbar, the temperature ± 15 K. No corrections due to the pressure effect on the thermocouple readings were made. The temperature was kept constant within ± 2 K during investigation of the electric resistance isotherms.

The hydrogen concentration in the Ni-Co-H samples was measured in the process of their desintegration at normal conditions with 3% error by collecting the released hydrogen into a scaled glass vessel, silicon being expelled from the vessel.

3. Results and Discussion

3.1 The T - P_{H_2} phase diagram of the $Ni_{40}Co_{60}$ -H system

Under high hydrogen pressure nickel experiences an isomorphous $\gamma_1 \rightleftharpoons \gamma_2$ transformation followed by a jump-like increase of hydrogen solubility and the parameter of the f.c.c. nickel sublattice [7]. In the T - P_{H_2} diagram the line of this transformation terminates in a critical point with the coordinates $620 < T_{cr} < 700$ K, $16 < (P_{H_2})_{cr} < 19$ kbar [8, 9]. An investigation of the T - P_{H_2} phase diagrams of the Ni-Co-H solutions with ≤ 30 at% Co has shown the doping of nickel with cobalt to increase the critical pressure [10, 11]. Fig. 1 represents the electric resistance isotherms of the alloy with 60 at% Co at step-wise increase and decrease of hydrogen pressure. In every point the sample was exposed up to the end of the resistance time drift $R(\tau)$ occurring after a pressure change in hydrogen atmosphere due to the diffusional

nature of the formation of Ni-Co-H solid solutions. The finite values of R are plotted in the figure. One can see the prominent jumps of $R(P_{H_2})$ dependences near $P_{H_2} = 42$ kbar at 523 K, the time $\Delta\tau$ needed for approaching the equilibrium values of R sharply increasing in the pressure intervals where the resistance jumps take place. Such a behaviour of electric resistance is characteristic of a phase transfor-

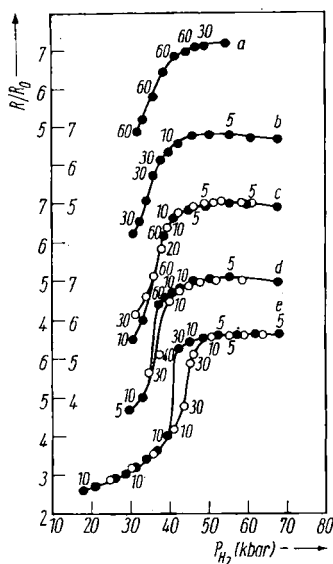


Fig. 1. Electrical resistance isotherms of the Ni-Co alloy with 60 at% Co in hydrogen atmosphere; ● at increasing pressure, ○ at decreasing pressure. The digits show the times $\Delta\tau$ in minutes for the resistance drift to terminate at fixed T and P_{H_2} after the pressure has been changed. The values $\Delta\tau$ at pressure increases are left of the curves $R(P_{H_2})$, at decrease right. R_0 is the resistance of the samples at normal conditions. (a) $T = 623$, (b) 598, (c) 573, (d) 548, (e) 523 K.

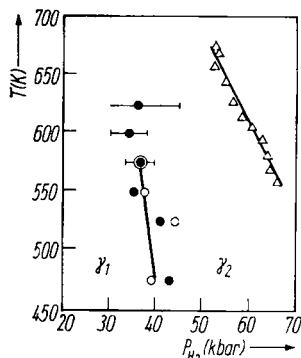


Fig. 2. T - P_{H_2} phase diagram of the $Ni_{40}Co_{60}$ -H system. ● pressures of the $\gamma_1 \rightarrow \gamma_2$ transition, ○ of $\gamma_2 \rightarrow \gamma_1$, Δ Curie points

mation of the first kind. An X-ray study ($P = 1$ atm, $T = 83$ K) of the specimen $Ni_{40}Co_{60}$ -H hydrogenized at 550 K and $P_{H_2} = 67$ kbar up to $n = 0.7 \pm 0.02$ has shown that metal atoms form an f.c.c. sublattice with unit cell volume being increased by $\Delta V_0 = (6.9 \pm 0.5)\text{\AA}^3$ as compared to that in a hydrogen-free alloy. This agrees with the dependence $\Delta V_0(n)$ for hydrogen γ -solutions in Ni-Fe [1] and Ni-Fe-Mn [2] alloys. So,

the first-order phase transformation observed in the $Ni_{40}Co_{60}$ alloy at 523 K and $P_{H_2} \approx 42$ kbar is likely to be the isomorphous $\gamma_1 \rightleftharpoons \gamma_2$ transformation.

As it is seen from Fig. 1, this $\gamma_1 \rightleftharpoons \gamma_2$ transformation has no hysteresis already at 523 K. Above 573 K the behaviour of the resistance isotherms becomes more smooth, and the pressure intervals where $\Delta\tau$ increases up to the values peculiar for $\gamma_1 \rightarrow \gamma_2$ and $\gamma_2 \rightarrow \gamma_1$ transformations rapidly increase. It is the behaviour of electric resistance that should be expected in Me-H systems at temperatures near T_{cr} owing to the decrease of the rate of hydrogen diffusion in the vicinity of the critical point [12]. The positions of the anomalies of $R(P_{H_2})$ isotherms for the alloy with 60 at% Co are plotted in the T - P_{H_2} phase diagram Fig. 2.

3.2 The spontaneous magnetization $\sigma_0(n)$

It was shown [13] that the hydrogen mobility in Ni-H solutions is so large that even at $T < 250$ K the separation into γ_1 and γ_2 phases occurs in accordance with the equilibrium T - C diagram. With decreasing temperature the two-phase region in the T - C diagram expands; in particular, the value of the minimum hydrogen solubility in the γ_2 -phase increases. In order to study at $T \leq 220$ K the magnetization of one-phase Ni-Co-H samples only the alloys were hydrogenized at temperature $520\text{ K} \ll T_{cr}$ and pressures different from those of the $\gamma_1 \rightleftharpoons \gamma_2$ transformation by not less than 3 to 5 kbar. The one-phase nature was verified by X-ray measurement in the present work for the $Ni_{40}Co_{60}$ -H specimen with $n = 0.7$ and in [10] for the $Ni_{70}Co_{30}$ -H specimen with $n = 0.65$.

The values of σ_0 represented in Fig. 3 for hydrogen solutions in the Ni-Co alloys with 30 and 60 at% Co and of the Curie points for the $Ni_{70}Co_{30}$ -H solutions were

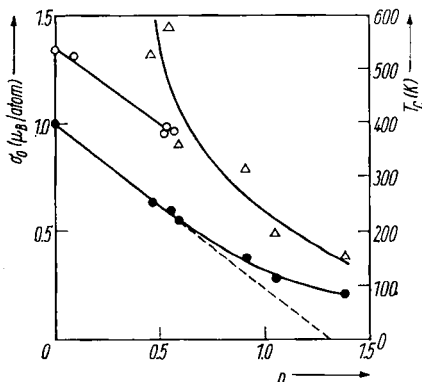


Fig. 3. Spontaneous magnetization σ_0 at $T = 0$ K (● for 30 at% Co, ○ for 60 at% Co) and the Curie points (Δ for 30 at% Co) in dependence on hydrogen concentration n for the Ni-Co-H system. (The magnetization is given in μ_B /atom of the Ni-Co alloy)

obtained using the equations of the theory of very weak itinerant ferromagnetism [14]. Note, that within the error of $\approx 5\%$ an extrapolation of the dependences $\sigma(T)$ to $T = 0$ K by the low $T^{3/2}$ of the spin wave theory yields the same values σ_0 for the investigated samples. As it is seen from Fig. 3, the magnitude of σ_0 for both the alloys decreases monotonously with increasing n . The $\sigma_0(n)$ dependence for the alloy with 30 at% Co is nonlinear with concavity towards the n -axis. Analogous deviation from linearity was observed for Ni-Fe non-invar γ -alloys at $n \gtrsim 0.8$.

The concentration $n \approx 0.8$ is peculiar for the Me-H solutions with f.c.c. crystal sublattice of the transition metal since in all the investigated solutions the character of the dependences $\Delta V_0(n)$ changes near this n [2, 15]. The nature of this effect is still obscure. For instance, an assumption exists that at $n > 0.8$ hydrogen in these metals begins to populate not only octahedral, but also tetrahedral interstitial sites [9]. It is not excluded, too, that even at $n > 1$ hydrogen continues to populate octapores alone, their number increasing with respect to the number of the lattice points due to the increase of the number of vacancies in the f.c.c. metal lattice at $n < 0.8$ (i.e. due to the formation of a f.c.c. subtractional solution by the metal atoms) [16].

Restricting ourselves to the data for $n < 0.8$ only, with a linear approximation of the dependences $\sigma_0(n)$ by the least squares technique we obtain $\partial\sigma_0/\partial n = -0.76$ and $-0.71 \mu_B/\text{atom}$ for the $\text{Ni}_{70}\text{Co}_{30}$ -H and $\text{Ni}_{40}\text{Co}_{60}$ -H solutions, respectively.

Nickel is described well by the model of itinerant ferromagnetism, and near $T = 0$ K it can be considered as a strong itinerant ferromagnet [17]. The dependence $\sigma_0(x_{\text{Co}})$ for Ni-Co alloys is close to linear, agrees with the Pauling-Slater curve, and has the slope $\partial\sigma_0/\partial x_{\text{Co}} \approx 1.05 \mu_B/\text{atom} = -1.05 \mu_B/\text{electron}$ [18], i.e. it is described well by the rigid band model for strong ferromagnets (x_{Co} is the atomic fraction of Co in the Ni-Co alloys). The $\sigma_0(x_{\text{Co}})$ dependence for these alloys seems to be mainly determined by the changes in electron concentration, the band structure varying weakly. According to [3, 4], the hydrogenation of the f.c.c. transition metals increases the degree of occupation of the d-band (by 0.4 to 1.0 electron/proton for Pd and Ni [3]). Hence, one can expect $0 > \partial\sigma_0/\partial n > -1 \mu_B/\text{atom}$ for the Ni-Co-H solid solutions. The sign and the order of magnitude of the experimental $\partial\sigma_0/\partial n$ values agree with these calculations.

3.3 The Curie points T_C

Fig. 2 shows the $T_C(P_{\text{H}_2})$ dependence for the $\text{Ni}_{40}\text{Co}_{60}$ alloy. The Curie temperature is seen to decrease on hydrogenation. The curve $T_C(P_{\text{H}_2})$ in the T - P_{H_2} diagram intersects the prolongation of the line of $\gamma_1 \rightleftharpoons \gamma_2$ phase transformation in the supercritical region ($T_C \approx 1200$ K at $P = 1$ atm for the $\text{Ni}_{40}\text{Co}_{60}$ alloy [18, 19]). Hence, this dependence is a continuous function of hydrogen pressure (and hydrogen concentration in the sample).

As it is seen from Fig. 3, the Curie temperature of the $\text{Ni}_{70}\text{Co}_{30}$ alloy (at $P = 1$ atm) also decreases with increasing hydrogen concentration. The error in T_C determination using Wohlfarth's equations [14] is ± 10 K when $T \lesssim 300$ K and grows up to ± 50 K at $T \approx 500$ K. The equations [14] are valid for very weak itinerant ferromagnets. In the case of the $\text{Ni}_{70}\text{Co}_{30}$ -H system they yield somewhat overestimated values for the Curie points: the measurements under high hydrogen pressure have shown that in the γ_2 -region of the T - P_{H_2} diagram of this system $T_C < 350$ K.

Following [1], we introduce the coefficients ξ relating the values of n and Δx_{Co} for every Ni-Co alloy:

$$\Delta x_{\text{Co}} = \frac{(\partial\sigma_0/\partial n)}{(\partial\sigma_0/\partial x_{\text{Co}})} n = -\xi n. \quad (1)$$

This equation establishes the correspondence between alloys with the same σ_0 , one containing x_{Co} cobalt and n hydrogen, the other one containing $x_{\text{Co}} - \Delta x_{\text{Co}}$ cobalt and no hydrogen. Under the assumption that the corresponding alloys have also close values of T_{C} and $(dT_{\text{C}}/dP)_{\text{in}}$ the semiquantitative description was given in [1] for the $\Delta T_{\text{C}}^{\text{exp}}$ dependences in the Ni-Fe-H system, where the index "in" designates an inert medium, $\Delta T_{\text{C}}^{\text{exp}}$ is the difference between the values of T_{C} in hydrogen and in an inert medium at the same pressure.

Under such an assumption in the case of Ni-Co alloys we have [1]

$$\Delta T_{\text{C}}^{\text{cal}} = \Delta T_{\text{C}}^{\text{n}} + \Delta T_{\text{C}}^{\text{P}} = \{T_{\text{C}}(x_{\text{Co}} - \xi n) - T_{\text{C}}(x_{\text{Co}})\} + \\ + \left(\frac{d}{dP} \{T_{\text{C}}(x_{\text{Co}} - \xi n) - T_{\text{C}}(x_{\text{Co}})\} \right)_{\text{in}} P,$$

since $T_{\text{C}}(P)$ dependences for the Ni-Co alloys are nearly linear [19]. For the alloy with $x_{\text{Co}} = 0.6$ at $n = 0.7$ equation (1) gives $x_{\text{Co}} - \xi n \approx 0.6 - (0.71/1.05) 0.7 \approx 0.1$. Using the values of T_{C} and $(dT_{\text{C}}/dP)_{\text{in}}$ from [18 and 19], at $P = 67$ kbar we obtain:

$$\Delta T_{\text{C}}^{\text{cal}} \approx (750 - 1200) + (0.66 - 0.74) 67 \approx -450 - 5 \approx -450 \text{ K}.$$

Note, that in contrast to the hydrogen solutions in the Ni-Fe invars [1, 2], where $\Delta T_{\text{C}}^{\text{n}}$ and $\Delta T_{\text{C}}^{\text{P}}$ are of the same order of magnitude, in the case of the Ni-Co-H system $|\Delta T_{\text{C}}^{\text{P}}| \ll |T_{\text{C}}^{\text{n}}|$ due to the small values $(dT_{\text{C}}/dP)_{\text{in}}$.

So, at $n = 0.7$ the $\text{Ni}_{40}\text{Co}_{60}$ -H solution has to have $T_{\text{C}} \approx 750$ K. This composition is attained at $P_{\text{H}_2} = 67$ kbar and $T \approx T_{\text{C}}$ ($P_{\text{H}_2} = 67$ kbar) ≈ 560 K (see Section 3.1). An analogous calculation shows that at $n = x_{\text{Co}}/\xi \approx 0.3(1.05/0.76) \approx 0.4$ the Curie temperature of the $\text{Ni}_{70}\text{Co}_{30}$ -H solution must decrease down to $T_{\text{C}}^{\text{Ni}} = 630$ K [18, 19, 9] (compare with the data of Fig. 3). So, in the cases of both $\text{Ni}_{40}\text{Co}_{60}$ and $\text{Ni}_{70}\text{Co}_{30}$ alloys, formula (1) yields the correct sign and order of magnitude of ΔT_{C} . The observed correlation between the behaviour of σ_0 and T_{C} of the Ni-Co-H solid γ -solutions (and Ni-Fe-H solutions, too, [1]) is of additional interest because these values are determined by the different physical parameters. The tendencies of the magnetization changes in Ni-Cr-H [20] and Ni-Mn-H [21] solutions obtained by electrochemical techniques show that such a correlation may be absent in these systems. It is to be noted that the magnetic properties of Ni-Cr and Ni-Mn alloys are anomalous [18], and further studies are needed for a better understanding of the properties of hydrogen solutions on their base.

4. Conclusion

Despite of a strong deformation of the band structures of transition metals on hydrogenation, the behaviour of the spontaneous magnetization at $T = 0$ K and of the Curie points for hydrogen solid γ -solutions on the base of a number of alloys (Ni-Fe, $\text{Fe}_{65}(\text{Ni}_{1-x}\text{Mn}_x)_{35}$, Ni-Co) can be qualitatively described considering hydrogen as a donor of a fractional quantity of electrons.

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