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The Structure of Raney Nickel

VII. Ferromagnetic Properties

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Magnetization-field data were measured on four different Raney nickels with a vibrating sample magnetometer at fields up to 14 kOe and temperatures from 4 to 600 K. The magnetization of the Raney nickel per gram Ni and the Curie points were substantially less than the corresponding quantities for bulk nickel. The magnetizations and the Curie points of the catalysts increased with the temperature of preparation and the temperature of pretreatment (evacuation). The data were interpreted on the basis of the catalyst containing solid solutions of hydrogen and/or aluminum, using available magnetic data for nickel solid solutions.

Raney nickel is prepared by removing aluminum from a nickel–aluminum alloy with aqueous alkali at 50–107°C. The Raney catalyst consists of a nickel component, which may contain aluminum (up to 4% according to phase diagrams), chemisorbed and possibly occluded hydrogen, and some or all of the following: unreacted alloy, alumina and residual alkali (*1–4*). The composition of different activated Raney nickels by careful special analyses has been reported in two papers as nickel, "metallic" aluminum, and alumina 75–80, 10, and 5 (*1*), and 92–93, 3.6–4.1, and 0.1 (*5*), respectively. The important result is that the catalyst contained substantial quantities of unoxidized aluminum; the differences probably reflect variations in the severity of the activation. The presence or absence of hydrogen in excess of that chemisorbed has been determined by measuring the hydrogen evolved on dissolving the catalyst in acid. Some workers have found substantial amounts of excess hydrogen (*6, 7*) and others have not (*2*). The nickel component is present as small crystallites of average diameters from 36–100 Å, and is the principal material contributing to the large surface area (*8*). The complexities of the structure of Raney nickel are exacerbated by variations in the original alloy and its activation and subsequent treatment. Papers from this laboratory (*8–12*) have to some extent clarified this situation, as catalysts prepared by several methods have been examined.

Alloying nickel with certain metals produces marked changes in ferromagnetism (*13*). For solid solutions of a number of Group I–V metals in nickel both the saturation magnetization at 0 K and the Curie temperatures decrease approximately linearly with atom fraction of the alloying element to zero and 0 K at an atom fraction of about $0.6/n$, where n is the number of s electrons in the metal added to nickel (*14*). For aluminum in nickel including supersaturated solid solutions the Curie points extrapolate to 0 K at an atom fraction Al of 0.19 (*15*). Older data for saturation magnetization at 0 K, involving only 3 Ni–Al alloys, extrapolate to zero at an atom fraction of Al of 0.22 (*16*). For nickel–copper alloys the magnetization and

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Curie point decrease linearly with increasing copper content reaching zero and 0 K at a copper content of about 53 atom% (*17*). Following the work of Hume-Rothery (*18*) and Sucksmith *et al.* (*17*), data for alloys may be interpreted on the assumption that the donation of about 0.55 electron to the nickel *d*-band eliminates its ferromagnetism. Chemisorption of hydrogen on nickel, well dispersed on silica, similarly decreases the magnetization about $-0.7\ \mu_B$ per hydrogen atom (*13*).

The literature contains many references to the formation of nickel hydride on nickel cathodes in electrolysis of aqueous solutions. For example, a 10 μm layer of hydride of approximate composition NiH was obtained (*19*). This material had a fcc structure with a lattice dimension of 3.721 Å; however, at room temperature the hydride decomposed to hydrogen and nickel in a few hours.

The principal reports extant on the ferromagnetism of Raney nickel are those by Kokes and Emmett (*1*) and by Mars, Scholten and Zwietering (*2*). Both groups found that heating the catalyst increased the magnetization at room temperature, and that the increase in magnetization was proportional to the volume of hydrogen evolved on heating. Kokes and Emmett interpreted these and other data on the basis of hydrogen held in the nickel lattice as an alloy, while Mars *et al.* showed strong evidence for the reaction of water with residual aluminum, presumably in a Ni–Al alloy, as the source of hydrogen. This polemic has not been resolved.

To gain information about the alloys or other phases present, magnetic data should be obtained over a temperature range wide enough to allow extrapolation to 0 K, as only at 0 K is true ferromagnetic saturation obtained (*20*). The presence of phases other than metallic nickel should contribute their magnetic moment, if any, to the overall magnetization of the sample. The presence of two or more ferromagnetic phases may be apparent from the thermomagnetic curve, as each ferromagnetic component should exhibit its characteristic Curie point.

The magnetic properties of greatest interest are the specific magnetization, in the present work given per gram Ni, and the Curie points. The magnetization is affected by other factors, notably particle size, and interpretation of the data is a complex problem. Selwood (*13*) and Hofer (*21*) have described experimental methods for making magnetic measurements on catalysts and ways of interpreting the data.

The present paper reports a detailed magnetic study of four typical Raney nickel catalysts evacuated at several temperatures in the range 25–500°C. A subsequent paper will present an interpretation of these data with respect to particle size and amount of hydrogen evolved on heating.

EXPERIMENTAL

The system used to measure the magnetic moment of the samples was a Princeton Applied Research Corp. vibrating sample magnetometer of the type described by Foner (*22*), together with a Magnion electromagnet capable of producing fields greater than 14 kOe. The principle of this instrument is that the sample is made to vibrate perpendicularly to the applied field; the vibrating sample produces an oscillatory field pattern that is proportional to the magnetic moment of the sample and the frequency and the amplitude of vibration. The oscillatory field induces an ac voltage in two fixed coils situated between the specimen and the poles of the magnet. A vibrating capacitor driven by the same vibrator produces an ac reference signal that is proportional to the voltage of the capacitor and the amplitude of the vibrator. Electronic balancing of the two signals produces an output proportional to the magnetic moment of the sample that is independent of the amplitude of vibration and amplifier gains. The sample is secured to the vibrator by the sample support tube and positioned between the magnet poles.

A requirement of this system is a small compact sample; considerable restrictions are imposed on the sample size and method of preparation by the geometry of the magnetometer and the pyrophoricity of Raney nickel. Cylindrical pellets, ⅛-in.

diameter, and weighing 140–220 mg, were prepared from an ethanolic or aqueous slurry of the catalyst in a Stokes Tablet machine, and were stored in the same medium until used. The pellets were ¼–5⁄16-in. in length and the pellet density after evacuation was about 3.0 g/cc. A pellet, wet with the storage fluid, was placed at the bottom of a closed 0.13-in. i.d. Pyrex tube that was attached to a ground glass joint. A length of narrow glass rod was sealed inside this tube to anchor the pellet at the end of the sample tube to prevent out-of-phase vibration in the magnetometer. The sample was then evacuated to a pressure of 10^{-5} Torr at room temperature and subsequently at any desired higher temperature, and the sample tube was sealed off under vacuum. The weight of the sample was determined after the magnetic measurements.

A sample tube was attached to the support tube by a teflon adaptor, and, in an applied field of 4–6 kOe, the position of the sample was adjusted along each of three mutually perpendicular axes so that the output signal was stationary with respect to small displacements. This adjustment is of the greatest importance if results for different samples are to be compared.

Measurements in the temperature range 77 K to ambient were made with a specially designed open Dewar flask. The sample could be thermostatted at 77 K liquid nitrogen, and measurements of higher temperatures could be made as the sample warmed up after the nitrogen had boiled off. Temperatures down to 4.2 K were achieved with a liquid-helium Dewar flask equipped with a sample heater to provide temperature control from 4.2 K to ambient. For measurements above room temperature, a sophisticated furnace equipped with a vacuum jacket to prevent damage to the detection coils was used. The sample chamber of the furnace was filled with helium gas to prevent corrosion and to maintain thermal conductivity between the heater element and the sample. Sample temperatures were measured by means of a thermocouple taped to the sample tube adjacent to the pellet.

The sample signal was measured by a manual potentiometer or by a digital voltmeter to give the magnetic moment in arbitrary units. The magnetometer was calibrated using a sample of pure bulk nickel and setting the σ_0 value equal to 57.50 emu. All specific magnetization values are expressed per gram of total nickel, and are denoted by σ. The saturation value of σ at any temperature is denoted by σ_s, and the value of σ_s at 0 K by σ_0. Corresponding magnetizations for massive nickel are denoted by σ', σ'_s, and σ'_0. The magnetic field was corrected for the demagnetizing field of the sample assuming the catalyst particles are present as spheres.

Each sample was investigated for evidence of magnetic hysteresis at ambient and the lowest and highest measurement temperatures in fields down to 1.7 kOe; below this level the accuracy of the field measurement was insufficient to allow significant measurements to be made, as the magnetization is very field dependent in this range. As the magnet employed did not have a field reversal switch, complete hysteresis loops could not be obtained. Hysteresis was not observed for any of the catalyst samples.

Catalysts

Details of the standard extraction procedures used for the preparation of Raney nickel catalysts in this laboratory, and the associated nomenclature, have been described previously (*10*). Four catalysts were studied: IIA was prepared by adding small portions of the aqueous NaOH to alloy A in water at 50°C as required to maintain a constant evolution of hydrogen. IIIA was prepared by adding the aqueous NaOH at one time to alloy A. The temperature reached the boiling point of the solution, about 107°C. IIA–B was prepared by heating IIA in aqueous NaOH at 50°C for 2 hr and then at 107°C for 2 hr. The catalyst was then washed with distilled water until a pH of 7 was obtained and then transferred to ethanol. COM was a Davison commercial catalyst.

Alloy A had a nominal composition of 50% Ni and 50% Al by weight, and con-

TABLE 1

Analysis of Catalyst Samples

Sample	Weight percent Ni	 Total Al	 Elemental Al
IIA	77.9	10.9	5.0
IIA-B	86.6	3.1	0
IIIA	86.5	3.9	0
COM	90.4	6.0	4.1

tained 50.8 wt% Ni. Catalysts IIA, IIIA, and IIA-B were stored in ethanol at 0°C and the commercial catalyst was stored in water at room temperature. For each type of catalyst a series of samples was prepared by evacuation at about 25, 100, 200, 300 and 500°C, respectively.

Samples were analysed for Ni and Al by standard chemical methods after the magnetic measurements were completed, and the analytical data are based on the weight of sample after evacuation. Within the uncertainties of sampling and analyses, the compositions were independent of evacuation temperature. The analyses in Table 1 include an estimate of the amount of metallic aluminum calculated on the basis of the evacuated catalyst containing only metallic Ni, metallic Al and $Al_2O_3 \cdot 3H_2O$. The

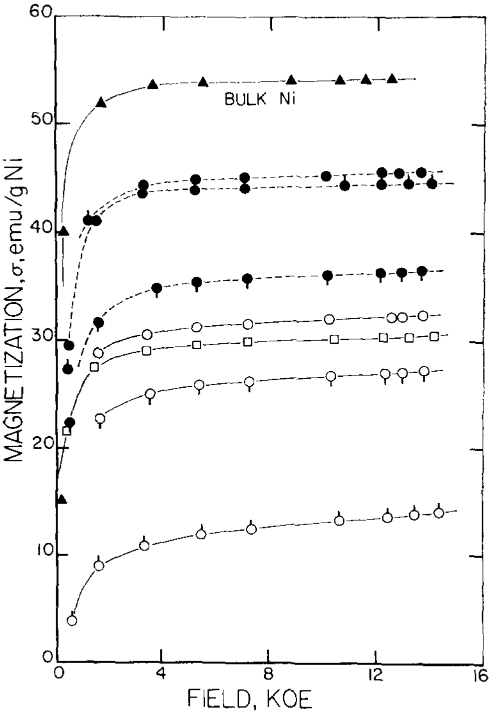

Fig. 1. Magnetization-field curves measured at 20°C. Catalysts and the evacuation temperatures in °C are denoted by the following symbols: IIA, 25° ♂, 500° ♦; IIA-B, 25° □; IIIA, 25° ○, 475° ●; and COM, 25° ♀, 500° ♦.

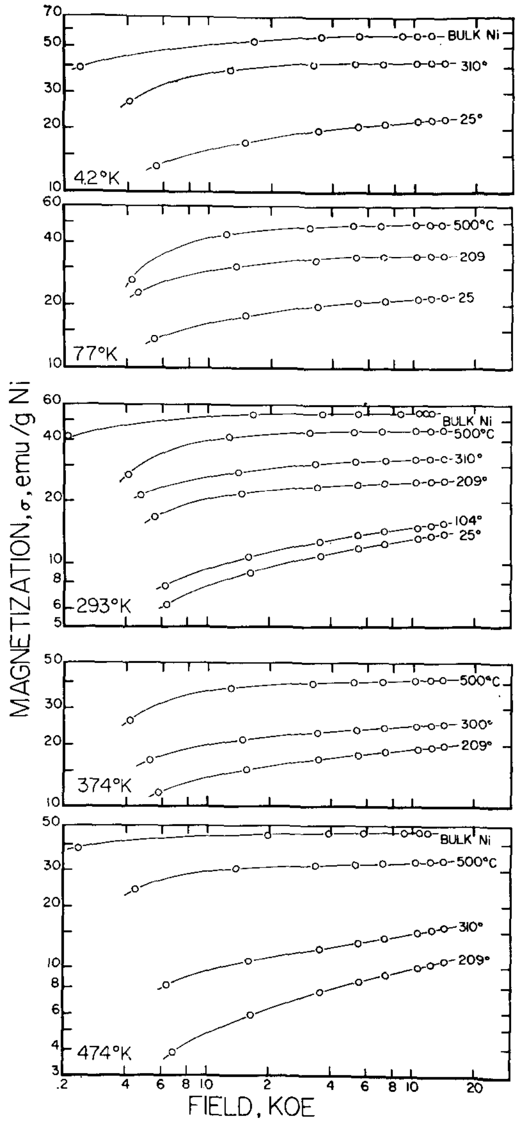

Fig. 2. Logarithmic plots of magnetization as a function of field for catalyst IIA measured at temperatures shown in lower left corner. Number on the right side denotes temperatures of evacuation.

values for metallic aluminum have large uncertainties for a variety of reasons, and the uncertainties of the numbers may be as high as ±1.0 or ±2.0.

Experimental Results

A sample of alloy A was studied in the magnetometer, but no traces of ferromagnetic behaviour was found.

Figures 1–4 present magnetization-field data on the four catalysts at a number of temperatures of measurement and different temperatures of evacuation. Magnetic measurements could not be made at temperatures greater than the evacuation temperature because of complications due to the evolution of hydrogen from the catalyst. Figure 1 presents linear plots for data for all catalysts measured at room temperature, the temperature at which Raney nickel is normally handled. In Figs. 2 to 4 the data are plotted on logarithmic scales. Table 2 presents the fractional magnetization σ/σ_s at a field of 5.6 kOe, and 3 temperatures of measurement. In all cases σ_s was determined by extrapolating plots of σ vs 1/H to infinite field.

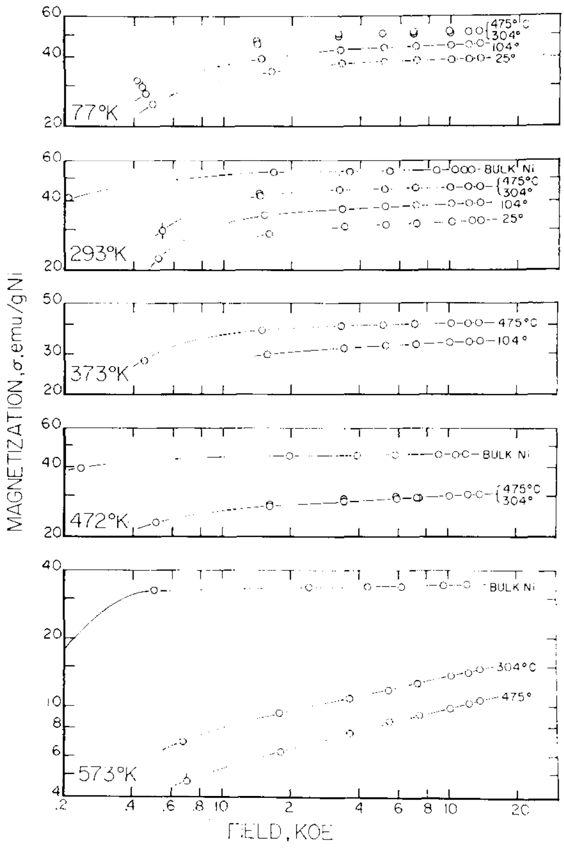

Fig. 3. Logarithmic plots of magnetization as a function of field for catalyst IIIA measured at temperatures shown in lower left corner. Number on the right side denotes temperatures of evacuation.

Figure 5 presents plots of saturation magnetization as a function of temperature. Data in these figures are of two types: The solid and dashed curves were obtained at short temperature intervals as the temperature of the sample was increased continuously at a field of about 14 kOe, and the points, which represent saturation magnetizations, σ_s, obained from curves such as given in Figs. 1–4. The points either fall on the curves or lie slightly above them. All of these curves terminate at the evacuation temperature of the sample. Table 3 summarizes specific magnetizations at 0 and 293 K and presents estimates of the Curie temperature for some of the thermomagnetic curves.

Figure 1 and Table 2 show that the magnetization σ, and fractional magnetization, σ/σ_s, for samples evacuated at room temperature increases with the severity of the conditions of preparation in the order IIA < COM < IIA-B < IIIA. These relationships hold for most conditions of measurement and evacuation temperature as shown in Figs. 2 to 4 with some exceptions; for example, for evacuations at 500°C the com-

TABLE 2

Fractional Magnetization in 5.6 kOe Field

Sample	Temp. of evacuation, °C	Temperature of measurement, K		
		4.2	293	473
IIA	25	0.873	.770	
	310	.963	.951	.780
IIA-B	25	.940	.958	
	299	.975	.973	.944
IIIA	25		.950	
	305		.964	.943
COM	25		.928	
	300		.964	.896

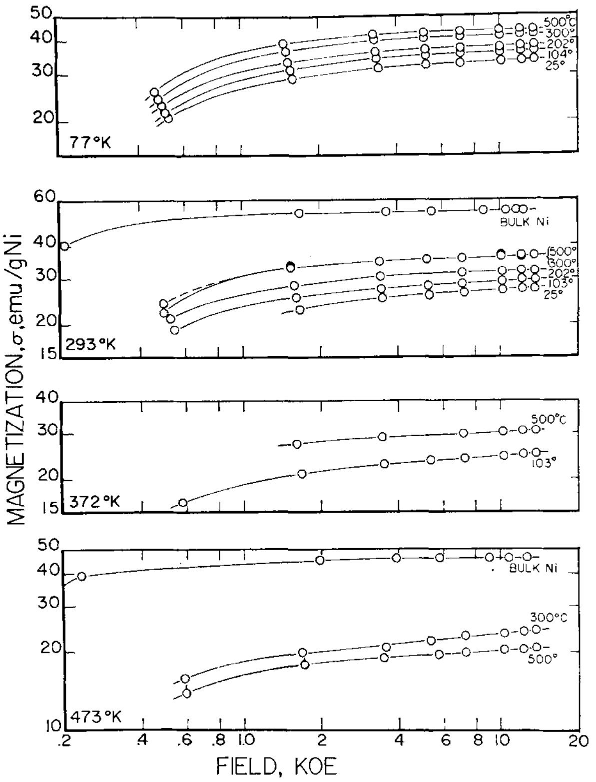

Fig. 4. Logarithmic plots of magnetization as a function of field for commercial catalyst, COM, measured at temperatures shown in lower left corner. Number of the right side denotes temperatures of evacuation.

mercial catalyst had a lower magnetization than IIA and IIIA. The combined effect of the preparation steps of sample IIA–B should be about equivalent to the preparation of IIIA.

For measurements at a particular temperature on the same catalyst the magnetization curves were displaced upward by roughly constant amounts as the evacuation temperature was increased. As the corresponding curves in the logarithmic plots are usually not an equidistance apart, we may conclude that the evacuation temperature changes both the amount and kind of magnetic material. In the high field region the slope of the magnetization field curves decreased with increasing magnetization, and the more severely treated sample, either by preparation or evacuation temperature, saturate more readily.

The thermomagnetic curves in Fig. 5 do not increase significantly as temperature is decreased from 77 to 4.2 K, and the catalysts had magnetizations substantially smaller than massive nickel at all temperatures. Unless the sample contains a material that magnetizes at temperatures below 4.2 K, e.g., very small crystallites, we must conclude that a significant part of the catalyst is not ferromagnetic, or is present in other ferromagnetic forms than metallic Ni.

If the sample is assumed to contain metallic Ni plus nonferromagnetic phases, the fraction of metallic Ni, σ_0/σ'_0, the ratio of the magnetization of the catalyst to that of massive Ni at 0 K, was as low as 37%, Table 3. This fraction increases to 90% for samples of catalyst IIA and IIIA as the evacuation temperature was increased. The ratio of the saturation magnetization of the catalyst to that of bulk Ni at 293 K was substantially less than corresponding values at 0 K but the difference becomes smaller for the more severely treated samples.

TABLE 3
SUMMARY OF SPECIFIC MAGNETIZATIONS AND CURIE POINTS

		0 K		293 K		
Sample	Temp. of evacuation °C	σ_0 emu/gNi	σ_0/σ'_0	σ_s emu/gNi	σ_s/σ'_s	Curie point, K
IIA	25	21.1	0.367	11.7	0.215	
	25	23.0	.400	13.8	.254	
	104			15.6	.287	
	209	35.4	.616	25.3	.465	∼440
	310	41.9	.729	32.5	.598	
	500	49.6	.863	44.6	.820	590 ± 10
IIA-B	25	39.3	.683	31.2	.574	
	299	46.2	.803	41.1	.756	600 ± 10
IIIA	25	40.0	.696	32.5	.598	
	104	46.2	.803	38.9	.715	
	204	44.3	.770	36.9	.678	565 ± 20
	304	52.0	.904	45.9	.844	580 ± 10
	475	52.1	.906	45.7	.840	585 ± 5
COM	25	34.7	.603	27.5	.506	
	103	37.4	.650	29.5	.542	
	202	38.8	.675	31.8	.585	
	300	42.3	.736	36.3	.667	∼540
	500	44.5	.774	36.5	.671	540 ± 10
Bulk Ni		57.50		54.39		631

Curie points were estimated from some of the thermomagnetic curves of Fig. 5; these values were substantially lower than the Curie point of bulk Ni. For catalyst IIA, some of the plots were essentially linear above 200 K, and Curie points could not be estimated.

DISCUSSION

Raney nickel contains small to moderate amounts of metallic aluminum and hydrogen, presumably as solid solutions in nickel, and the crystallite size is small. These factors complicate the interpretation of magnetic data (cf. footnote, p. 48 of Ref. 13).

Particle sizes from X-ray broadening (*8*) were for catalyst IIA 36, 40, and 57 Å for evacuation at 25, 310 and 500°C, respectively; for IIIA 52 and 57 Å for evacuation at 25 and 130°C; and for the commercial catalyst 50, 61, 75, and 104 Å for evacuation at 25, 130, 300 and 490°C, respectively. The unit-cell dimension of Ni in these preparations varied from 3.53 to 3.55 Å compared with 3.524 Å for bulk Ni.

The specific magnetization per gram Ni increased substantially with the severity of the preparation or evacuation. The temperature of preparation or of the final aqueous (NaOH) treatment was more effective in increasing magnetization and particle size (*8*) than evacuation at substantially higher temperatures. Increasing the temperature of aqueous treatment from 50–107°C was more-or-less equivalent to increasing the evacuation temperature from 100 to 300 or 400°C.

At all temperatures the magnetization of catalysts per gram Ni was significantly smaller than that of bulk Ni. The magnetization increased only slightly from 77 to 4 K, suggesting that the fraction of very small particles was small. Probably nickel alloys containing aluminum and hydrogen are primarily responsible for the lower magnetizations of the catalysts. These alloys could be either nonferromagnetic or have a lower magnetization and a presumably lower Curie point than bulk Ni. The small particle sizes would also lower the magnetization, but crystallites with diameters of about 50 Å would be expected to

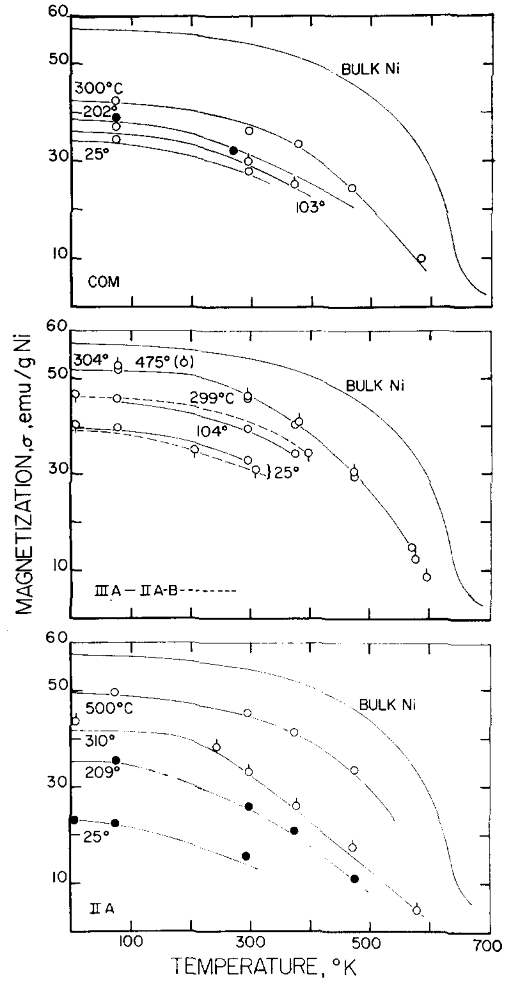

FIG. 5. Thermomagnetic curves for Raney nickel. Curves were obtained at about 14 kOe and points represent saturation magnetization.

have the same Curie point as bulk nickel. For samples evacuated at 300°C or higher temperatures, the catalyst had substantially lower Curie points than bulk nickel. Any reasonable extrapolation of curves for catalysts evacuated at lower temperatures suggests that their Curie temperatures would be even lower. Some thermomagnetic curves were essentially linear in the region where the Curie point would be expected.

Based on the more recent work on Ni–Al (*15*) and Ni–Cu (*17*) solid solutions, we propose as approximations for Ni–Al and Ni–H solid solutions of uniform composition:

$$T_c = 631(1 - 1.82nx) \qquad (1)$$

$$\sigma_0^* = 57.5(1 - 1.82nx) \qquad (2)$$

where the Curie point, T_c is given in K, σ_0^* is the saturation magnetization at 0 K per gram of alloy in emu, $n = 1$ for H and $n = 3$ for Al, and x is the atom fraction of H or Al. Here we assume that copper and hydrogen in solid solution affects magnetization similarly. According to Eq. 2 an atom fraction of 0.55 of H or Cu eliminates ferromagnetism, and 57.5 corresponds to 0.606 μ_B. The terms in parentheses in Eqs. 1 and 2 could be written as $[1 - 1.82(3x_{Al} + x_H)]$ to account for the effects of both solutes. Table 4 presents the atom fractions of Al and H by Eq. 1 to decrease the saturation magnetization at 0 K to the observed value if Al or H were present alone in solution in the nickel.

If the composition of the nickel solid solutions in Raney nickel is uniform, and only so, the Curie point of the catalysts can be calculated from a combination of Eq. 1 and 2:

$$T_c = 631\sigma_0^*/57.5 \qquad (3)$$

The calculated values in Table 4 are smaller than the observed Curie points. These discrepancies would be expected if the concentration of the H and/or Al in the Raney nickel was not uniform, i.e., the thermomagnetic curve is a composite of a spectrum of curves with different Curie points. This postulate would also explain the thermomagnetic curves that are essentially linear in the region where the Curie point might be expected.

Lattice spacings for solid solutions of Al in Ni increase about linearly with Al content; e.g., for 7.5 atom% Al, 3.5380 Å compared with 3.5240 Å for pure Ni (*20*). The lattice spacing of NiH was reported as 3.721 Å (*23*). For Raney nickel lattice dimensions of 3.53–3.55 Å were found; however, these values have moderately large uncertainties due to line broadening, and generally, the lattice spacings do not vary in a consistent way with severity of preparation or subsequent evacuation.

We interpret the present magnetic data

TABLE 4

DATA CALCULATED FROM EQUATIONS 1–3

		Maximum atom fraction of solute[a]		Curie temperatures, K	
Sample	Evacuation temp. °C	Aluminum	Hydrogen	Calculated	Observed
IIA	25	0.1160	0.3480	232	~300
	209	.0797	.2389	357	~440
	310	.0606	0.1819	422	
	500	.0381	.1143	500	~590
IIA-B	25	.0581	.1743	431	
	299	.0361	.1083	506	~600
IIIA	25	.0557	.1672	439	
	104	.0361	.1083	506	
	204	.0422	.1265	486	~565
	304	.0176	.0528	570	~580
	475	.0172	.0517	572	~585
COM	25	.0796	.2389	357	
	103	.0715	.2146	385	
	202	.0673	.2018	399	
	300	.0567	.1702	436	~540
	500	.0502	.1507	458	540

[a] From Eq. 2 assuming that the nickel solid solution contains only aluminum or hydrogen. Chemisorbed and dissolved hydrogen would be expected to affect magnetic properties in a similar way.

as indicating that nickel in Raney nickel is present as a solid solution containing aluminum and/or hydrogen and that the composition of the nickel solid solution is not uniform. These conclusions are based on the following arguments: (a) The small crystallite size of "nickel" in the catalyst, about 50 Å, would be expected to cause changes in magnetization-field data and thermomagnetic curves compared with massive Ni. The saturation magnetization at 0 K, however, should not be influenced by particle size, and the Curie points of 50 Å particles should be essentially the same as for massive nickel. (b) The saturation magnetization extrapolated to 0 K is substantially smaller than that of massive nickel, and the Curie points are lower. The lower Curie temperatures seems to eliminate the possibility of the catalyst containing pure nickel plus a nonferromagnetic nickel component. (c) Curie temperatures estimated from Eq. 3 are lower than the observed values, suggesting that the composition of the nickel solid solution is not uniform. This conclusion is consistent with the nature of the original Raney alloy and the method of activation.

On this basis, the increase in magnetization and Curie point with increasing evacuation temperature results from removal of aluminum and/or hydrogen from the nickel solid solution. Whatever the nature of this process, it is fairly effective, as evacuation of samples IIA and IIIA at 500°C increases the saturation magnetization at 0 K to 86 and 91% of that of bulk nickel. If Argument (c) is valid, the nickel solid solutions of different composition may have different lattice spacings that will contribute to the X-ray diffraction line broadening by small particles. Thus, estimates of average particle size by this method may be too low. Particle sizes calculated from surface areas are about 60% larger than those from line broadening (*8*).

We note here that the present magnetic data agree substantially with magnetic studies published very recently by Prettre and co-workers (*24*). These results will be discussed in the subsequent paper.

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