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Photoelectric Work Function Measurements on Nickel–Copper and Nickel–Gold Alloy Films

Clean Surfaces and Adsorption of Ethylene and Carbon Monoxide

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The work function Φ and the change in work function ΔΦ caused by the adsorption of CO or C_2H_4 have been measured as a function of the overall composition of equilibrated Ni–Cu and Ni–Au alloy films. The measurements reveal that Φ as a function of bulk (average) composition of the alloy films has the same character for alloy films annealed below the critical temperature T_c, where two phases coexist (a Ni-rich phase and a Cu- or Au-rich phase), as well as for films annealed above T_c where only one phase is found. There always appears to be a broad range of concentrations where Φ is independent of the composition. Both the Φ and ΔΦ measurements indicate the surface in this concentration range to be Cu rich (about 20 atom% Ni) or Au rich (about 10 atom% Ni). The critical temperature T_c of Ni–Cu alloys was checked. The results agree with the value predicted by Meijering. The C_2H_4 adsorption experiments reveal that on Ni–Au surfaces less deep dissociation occurs and more partially hydrogenated C_2H_4 species are present than in the case of Ni–Cu alloys. The results indicate that the surface of Ni–Cu alloys within the concentration range of constant surface composition contains larger Ni clusters than in the case of Ni–Au alloys.

INTRODUCTION

This paper deals with nickel alloys, and the study has two main aspects. The first is to investigate the changes in the adsorption behavior of C_2H_4 caused by alloying of nickel with an inactive element and the second is to contribute to the solution of some problems of the surface and phase composition of Ni alloys which segregate below the critical temperature T_c.

Previously, the adsorption of C_2H_4 and its interaction with hydrogen in the adsorbed layer was studied by measuring the photoelectric work function Φ of evaporated pure metal films (*1*). Various metals were studied and the following forms of C_2H_4 adsorption were detected. On Cu and Au, C_2H_4 was adsorbed only weakly and this adsorption was accompanied by a decrease in Φ ($\Delta\Phi < 0$). On Ni, Pd, and Pt, the first doses of admitted C_2H_4 were adsorbed with dissociation of C–H bonds which results in $\Delta\Phi > 0$ on Ni and Pd and $\Delta\Phi < 0$ on Pt. Part of the C_2H_4 from the consecutive doses was hydrogenated in the adsorbed state and the half-hydrogenated species were responsible for the decrease in Φ on Ni, Pd, and Pt. The decrease $|\Delta\Phi|$ measured for these metals increased in the same order as the "hydrogenation activity" of the metals increased, namely, Ni < Pd < Pt, or the "dehydrogenation power" decreased (*2*). Finally on these metals, a weak adsorption of C_2H_4 also occurs, causing Φ to decrease. On pure metals, C_2H_4 is thus adsorbed in various forms which, depending on the metal, differ in the degree of dissociation of the C–H bonds, and the various species cause different changes in the work function Φ.

Data on work function changes, $\Delta\Phi$, of alloys upon C_2H_4 adsorption are completely missing in the literature. However, there are good reasons why information is needed. Alloying causes important changes in the selectivity and activity of metals in the reactions of hydrocarbons (*2*, *3*), and this must be connected with differences in the composition of the adsorbed layer (adsorption complexes) on pure metals and alloys. The measurements of $\Delta\Phi$ upon adsorption alone cannot solve problems of the chemical composition of adsorption complexes but do contribute to the solution. In any case, the $\Delta\phi$ values are valuable characteristics of the complexes.

Recently, much effort has been made to determine the surface composition of alloys. Nevertheless, some problems still remain unsolved. For the systems like the ones studied in the present paper, namely, Ni–Cu and Ni–Au alloys, the experiments on chemisorption (*4*, *5*), activity (*6*), and work function measurements (*7*) led previously to the following conclusion (*8*). In a certain region of temperatures, under the so-called critical temperature T_c, and concentrations a miscibility gap occurs where two phases, a Ni-rich and a Cu- (or Au-) rich phase, coexist at equilibrium. Films composed of two coexisting phases are built up of crystallites of a cherry-like form: a kernel which is formed by the Ni-rich phase and an external shell formed by the Group Ib metal-rich alloy. Many of the existing data are explained by this model consistently, but some puzzling problems exist as well. One of these is the apparently identical surface composition (near to that of the Ib metal-rich phase) for the two-phase as well as for the one-phase materials; this is indicated by chemisorption (*9*) as well as catalytic experiments (*10*). To check this point and, possibly, in order to gain new evidence for this phenomenon, we performed the experiments described below with a series of Ni–Cu alloys equilibrated *above* and *below* the critical temperature. Because of the limitations of the apparatus used by us we draw on the Auger spectroscopic data of Williams and Boudart (*11*) obtained with Ni–Au alloys annealed at $T > T_c$ instead of performing our own experiments with Ni–Au films equilibrated above the critical temperature.

TABLE 1

Values of the Critical Temperature T_c Given in the Literature

T_c (°C)	Reference
800	Calculated in Ref. (*8*) according to data of Ref. (*12*)
320	Calculated in Ref. (*13*) according to data of Ref. (*12*) and (*14*)
177	Estimated by Meijering (*15*) according to the data on the Ni-Cr-Cu system

In course of the present investigation it appeared that the critical temperature for Ni–Cu alloys is by no means certain. The literature offers the values of T_c given in Table 1. The value by Elford *et al.* (*13*) is usually considered to be the most reliable.

EXPERIMENTAL

For details on the experimental technique the reader is referred to previous articles (*16*, *17*). The main features were as follows.

The experiments were performed in a phototube described before as tube II. The alloy films, of average thickness 25–30 nm, were prepared by successive evaporation of both metal components on a quartz carrier and annealed at various temperatures for 30 to 40 hr.

Nickel films were evaporated from a Ni wire directly. Gold and copper were evaporated from these metals mounted on a multihairpin W filament. During evaporation and annealing the pressure did not exceed 10^{-9} Torr. Ni–Au alloys were annealed at one temperature (420°C), while for Ni–Cu three temperatures were chosen, namely, 165, 215, and 420°C.

After the annealing procedure was finished gases were admitted slowly until a pressure of $2\text{–}8 \cdot 10^{-3}$ Torr for C_2H_4 and 10^{-4} Torr for CO was reached (pressures are uncorrected readings of the ionization gauge in N_2 equivalents). During the admission itself no pressure measurements were performed because a working ionization gauge would change the composition of the gas phase. The gases used were of 99.95% purity for C_2H_4 and 99.997% for CO (L'Air Liquide, Bruxelles).

As a rule the photoelectric current was monitored at a constant wavelength of the irradiated monochromatic light. At several stages of the gas admission, the flow of gases was interrupted and the work function determined by measuring the photocurrent at various wavelengths. Thereafter the admission of gases was continued. In some experiments the interaction of the adsorbed layer of C_2H_4 with admitted H_2 (purity 99.997%) or of an adsorbed layer of H_2 with admitted C_2H_4 was also followed in the way described.

The films used for the photoelectric measurements are alloys of continuously varying composition. Chemical and structural (X-ray diffraction) analysis of the films was performed after photoelectric measurements when the film has been taken out of the apparatus and cut into several strips. Chemical analysis of the strips was performed by nondispersive X-ray fluorescence [see Ref. (18)] or, in the case of one-phase Ni–Cu films, by X-ray diffraction analysis using the lattice constant from Pearson's "Handbook of Lattice Spacings" (*19*).

RESULTS

Phase Composition of the Films

The Ni–Au films equilibrated at 420°C were composed, in full agreement with the known phase diagram, from two phases. Strips of a varying average Ni–Au composition showed a varying ratio of the two alloy phases present while the position of the diffraction peaks remained at the expected diffraction angles [see Ref. (*18*)].

The Ni–Cu films were annealed at three different temperatures. It appeared that after equilibration at 420 and 215°C the films were formed of one phase only. For an illustration of this fact, in Fig. 1 a diffraction pattern is shown of an alloy with an average composition of 49 atom% Ni. The position of the peak corresponds well with the position expected for one-phase alloys.

The situation is different when the Ni–Cu films are annealed at 165°C. The X-ray diffraction pattern (see Fig. 1) indicates the presence of two phases, a Cu-rich one and a Ni-rich one. The pattern is obtained after 40 hr of annealing. It is highly probable that at this temperature two phases

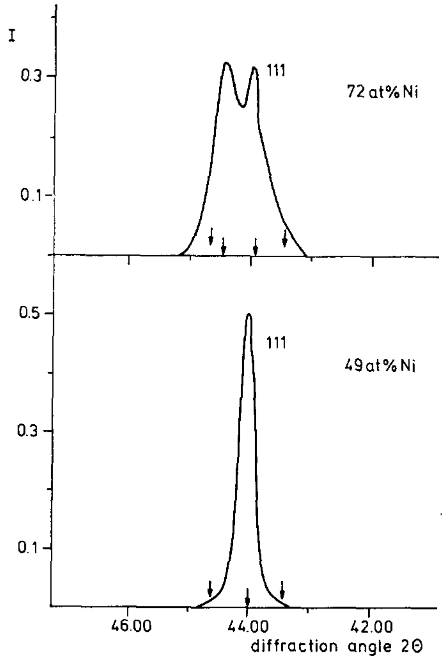

FIG. 1. X-ray diffraction patterns of a two-phase Ni–Cu alloy film annealed at 165°C (upper part) and of a one-phase Ni–Cu alloy film annealed at 420°C (lower part).

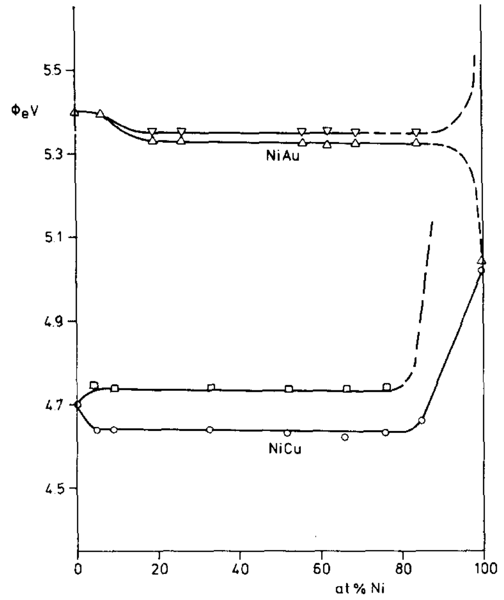

FIG. 2. The work function Φ of Ni–Cu and Ni–Au alloy films as a function of the overall composition. (○), Equilibrated (420°C) Ni–Cu films; (□), after admission of 10^{-4} Torr CO to the Ni–Cu alloy film; (△), equilibrated (420°C) Ni–Au film; (△), after admission of 10^{-4} Torr CO to the Ni–Au alloy film.

really exist at equilibrium, but on the other hand the breadth of the peaks and the bad resolution indicate that the films are not homogeneous and thus not at full equilibrium.

Films which have been annealed and homogenized above the critical temperature T_c do not show any detectable segregation of phases when they are brought back to temperatures below T_c. However, it is known that they segregate at low temperatures when the structure of the film is made defective by, e.g., formation and decomposition of hydrides (*33*).

Work Function of Ni–Cu and Ni–Au Films

Figure 2 shows the work function Φ as a function of the bulk composition of the Ni–Cu films. The data shown are for a film equilibrated at 420°C but similar courses of Φ for the other films equilibrated at 215 or 165°C are found. It is remarkable, indeed, that the same independence of Φ on the bulk composition in a broad range of concentrations is found for one-phase alloys (equilibrated above T_c) as well as for films which contain two phases. The emission constant variations were also similar for the one- and two-phase systems.

The course of Φ found for Ni–Au films as a function of concentration looks very much like the one measured for Ni–Cu and Pt–Au alloys. A broad plateau for all concentrations within the miscibility gap occurs.

Work Function of Alloys after CO Adsorption

In the broad range of Ni concentrations the change in Φ caused by adsorption of CO at 293 K (ΔΦ) is also constant (Fig. 2). The ΔΦ value in this region of concentrations is equal to ~0.11 eV for Ni–Cu films and ~0.04 eV for the Ni–Au films.

Work Function of Films after C_2H_4 Adsorption

The photocurrent monitored during the continuous admission of C_2H_4 on pure Ni reveals the following behavior. It decreases first (increase in Φ), reaches a minimum, and starts to increase again (decrease in Φ) as is shown in Fig. 3. It has been checked at several stages of adsorption that the variations in the photocurrent are indeed

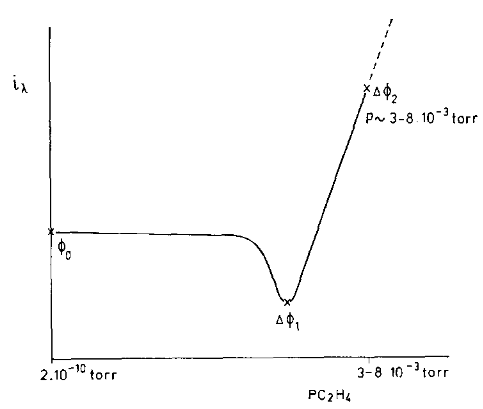

FIG. 3. Electron emission current observed with pure Ni as a function of ethylene pressure.

due to the corresponding changes in Φ. With pure Au or Cu only, a decrease in Φ is observed.

The photocurrent measured with Ni–Cu and Ni–Au alloys decreases monotonically when C_2H_4 is being admitted to the films. In this respect the behavior of the photocurrent resembles that of pure Cu or Au, respectively (Fig. 4).

Values of changes in Φ at the maximum increase ($\Delta\Phi_1$) and the decrease at $2\text{–}8 \cdot 10^{-3}$ Torr denoted as $\Delta\Phi_2$ are presented in Table 2. Table 2 also gives the $\Delta\phi$ values ($\Delta\Phi_3$) found after prolonged pumping ("irreversibly" bound species) of the system after the films had been exposed to C_2H_4, at the highest pressure used here ($2\text{–}8 \cdot 10^{-3}$ Torr).

Interaction of C_2H_4 with H_2

When some of the films were exposed to C_2H_4 ($\Delta\Phi_2$), the gas phase was removed subsequently ($\Delta\Phi_3$) and H_2 was admitted thereafter up to a pressure of $5 \cdot 10^{-3}$ Torr at 293 K. After 18 hr the gas phase was pumped off again and the $\Delta\Phi_4$ value determined (see Table 2).

In some other experiments the films were precovered by irreversibly bound H_2 (at 293 K) prior to the admission of C_2H_4. On the Ni alloy films even at $5 \cdot 10^{-3}$ Torr H_2, no change in Φ by adsorbed H_2 could be measured, in contrast with pure Ni where a $\Delta\Phi \sim +0.13$ eV (*1*) is observed at $5 \cdot 10^{-3}$ Torr H_2. The Φ values found for C_2H_4 on pure Ni as well as on Ni alloys when these are precovered by adsorbed hydrogen are lower than those observed with the films without preadsorbed hydrogen (Table 3).

TABLE 2

Selection of Representative Work Function Changes Caused by Ethylene Adsorption and by Further Treatment on Ni and Ni Alloys[a]

Metal	$\Delta\Phi_1$ (eV)	$\Delta\Phi_2$ (eV)	$\Delta\Phi_3$ (eV)	$\Delta\Phi_4$ (eV)
Cu	—	−0.38	0	0
Ni-Cu	—	−0.40	−0.05	+0.13
Ni	+0.13	−0.46	−0.34	−0.25
Ni-Au	—	−0.45	−0.17	−0.07
Au	—	−0.46	0	0

[a] All changes in Φ (ΔΦ) are related to the Φ value of the clean metal, before adsorption. $\Delta\Phi_1$ = observed increase in Φ after C_2H_4 dosing. $\Delta\Phi_2$ = decrease in Φ after admission of $2\text{–}8 \cdot 10^{-3}$ Torr C_2H_4. $\Delta\Phi_3$ = change in Φ after evacuation of the system. $\Delta\Phi_4$ = change in Φ caused by exposure of the films with irreversibly adsorbed C_2H_4 to hydrogen at $5 \cdot 10^{-3}$ Torr. After 18 hr the gas phase had been pumped off.

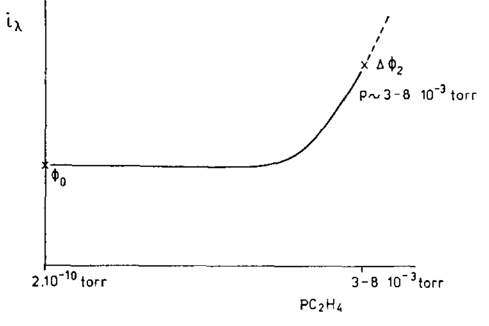

FIG. 4. Electron emission current observed with pure Cu, pure Au, Ni–Cu, and Ni–Au as a function of ethylene pressure.

DISCUSSION

First, the problem of the correct critical temperature, T_c, of Ni–Cu alloys will be discussed because it is of relevance for other questions studied.

The X-ray diffraction analysis of Ni–Cu films prepared at different temperatures has led to the conclusion that when the films are equilibrated at 215 and 420°C they contain only one phase (a complete miscibility). In films prepared at 165°C two phases are present. These results mean that the critical temperature lies below 215°C but above 165°C. It might be objected that perhaps the thin films have a lower T_c than macrocrystals, because it is on thermodynamic grounds unfavorable to separate

TABLE 3

A Comparison of the Decrease in Φ for Clean Surfaces and for Hydrogen-Precovered Surfaces, when Exposed to 2–$8 \cdot 10^{-3}$ Torr of C_2H_4 and Then Evacuated

Metal	$\Delta\Phi_3$ Pure	$\Delta\Phi_3$ H_2 covered
Ni	-0.34	-0.59
Ni-Cu	-0.05	-0.15
Ni-Au	-0.17	-0.26

phases when particles of a solution phase are too small (*23*, *25*). However, such an effect can be expected only with particles much smaller than those present in films (*25*, *26*) so that it seems to be justified to conclude that the T_c of the Ni–Cu system indeed lies between 215 and 165°C. If we compare our data with the predictions made by various authors, the T_c predicted by Meijering (*15*) is in very good agreement with the reality.

From the experiments it also became obvious that a film once homogenized above T_c does not segregate measurably into two phases during a prolonged annealing below T_c. Evidently, the presence of lattice defects (*33*) (which disappear during the homogenizing of the film) and the presence of a larger surface area prior to the equilibration are necessary conditions for an equilibration to proceed fast enough to be observable at the annealing temperature applied.

The work function Φ as a function of bulk (average) composition of the alloy films has the same character for all films studied; namely, there is always a broad range of concentrations where Φ is independent of the composition. The dependence is the same for all films irrespective of whether one or two phases are present in the bulk. This is a remarkable situation which evokes the principal question of whether Φ measurements reflect the surface composition of alloys at all properly. This point is the more important because there is some controversy with regard to the surface composition of Ni–Cu alloys as determined by various authors using different methods.

Work function measurements on metal A covered by a monolayer of metal B show that the system reveals a work function Φ of pure metal B (*20*). This proves that Φ is a parameter very sensitive for the surface layer. This statement is confirmed by several other results [see e.g. Ref. (*21*)]. However, up to now there is no satisfactory theory for the work function of alloys as a function of composition. A theory published recently (*22*) showed that the variation of Φ with alloying falls below the linear interpolation between the Φ's of the pure metals. How much of the nonlinearity experimentally found is due to the surface dipole contribution ("relaxation" of electrons at the surface) to Φ is not known exactly.

Nevertheless, the following conclusions with regard to the work function measurements as an analytical tool for determination of the surface composition can be made in any case: Changes in Φ do reflect the variation in composition, and when Φ is constant the surface composition is constant as well.

Changes in Φ on the series of Ni–Cu alloys are consistent with the results of H_2 chemisorption (*4*, *5*) at $T \approx 300$ K. This adsorption proceeds selectively on Ni only. Adsorption per unit surface area is independent of the alloy bulk composition in a broad range of composition and the results are almost the same for films prepared at $T \approx 180$–200°C and powders prepared at 200 or 420°C, respectively. Moreover, from the amount of adsorbed H_2 we may conclude that the surface composition is 15–20 atom% Ni.

On the basis of the data just mentioned, we conclude that the surface composition of various Ni–Cu films studied here was indeed the same function of the average bulk composition and it was independent of the phase composition of films. Evidently, the surface composition of the one-phase Ni–Cu films is the same as the surface composition of the Cu-rich alloy which is stable under T_c. (The reason is not yet clear, but in three dimensions the alloy with about 20% Ni reveals the highest $|\Delta G|$ value of alloy formation, which points to a particular stability of the alloy with this composition. Another fact of relevance is that the phase separation starts at structural defects such as the surface itself. These two pieces of information do not explain the phenomenon but perhaps make it less surprising.)

This also appears to be the case with the Ni–Au films. The surface composition of the two-phase Ni–Au films investigated in the present work was namely about equal to that determined by Auger spectrometry (*11*) for a Ni–Au alloy annealed above the critical temperature ($\sim$10 atom% Ni). The surface composition of the two-phase Ni–Au films is estimated here by comparing the change in Φ caused by CO adsorption (selectively on Ni at 293 K) on the Ni–Cu films (0.11 eV) with the change in Φ observed on Ni–Au alloys (0.04 eV). According to these two figures and because the surface content of Ni in the Ni–Cu alloys is probably between 15 and 20% Ni, we estimate the Ni surface content of the Ni–Au alloys to be 10 ± 5% Ni.

The films used for this research (and the films used in various previous work as well) are prepared in such a way that Cu or Au is condensed first on the cathode carrier and then covered by Ni. Already after a rather short equilibration time the vacuum-side surface is formed by the Cu-rich or Au-rich alloy (*8, 20, 21*), irrespective (within certain limits, of course) of the temperature of equilibration. This can be easily understood by means of the model suggested by Sachtler *et al.* for Ni–Cu (*8*). Cu has a much higher migration rate than Ni so that the Ni crystallites are soon covered by a Cu-rich layer. This process takes place even at room temperature with such a rate that the migration is visible by eye (*8*). Next to the surface migration Cu also penetrates into Ni while Ni is being dissolved slowly in the Cu layer (the first penetration is faster, because this system reveals a Kirkendall effect) up to the concentration equal to that in the Cu-rich phase stable at a temperature below T_c. When $T > T_c$ and the equilibration time is sufficiently long the Cu-rich shell and the Ni-rich kernel of crystallites disappear during a prolonged equilibration, and a homogenous solution is formed. The solution is homogeneous except the outermost layer which is enriched by Cu even at equilibrium. Only below T_c does the surface segregation extend into the bulk of the alloy. Recently, such a model has been analyzed exactly by a general theory (*23*).

Having in mind the picture of the surface composition as suggested above, the results obtained with adsorption of gases and the changes in $\Delta\Phi$ upon adsorption will be discussed. We shall start with CO adsorption.

The change in Φ ($\Delta\Phi$) upon adsorption of CO is on Ni–Cu alloys about 10 times and on Ni–Au alloys about 25 times lower than on pure Ni (*34*). However, according to the results of volumetric adsorption measurements the Ni content (*4, 5*) of Ni–Cu alloy surfaces should be only four to six times lower than that on a pure Ni surface. The infrared spectra (*24*) of the Ni–Cu/CO system showed that there is actually no controversy between these two results. Infrared spectra revealed that one of the forms of the adsorbed CO disappears upon alloying relatively more than the other one. The form more affected is that which needs for its adsorption sites among several (two, three) Ni atoms (surface holes) and which is characterized py a strong back-donation (back-donation increases $\Delta\Phi$). Therefore, it is not surprising that the $\Delta\Phi$

after CO adsorption on alloys is lower than expected according to the Ni content and a simple linear dependence of $\Delta\Phi$ on the amount of CO adsorbed.

From previous C_2H_4 adsorption experiments on pure metals (*1*) it became evident that, on Ni, C_2H_4 was adsorbed first dissociatively causing the increase in Φ. This was followed by formation of a complex which became partially hydrogenated and caused a decrease in Φ. The adsorption of C_2H_4 on Ni–Cu alloys causes only a decrease in Φ ($\Delta\Phi_3$), and the decrease is five times lower than for pure Ni. However, we believe that the correspondence of this decrease (five times) with the expected Ni content decrease is rather incidental. It is because the $\Delta\Phi_3$ effect is the sum of the contribution of deeply dehydrogenated (Φ-increasing) complexes as well as the partially hydrogenated (Φ-lowering) complexes. We can see this on the effect of the subsequent hydrogenation ($\Delta\Phi_4$ effect) which is quite different on Ni and on Ni–Cu. The $\Delta\Phi_3$ value measured for Ni–Au films is larger than that found for Ni–Cu films (see Table 2). We suggest an explanation based on the following considerations.

Various pieces of information on the dissociative adsorption of C_2H_4 (or of similar molecules like butenes, cyclopropane, etc.) and its self-hydrogenation show that it is necessary to distinguish a simple (single) dissociation (one C–H bond broken) and a multiple or deep dissociation (more C–H bonds broken and to some extent also the C–C bonds). There is evidence (*27*) that the deep dissociation is a process which needs more sites on the surface (larger ensembles) to proceed. By alloying, the number of larger ensembles decreases, but they do not disappear completely. First, even in random solutions, there is always a certain probability of finding ensembles with two, three, or four Ni atoms. Second, Ni–Cu alloys reveal clustering of Ni in the bulk (*28*) and the same can be expected for the surface. Therefore, we expect that alloying must decrease the degree of dissociation of C_2H_4 but should not exclude it completely, at least at concentrations of Ni corresponding with the plateau of the Φ in a broad range of concentrations.

The first doses of admitted C_2H_4 do not cause an increase in Φ, typical for hydrogen made free from adsorbed C_2H_4, on alloys. However, this is still an insufficient proof for the absence of (deep) dissociation. Pure H_2 admitted to Ni–Cu alloys does not increase Φ measurably either. Deep dissociation is thus not excluded, but, of course, it proceeds to a smaller extent on alloys as compared with pure Ni.

When a layer formed by C_2H_4 adsorption on Ni–Cu alloys has been hydrogenated for 18 hr and the weakly bound species pumped off afterwards, a positive $\Delta\Phi_4$ value (see Table 1) resulted. This can best be explained by the presence of small amounts of nonreactive, deeply dehydrogenated or carbonaceous species (*29*). If this is a correct explanation we have to conclude that after prolonged hydrogenation and evacuation of the adsorbed layer there are relatively more carbon deposits on Ni–Cu than on pure Ni or on Ni–Au alloys. The question arises whether there is any reason to expect this behavior.

Recently, Van Barneveld and one of us (*30*) studied the hydrogenation reaction and self-poisoning phenomena with benzene on Ni and Ni–Cu alloys. The conclusion was reached that Ni is more sensitive for poisoning than Ni–Cu alloys, but, when the catalysts are poisoned upon reaction at high temperatures, then this poisoning appeared to be more irreversible on alloys than on Ni. Other investigations (*31*) showed that with Ni–Cu a complete disappearance of hydrogenolysis by alloying was not achieved. Only a diminishing of the contribution of this reaction was achieved up to the activity in hydrogenolysis which was also expected for pure Cu.

Other information which should be mentioned is that according to the conductivity and magnetic measurements (*32*) the Ni clusters are larger in Ni–Cu than in Ni–Au alloys. Diluting of active sites leads to a slowing down (or elimination) of hydrogenolytic splitting of hydrocarbons and should thus be more pronounced with Ni–Au than with Ni–Cu. Moreover, Au is less active in chemisorption than Cu, so that the hydrogenolytic activity of Ni–Au alloys may fall to a very low value or even disappear.

The explanation of the data presented in this paper is then suggested as follows. By adding Cu to Ni, the multisite reactions like splitting of C_2H_4 are decreased in extent, but the reactions for recovering the surface by the hydrogenation of carbonaceous species are also slowed down. Therefore, on Ni–Cu there is relatively *more of the deeply dissociated species left* after hydrogenation than on pure Ni. Dilution of Ni in Au is, however, greater than in Cu and as Au is more inactive than Cu and cannot assist the splitting of, for example, C_2H_4, *less of the deeply dissociated species is formed* on Ni–Au. Therefore, $\Delta\Phi_4 > 0$ for Ni–Cu but $\Delta\Phi_4 < 0$ for Ni–Au.[1]

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[1] Catalytic experiments with Ni-Au in order to check these ideas with other reactions are in progress in our laboratory.

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