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Adsorption and Desorption of Carbon Monoxide from Nickel and Nickel–Copper Alloys

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The extent of CO adsorption has been measured at 295 K and the thermal desorption of CO has been followed on Ni and Ni–Cu films prepared in an ultrahigh vacuum apparatus. The total extent of adsorption revealed a different behavior than the extent of hydrogen adsorption studied previously; an explanation involving gas-induced surface enrichment of alloys is suggested. An irreversible gas-induced enrichment has also been observed upon repeated runs of the thermal desorption of CO. The thermal desorption reveals the existence of two weakly bound states γ_1 and γ_2 and two more strongly bound states α_1 and α_2 on Ni and Ni alloys. Cu reveals only the weakly bound states γ_1 and γ_2. The population of various states varies with the Cu content as well as the chemisorption bond strength of the α_2-species. Suggestions are made on the adsorption modes of CO.

INTRODUCTION

The formation of Ni–Cu alloys is endothermic; therefore, below a certain critical temperature (T_{cr}), coexistence of two phases in equilibrium must be expected. In the literature (*1*, *2*) several phase diagrams were suggested with T_{cr} varying from 320 to about 800°C. However, recently Franken (*4*) from our laboratory has established that the critical temperature is actually much lower. The critical temperature is found to be very near to the value predicted by Meijering (*3*), around 170°C. Because of this correction in T_{cr} the form of the phase diagram and the composition of the two phases in equilibrium at $T < T_{cr}$ became uncertain. However, it seems to be a safe estimate that the composition of the Ni-rich α phase is several percentages lower than 98% Ni and the composition of the Cu-rich β phase is 20–25% Ni, at temperatures of 100–150°C.

There is already substantial information available on the surface composition of Ni–Cu alloys. According to work function measurements (*4*) the surface composition of Ni–Cu alloys is almost constant in a broad range of concentrations (about 90–20% Ni) and it is very important to note that it is the same for alloys annealed at $T > T_{cr}$ as well as at $T < T_{cr}$; the same surface composition was found at temperatures from 165 to 400°C. The work function measurements thus fully confirm the conclusions made earlier on the grounds of hydrogen adsorption (*5–8*). It is an interesting point that hydrogen adsorption measurements (*5–8*) led to the same results for films annealed at 200°C[2] and for powders prepared and equilibrated at 450°C.

Auger spectrometry has also been applied to this system. The materials investigated were either polycrystalline powders or

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[2] When these films were found to be composed of two phases (*1*), it was because the time of annealing was insufficient for full equilibration.

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monocrystals. Earlier papers (*9, 10*) on this subject used for analysis the high energy peaks (0.7–0.9 keV) and the authors concluded that the composition of alloy surfaces was the same as that of their bulk. However, more recent papers (*11, 12*) which used the low energy peaks (~0.1 keV) for analysis found that the surface was strongly enriched in Cu.

These papers (*11, 12*) thus confirmed the results obtained by hydrogen adsorption and work function measurements. The difference in results obtained from high and low energy peaks shows, moreover, that the surface Cu-enrichment is limited and there is more Ni in the subsurface layer so that the electrons of 0.7–0.9 keV which bring information on the average composition of a thicker layer than the electrons with about 0.1 keV energy do not indicate any enrichment in Cu.

However, there were also some results in the literature which did not fit the picture as obtained from hydrogen adsorption, Auger spectrometry and work function measurements. Two groups of authors (*13, 14*) found that the extent of CO adsorption varied linearly with the Ni bulk content in an apparent contradiction to the hydrogen adsorption. Also, the selectivity in hexane reforming reactions (where –C– atoms participate as in the CO adsorption) showed variations with the Ni concentration in the region of concentrations where according to the hydrogen adsorption the number of Ni atoms in the surface should have remained constant (*15*). These open questions and the fact that nothing was known on the influence of alloying on the distribution of adsorption sites according to their energy were the reasons why this research was started.

EXPERIMENTAL METHODS

Apparatus, Materials, Procedure

The ultrahigh vacuum apparatus used and the experimental procedure were the same as in our earlier papers (*16, 17*). As in our previous work, various programs were used and are summarized in Table 1. The second column in this Table indicates the mode of adsorption which preceded desorption, either adsorption entirely at 78 K or preadsorption at 298 K, followed by cooling the film to 78 K in the presence of CO. The time for which CO was in contact with the film at the standard pressure (10×10^{-3} Torr at 295 K and about 2×10^{-3} Torr at 78 K) is indicated by t_a; t_p stands for the time period of pumping.

Thermal desorption was followed upon pumping by a Vac-ion pump. The temperature was raised from 78 to 473 K at a rate of about 0.67 K/sec. For other details, see Refs. (*16, 17*).

The phase and chemical composition was checked by X-ray diffraction. In spite of the same procedure being used in all cases (annealing at 200°C for 20 hr), several films showed the presence of two separate phases. According to the existing experience, the surface of these films should be formed mainly by the phase with the higher Cu content. In Fig. 1 (see below) the Ni concentrations indicated are those corresponding with the position of the diffraction maxima observed with the given sample. Full points are for films with two phases, they are plotted at the concentration corresponding to the phase with the higher Cu content.

RESULTS

Adsorption Measurements

Adsorption of CO is fast both at 295 and 78 K. The extent [n (295 K)] of CO adsorption at 295 K on a virgin film, at the pressure of 2×10^{-3} Torr has been determined as a function of alloy composition. The results are collected in Fig. 1. The Ni concentrations indicated are those corresponding with the X-ray diffraction maxima. The roughness factor of the films determined by Xe adsorption at 78 K

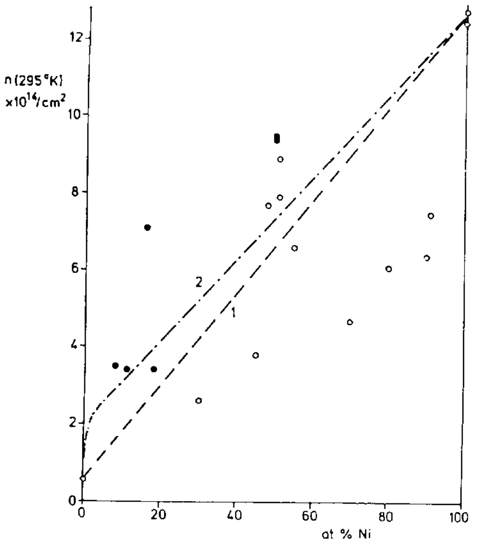


FIG. 1. Amount of carbon monoxide adsorbed per cm^2 of geometric surface area as a function of film composition. In this figure, the film composition is taken as corresponding with the X-ray diffraction maximum. (○) One phase films; (●) two-phase detected, a point is plotted at the composition of the Cu-rich phase; (1) linear function found by Engels *et al.* (*14*); (2) linear function found by Lyubarskii (*13*).

varied in the range 1.4–1.7 for Ni and all alloy films, and for Cu film it was 2.1. There was no significant trend in f as a function of film composition.

When the film is cooled from 295 to 78 K an additional amount of CO is adsorbed. At 78 K a considerable part of the amount [n_b (78 K) or n_e (78 K); according to the respective programs] totally adsorbed is adsorbed on Cu. For a given film, n_e (78 K) is about 65–80% of n_b (78 K). Evidently, a part of CO can be adsorbed by an activated process as found earlier with films sintered at lower temperatures (*18*).

It is known from the literature (*19–21*) that CO disproportionates on Ni at temperatures above 100°C. By disproportionation CO_2 is being released and carbon deposited on the surface. Therefore, when the adsorption/desorption cycle was repeated with the same film in the repeated runs, desorption of CO_2 was observed. CO_2 is desorbed in two peaks, one at 200–250 K and another around 470 K. During the runs repeated with the same film, about 60 (Ni)–70 (alloys)% of the n_b (295 K) value for the virgin film could be readsorbed. About 2% of the CO adsorbed appeared in the following desorption run as CO_2.

Thermal Desorption

The desorption profile is different for the different programs (see Table 1, for programs). Figure 2 (upper part) shows desorption spectra for pure Ni, programs (b) and (e). We can distinguish a variety of states according to the position of peak maxima and/or shoulders, γ_1 at 120 ± 30 K, γ_2 170 ± 30 K, α_1 at 315 ± 20 K and α_2 at about 455 K. We denote the part of CO which did not desorb at 475 K as a β state. Figure 2 (lower part) shows desorption spectra for pure Cu. Note the marked difference between the behavior of pure Ni and pure Cu films.

Figure 3 shows the desorption profiles for a film with about 8% Cu. The decrease of the α_1 and α_2 peaks compared with pure Ni can already be clearly seen. (Note:

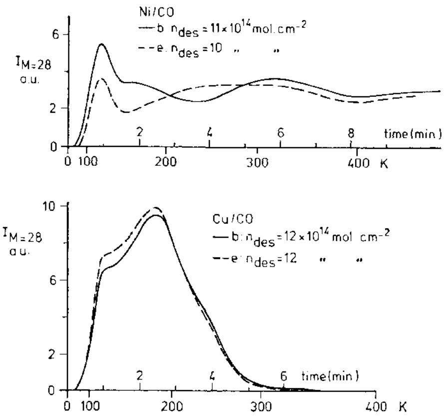


FIG. 2. Desorption profile of CO for various programs (see Table 1). Total amounts desorbed indicated. Upper part: pure Ni film; lower part: pure Cu film.

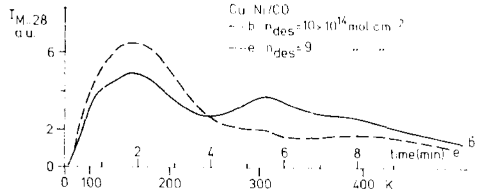


FIG. 3. Desorption profile of CO, alloy film of 92% Ni for various programs (see Table 1). Total amounts desorbed indicated.

TABLE 1

Adsorption Programs for Monolayer Coverage

Type	Temp range adsorption (K)	t_a (min)	t_p (min)
a	295–78	30	10
b	295–78	10	10
c	295–78	2	10
d	295–78	10	2
e	78	—	10

the units of the coordinates in Figs. 2 and 3 are directly comparable.)

The particular profile shown in Fig. 4 is for 30% Ni alloy but it is representative for the desorption from alloys in a wide composition range around this value. It can be seen that the α_1 peak increases slightly with increasing adsorption time t_a [programs (a) and (b)].

The desorption profile changes in a characteristic manner when the adsorption/desorption cycle is repeated several times with the same film. This can be seen from Fig. 5; with increasing number of runs, the α_1 peak decreases (absolutely) but simultaneously the γ_2 peak peak decreases. This reflects irreversible changes in the surface composition, namely, when comparing desorption profiles from alloys with varying composition we saw that with increasing Cu content the relative height of peak γ_2 increases while that of α_1 decreases. Therefore, a most straightforward explanation of the results presented in Fig. 5 is that with repeated runs the Ni content in the surface increases and that of Cu decreases, irreversibly under the given conditions.

The position of the three maxima, γ_1, γ_2, and α_1 does not show any systematic variation with alloy composition. Only the positions of the α_2 peak and of the CO_2 desorption (Figures 6 and 7) seem to be systematically shifted by alloying.

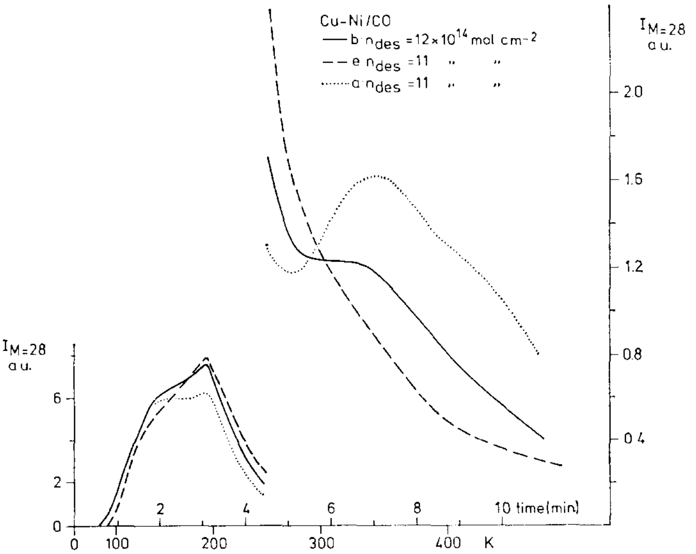
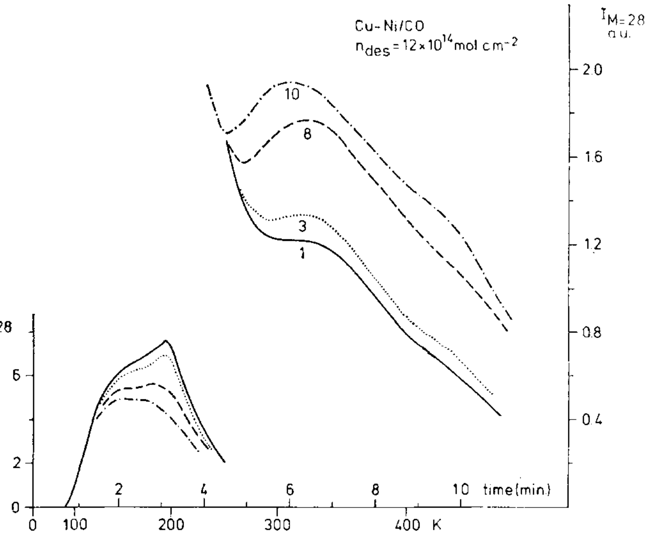


FIG. 4. Desorption profile of CO, alloy film, 30% Ni, various programs (see Table 1). Total amounts desorbed indicated.



IG. 5. Desorption profile of CO, alloy film, 30% Ni, b-type adsorption repeated with the same film. Run numbers indicated.

DISCUSSION

Surface Composition of Alloys

Let us first summarize the facts most relevant for the discussion.

1. Three independent methods, viz, work function measurements (*4*), hydrogen adsorption (*5, 6*) and low energy Auger spectrometry (*11, 12*) led to the same conclusions with respect to the alloy surfaces: the composition varies only marginally in a rather broad composition range and the surface of alloys is enriched in Cu. Slow-ion-back-scattering confirms this picture (*22*). There are good reasons to believe that all these methods reflect the characteristic features of alloy surfaces *in vacuo* correctly.

2. Hydrogen adsorption of films (*5, 6*) and on powders (*7, 8*) has the same character. Figure 8 summarizes the data schematically. According to point (1) this is more or less the curve of surface vs bulk composition. However, CO adsorption on the Ni–Cu system deviates from a picture like that in Fig. 8 quite substantially (see Fig. 1). First, the reproducibility of the results (scattering of points) is worse than with hydrogen on Ni–Cu (*5, 6*) or CO adsorption with other systems [Pd–Ag

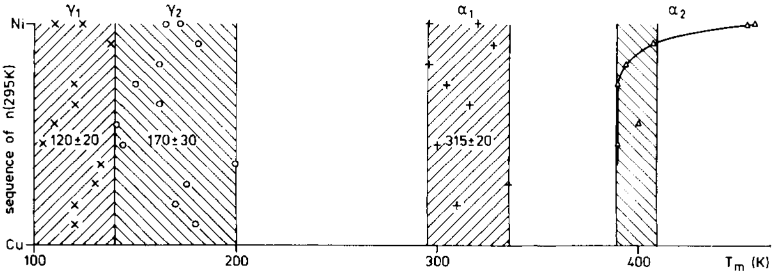


FIG. 6. Temperature of (shoulders) desorption profile maxima T, for various adsorption states (γ_1, γ_2, α_1, α_2) as a function of the total amount adsorbed n (295 K).

(*29*), Pt–Au (*23*)]. Second, the extent of CO adsorption does not vary in parallel with the Ni surface concentration. The CO adsorption extent decreases with the Ni bulk concentration more or less linearly in contrast to the behavior of hydrogen on the same series of Ni–Cu alloys (compare Figs. 1 and 8). However, such a discrepancy is not observed with, for example, the related Pt–Au system (*23*). With this system both H_2 and CO adsorptions led to identical conclusions, giving an overall picture like that in Fig. 8. Therefore, the two points mentioned above should be related to the specific behavior of the Ni and CO system.

Which features distinguish the Ni/Cu–CO system from other similar ones? For example, the corrosive character of CO adsorption even at very low pressures is a known fact (*24*) for a long time. Moreover, with Ni the formation of Ni carbonyls is possible at room temprateure and pressures as low as several Torr (*24*, *25*). Therefore, it can be reasonably expected that under the conditions applied when measuring the data for Fig. 1, serious changes in the surface structure of Ni–Cu alloys may occur due to the adsorption process itself. We know (see above) that the uppermost layer of Ni–Cu alloys *in vacuo* is enriched in Cu but the Ni concentration is increased to its bulk level in the subsurface layer(s), the average over several layers being almost equal to the bulk composition. We believe that due to the corrosive character of CO adsorption, Ni atoms of the subsurface layer become also accessible to CO molecules so that the total extent of CO adsorption varies more or less linearly with the bulk and not with the surface concentration of Ni. In fact, the gas-induced segregation of Ni to the surface cancels the Cu-enrichment of the surface *in vacuo*. A part of the Ni atoms attracted to the surface stays there irreversibly after CO desorption, as can be seen in Fig. 5.

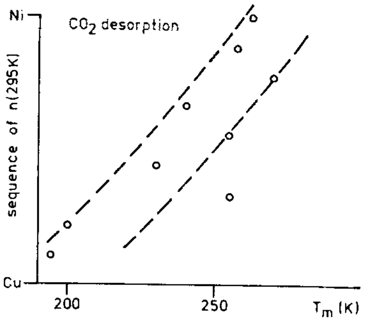


Fig. 7. Temperature of desorption profile maxima for CO_2 desorption as a function of the total amount adsorbed *n* (295 K).

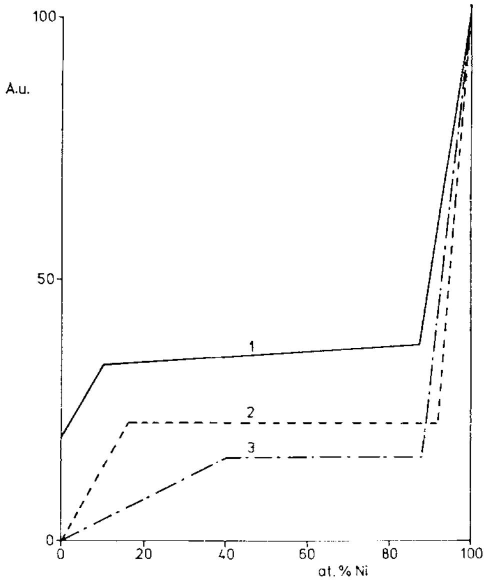


Fig. 8. Total amount of hydrogen adsorbed at 295 K as a function of film or powder. Composition: (1) Ref. (*7*); (2) Ref. (*5*); (3) Ref. (*8*).

Relying on this explanation, we can derive even more detailed conclusions by comparing the data in Fig. 1 on the one hand and the data of infrared (*26*), catalytic (*15*) and work function (*4*, *10*, *27*) measurements, on the other.

Work function changes ΔΦ caused by CO adsorption (*4*, *27*) follow a curve as a function of Ni bulk concentration like that in Fig. 8. The same holds for the catalytic activity in those reactions where ensembles of several Ni atoms are required for the reaction to occur [such reactions are, e.g., methanation of CO (*21*), disproportionation of CO (*21*) or hydrogenolysis of hydrocarbons (*6, 15, 28*)]. The difference between the behavior of $\Delta\Phi_{CO}$ (*4, 27*) and n_{CO} (295 K) (*13, 14,* this paper) as functions of the Ni content can be understood if the Ni atoms "attracted" (more precisely, "made accessible") to the surface were predominantly *isolated* atoms. On isolated atoms the back-donation is lower and only one form of the states detectable by infrared is possible (*26*). Also the $\Delta\Phi$ by CO is lower on sites with less back-donation. Therefore, the total extent of CO adsorption n (295 K) follows a different curve than the $\Delta\Phi$ effect or the activity in reactions requiring large ensembles.

Adsorption/Desorption States of CO

Let us now turn our attention to the desorption of CO and the identification of various states detected by temperature programmed desorption. There can probably be little doubt about the molecular character of the CO adsorption in γ_1 and γ_2 states. These states are observable on Ni as well as on Cu and the heat of adsorption is 10 ± 2 kcal/mole at most.

The α_1 state is absent on Cu and it is typical for Ni. Its population on alloys varies with the Ni content in alloys (compare Figs. 3 and 4). The position of the maximum of the α_1 desorption peak does not vary systematically with the composition of alloys. This reminds one of the infrared data: the population of various states detected by infrared varies strongly with alloying but the position of the infrared absorption maxima varies only marginally (*26*). Therefore, we ascribe the α_1 state to the adsorption of CO on Ni atoms with little or no interference of the Cu environment.

The situation is different with the α_2 state and CO_2 desorption. In contrast to the α_1 state, a systematic difference between Ni and alloys can be observed. The α_2 state desorbs at temperatures where CO dissociation is already possible (*19–21*) and we observe that alloying makes the desorption easier. Because a similar shift of comparable importance is absent in the infrared spectra (*26*), the α_2 state cannot *directly* be identified with one of the states detected by infrared. We are inclined to ascribe the α_2 peak to the desorption which either follows a recombination of "C" and "O" particles (*20*) or an adsorption of CO horizontal on the surface. In both cases the effect of alloying can be easily understood if some of the "O" particles or the "O" end of the CO molecules were bound on alloys to Cu instead of to Ni atoms. In a similar way, desorption of CO_2 should be preceded by desorption or even recombination of "CO" and "O," both attached to different components of the alloys.

In conclusion the following can be added. We saw that CO adsorption can supply useful information on the surfaces of Ni–Cu alloys but it is evidently less suitable for surface titration of Ni atoms than, e.g., hydrogen. The difference in the results of "titration" of Ni by H_2 and CO cannot be explained by the difference in ratio (H_2/CO) of the amounts adsorbed on the same surface area of pure Ni and Ni–Cu alloys, because with the Pt–Au (a system very similar to the Ni–Cu system)(*17, 23*) the ratio of both adsorptions (H_2/CO) was constant for Pt and all alloys. However, as has been shown, they can be explained by the corrosive action of CO adsorption.

Furthermore, by considering all available data a consistent picture of the Ni–Cu surfaces can be suggested which, however, requires a certain modification of some models (*27*) used earlier to explain data on Ni–Cu alloys.

Note added in proof. At the time this paper was being printed, a paper by K. Y. Yu, D. T. Ling, and W. E. Spicer, *J. Catal.* **44**, 378 (1976) appeared. The reader should notice the difference in the experimental procedure in that paper and in ours. Yu *et al.*

worked with the same exposure with all alloys and let CO adsorb at 173 K; this led to coverages lower than at saturation and probably varying with surface composition. CO molecules then reach their equilibrium positions only upon heating (compare the results of this paper for programs b and e), which process intervenes with desorption.

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