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Adsorption Studies with Cu/Ni Alloys

G. Ertl; J. Küppers



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(3) In the presence of an adsorbate the most favorable composition of the surface will be characterized by an enrichment with respect to the interior of that element which forms the strongest bonds with the adsorbate.

By photoelectric measurements we could show that, indeed, the latter type of surface reconstruction takes place. In the presence of carbon monoxide the surface of a Au/Pt alloy becomes enriched with Pt⁷ and that of Ag/Pd alloy with Pd.⁵ These surface reconstructions take days at room temperature and hours at a temperature of 100°C. Upon desorption of the gas at elevated temperature, this reconstruction is reversible.

The work function of the alloy then returns to the value prior to adsorption of CO.

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Adsorption Studies with Cu/Ni Alloys

G. Ertl and J. Küppers

Institut für Physikalische Chemie und Elektrochemie, Technische Universität, 3 Hannover, Germany
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The adsorption of oxygen and carbon monoxide at clean (110) faces of Cu/Ni alloys with 16, 45, 60, and 77% Ni content has been studied by means of LEED, Auger electron spectroscopy, work function measurements, and flash desorption. The results are compared with the behavior of the elementary metals. After proper preparation no phase segregation within the alloys could be detected and the surface and bulk compositions were shown to be identical by Auger spectroscopy. The adsorption of oxygen causes at first the appearance of a 2×1 structure on all surfaces, as is the case with Cu (110) and Ni (110). The corresponding change of the work function increases continuously with increasing Ni content. Further oxygen exposure leads to the formation of a c6×2 structure as on Cu (110) on a 16% Ni crystal, and to disordered adsorption at room temperature with the other samples. However, the 77% Ni surface develops a 2×2 structure after annealing. CO forms different ordered structures (1×2, 2×1 and c2×2 with the alloys. The adsorption energy of CO on the 45, 60, and 77% Ni samples is similar to that on Ni (110); the binding is somewhat weaker on the 16% Ni surface. Detailed measurements with the 60% Ni surface showed that the heat of adsorption is constant over a wide range of coverages. The results are discussed qualitatively from the point of view of the electronic structure of Cu/Ni alloys and the theory of chemisorption.

Introduction

Of fundamental importance for the theory of chemisorption and catalysis is the question whether the interaction between adsorbate and surface may be treated as a localized problem ("surface molecule") or if collective phenomena of the electronic structure of the metal play the dominant part. The problem can be tackled experimentally by studying with alloys of metals with different adsorption behavior, for example elements from the groups VIII and Ib of the periodic table. Besides these theoretical aspects such systems are of practical interest since mixed catalysts are frequently used and possess, in some cases, extraordinary properties.

Numerous investigations with Cu/Ni alloys have been made in the past,¹ but the results were frequently contradictory and no clear conclusions could be

drawn. Certainly one reason for this was the unknown surface structure and cleanliness of the (polycrystalline) samples. More important still is the fact that the composition of the surface may deviate considerably from the nominal bulk composition as has been shown for example by Sachtler *et al.*²

A reinvestigation of these problems with well-defined single crystal surfaces of known composition therefore seemed to be necessary. We have therefore investigated the adsorption properties of single crystals of Cu/Ni alloys. We report here the results obtained from the adsorption of O₂ and CO on clean (110) faces of Cu/Ni alloys with nickel contents of 16, 45, 60, and 77%. Some work function measurements have also been made with a surface containing 71% Ni. The results are compared with the properties of the elementary metals.

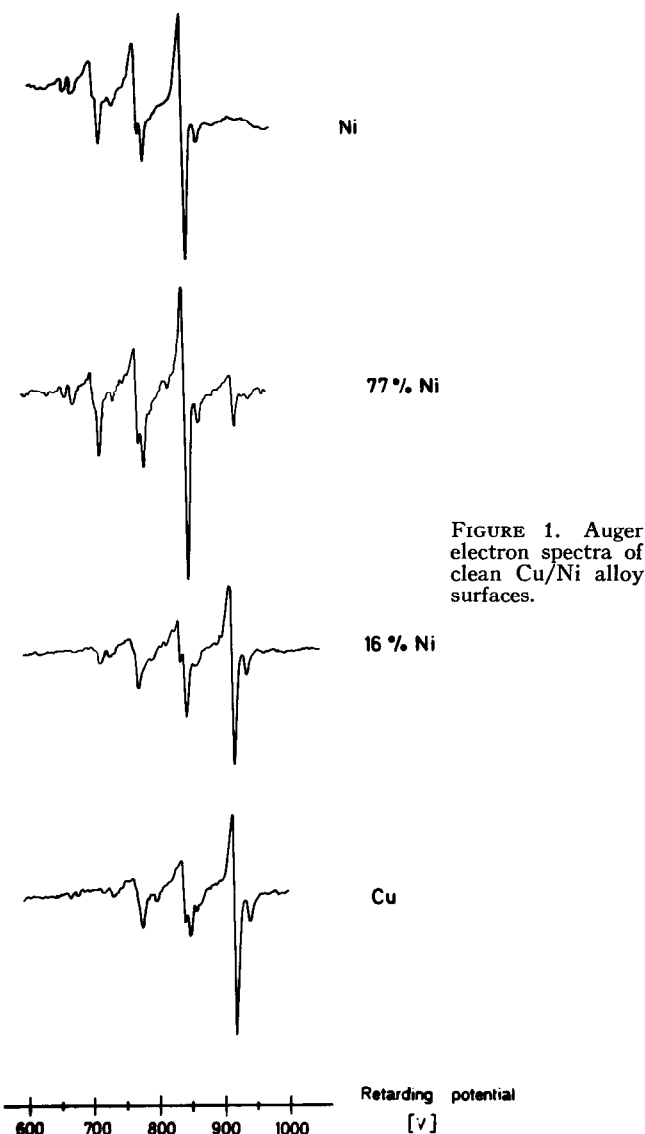


FIGURE 1. Auger electron spectra of clean Cu/Ni alloy surfaces.

I. Experimental

The experiments were performed with a four grid LEED system (Varian 120) with the addition of a glancing angle electron gun for Auger electron spectroscopy. Variations of the work function were measured with an electronically self-compensating Kelvin method using oxidized tantalum as the reference electrode. Mass spectra and flash desorption curves were recorded with a quadrupole mass filter (Finnigan).

The alloy single crystals (Metals Research) were oriented by x-ray diffraction and cut with a spark erosion machine within $\frac{1}{2}^\circ$ of the desired orientation. The used samples were cylindrical slices of 5–7 mm diameter and 1 mm thickness. These samples were mechanically polished and cleaned in the diffraction chamber by prolonged argon ion bombardment and careful annealing. The main contaminants were sulfur, carbon and oxygen as detected by Auger spectroscopy. Sulfur contamination causes in all cases an ordered $c(2 \times 2)$ structure as already reported previously for

the (110) planes of Cu³ and Ni.⁴ The concentration of impurities was always reduced to below the detection limit of our Auger spectrometer before adsorption studies were begun. The clean surfaces show sharp and bright diffraction spots and low-background intensities in the LEED pattern which must be attributed to only small differences between the (dynamical) scattering factors of Cu and Ni atoms.⁵

II. Surface Composition

Before discussing the surface composition the problem of bulk homogeneity must be considered, for in thermodynamic equilibrium Cu/Ni alloys segregate into two phases at lower temperatures, the critical temperature being in the range below 300°C.^{6,7} However a series of recent investigations by means of neutron scattering,⁸ magnetic measurements,⁹ and Mössbauer spectroscopy¹⁰ revealed that no or only minor deviations from randomness exist, provided that the samples had been homogenized at higher temperatures and then cooled down not too slowly. At temperatures below 500°C the rate of diffusion of Ni in compact Ni/Cu alloys is very small¹⁰ and therefore the configuration above the critical temperature is frozen in. The diffusion velocity may be enhanced by structural defects: This seems to be the reason why evaporated films as used by Sachtler may be equilibrated by prolonged heating at 200°C.

In our experiments the compact samples were carefully annealed above 500°C and thereafter quenched to room temperature. No indications of phase segregation have been found.

As already mentioned the composition of the surface of an alloy may differ considerably from that of the bulk. Unique information can be obtained by means of Auger electron spectroscopy. The spectra of Cu and Ni may be distinguished in particular in the region of

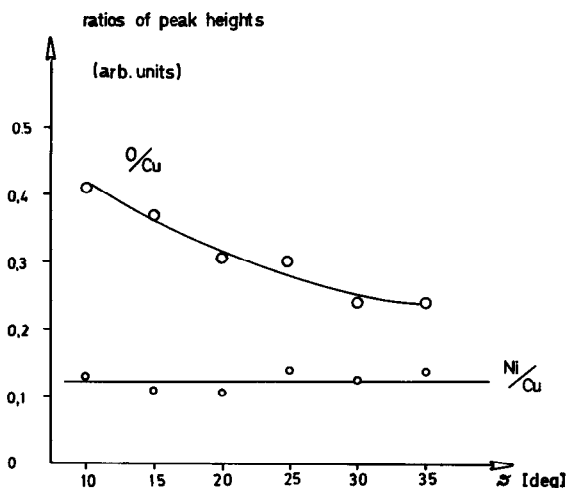


FIGURE 2. Variation of the ratio of Auger peak heights of an oxygen covered 16% Ni surface as a function of the angle between the incident electron beam and the surface.

higher energies: Ni shows a clearly resolved peak at about 720 eV and Cu at 930 eV. It has been shown explicitly⁵ that the heights of these peaks are a direct measure of the concentration of the corresponding element. Figure 1 shows the Auger spectra of clean surfaces of Cu and Ni and of two alloys. The analysis of these spectra shows that in all cases where the samples had been carefully annealed before hand, the compositions of the bulk and the surface were identical. A further check can be made by recording Auger spectra with different angles of incidence ϑ between the surface and the exciting electron beam. The ratio of the peak heights of two elements should vary with ϑ if a concentration gradient exists in the direction perpendicular to the surface because of the varying contribution of the surface atoms to the total emission current. An example of this is shown in Fig. 2 for an oxygen covered sample (16% Ni). The ratio O/Cu increases strongly with decreasing glancing angle ϑ whereas the ratio Ni/Cu remains completely constant. In this connection it must be noted however that the surface composition may be strongly influenced by the pretreatment of the sample, as also found by Ono *et al.*¹¹ This would therefore appear to be a main cause of the confusing results obtained earlier where the surface concentration was an unknown factor.

III. Adsorption of Oxygen

Oxygen is strongly chemisorbed on copper and on nickel. At the (110) faces of both metals ordered 2×1 structures are formed with small O_2 exposures. Obviously the oxygen atoms have the same geometrical configuration on both metals at this coverage ($\theta = \frac{1}{2}$). With all alloys the LEED pattern shows also ordered 2×1 structures, which is not very surprising, with sharp and intense "extra" spots (Fig. 3).

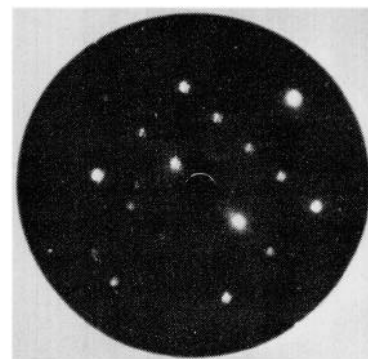


FIGURE 3. LEED pattern of the oxygen 2×1 structure on a 60% Ni surface. $u = 125$ V.

The increase $\Delta\varphi$ of the work function corresponding to the 2×1 structures is plotted in Fig. 4 as a function of the alloy composition. As the surface structure is the same in all cases the values represent equal coverages. With one exception (at 45% Ni) $\Delta\varphi$ increases continuously with increasing Ni concentration which implies that the adsorbed oxygen atoms become more negative.

Upon further exposure to oxygen the situation becomes more complicated: Increasing the coverage on a Ni (110) face leads to a continuous transition from the 2×1 to a 3×1 structure¹²; at a Cu (110) face regions with a 2×1 structure transform into domains with a $c(6 \times 2)$ structure.¹³ Obviously the kind of interaction between adsorbed oxygen atoms differs fundamentally between Ni (110) and Cu (110) for $\theta > \frac{1}{2}$, which reflects upon the nature of the chemisorption bond.

Additional exposure to oxygen of the 16% Ni surface leads to the formation of the same $c(6 \times 2)$ structure as on pure copper. It is rather improbable that this behavior is due to the existence of large regions of only Cu atoms at the surface, since the adsorption of CO on this alloy differs markedly from that on Cu (110). Moreover no variation of the surface composi-

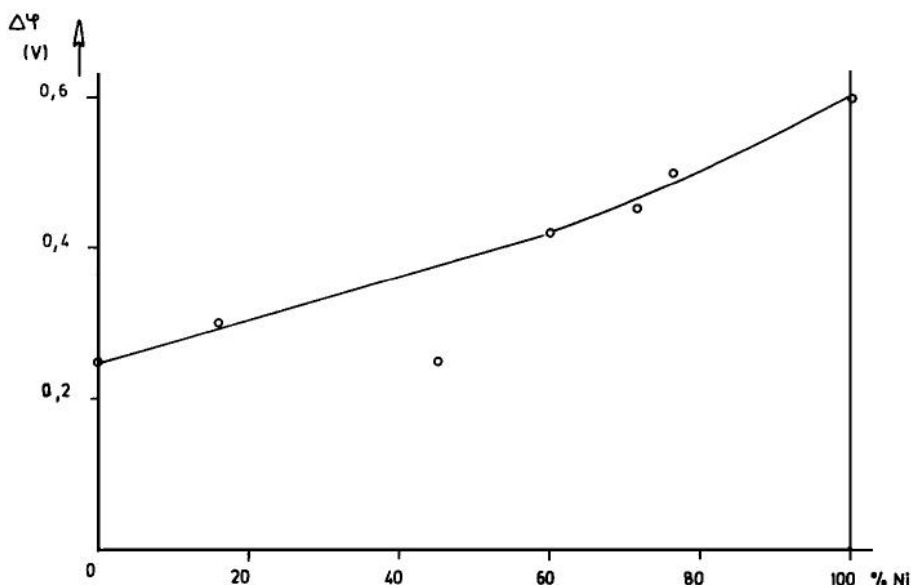


FIGURE 4. Increase $\Delta\varphi$ of the work function for the $O 2 \times 1$ structures as a function of the alloy composition.

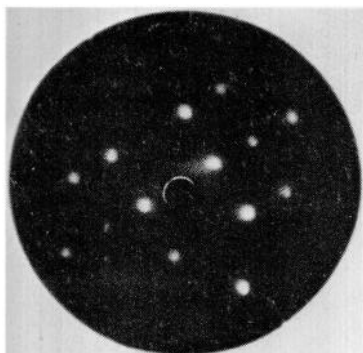


FIGURE 5. LEED pattern of the oxygen 2×2 structure on a 77% Ni surface. $u = 70$ V.

tion after oxygen adsorption could be detected in the Auger spectra. It appears therefore that the influence of the Cu atoms extends even to the chemisorption bonds with Ni atoms.

A further increase of the oxygen exposure causes the gradual disappearance of extra spots and an increase of the background intensity—similar to Cu (110) with the beginning of bulk oxidation.

The 45%-Ni alloy also adsorbs more oxygen after completing the 2×1 structure. However, this adsorption is random, which means it leads only to an increase of the background intensity. After strong oxidation some enrichment of nickel in the surface region can be detected in the Auger spectrum.

The alloys with 60% and 77% Ni show a similar behavior: Adsorption of oxygen at room temperature causes as with the 45% alloy an increase of the background intensity. However, with the 77% Ni surface after briefly annealing at about 200°C intense spots of a 2×2 structure appear in the diffraction pattern (Fig. 5). An exposure to oxygen of the clean surface at 200°C leads directly to the formation of the 2×2 structure without any detectable variation of the

Cu/Ni ratio in the surface. Again further oxygen exposure initiates bulk oxidation and high background intensity. The formation of the 2×2 structure is surprising as such a structure has never been observed with either Cu (110) or Ni (110) surfaces.

IV. Adsorption of Carbon Monoxide

At room temperature and at pressures below 10^{-4} Torr CO does not adsorb on Cu (110) surface to any measurable extent¹⁴ owing to the low heat of adsorption.¹⁵ At lower temperatures adsorption occurs on polycrystalline films and on (100) planes accompanied by a decrease in the work function.¹⁶ On the other hand, CO is chemisorbed by a Ni (110) surface causing an increase in the work function.¹⁷ Desorption occurs above 100°C.¹⁷ Therefore, the two metals differ considerably with respect to their adsorption behavior towards CO.

Chemisorption of CO at room temperature was observed with all alloys and with an increase of the work function in all cases. The maximum values of $\Delta\varphi$ are plotted in Fig. 6 as a function of the alloy composition. It must be noted, however, that these values probably do not coincide with equal coverages as was the case with Fig. 4 for the O 2×1 structures. Even so the tendency for stronger negative polarization of the adsorbed particles with increasing Ni concentration is quite clear. For CO adsorption on Ni (110) no exact value for $\Delta\varphi_{\max}$ is available, but for polycrystalline samples values of more than 1 V are reported.¹⁸

An estimate of the heat of adsorption can be derived from flash desorption spectra. Using a heating rate of 2°C/sec the alloys containing 45 to 77% Ni and the elementary Ni (110) face showed a desorption peak at about 110°C, indicating that CO has about the same

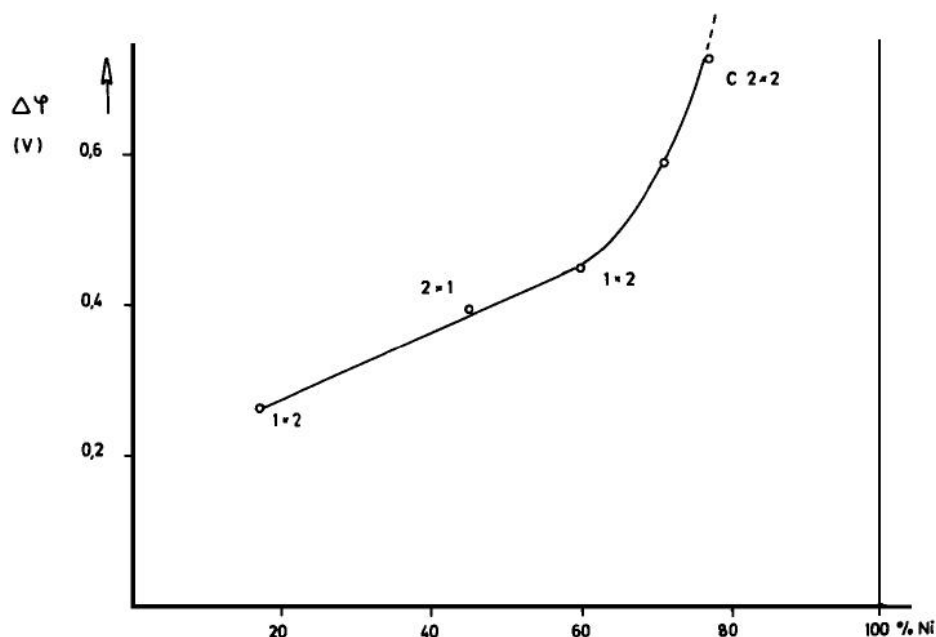


FIGURE 6. Maximum increase $\Delta\varphi_{\max}$ of the work function after CO adsorption as a function of the alloy composition.

heat of adsorption on all these surfaces with one binding state at room temperature. (With higher rate of flashing the desorption maximum is shifted up to about 180°C. Simultaneously the activated transformation into more tightly bound states may compete with the desorption process, as was observed for 45% Ni (110) and Ni (110)⁵ and for Ni (100) by Onchi and Farnsworth.¹⁹ This will be discussed elsewhere.) The alloy with 16% Ni shows a desorption peak at 75°C which means CO is bound more weakly on this plane.

Although no quantitative information about the adsorbed amounts could be derived from the recorded desorption spectra, the areas below the desorption peaks were comparable in size for all crystals. That means the maximum coverage seems to be similar on all surfaces. Further evidence for this is given by the LEED observations which are described below.

Adsorption isotherms have been derived for the 60% Ni alloy from measurements of $\Delta\varphi$ as a function of CO pressure at different temperatures up to 190°C. Figure 7 shows a plot of $\ln p_{\text{CO}}$ versus $1/T$ for different values of $\Delta\varphi$. Isothermic heats of adsorption ΔH_{ad} can be obtained from the slopes of these lines using the Clausius-Clapeyron equation. The figure shows that all the lines between $\Delta\varphi = 25 \text{ mV}$ ($\cong 0.06 \Delta\varphi_{\text{max}}$) and

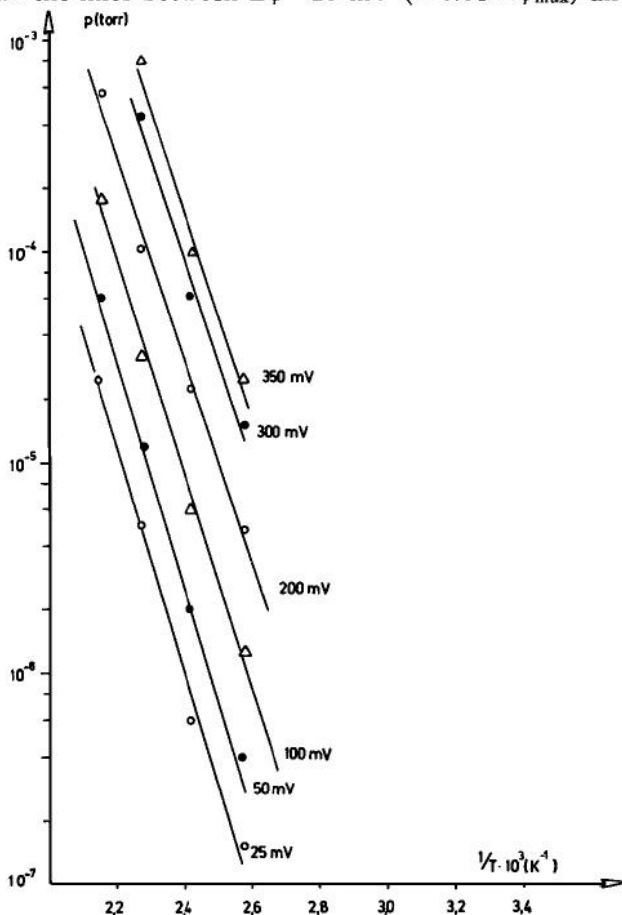
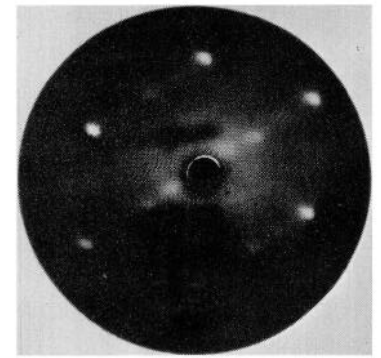
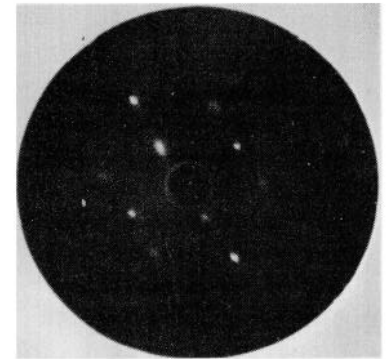


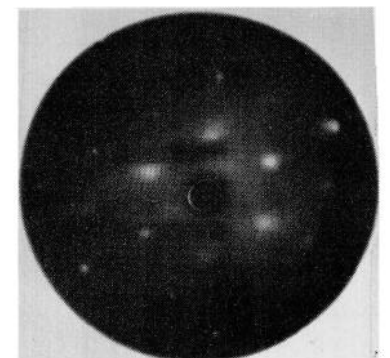
FIGURE 7. Plot of the logarithm of CO pressure versus the reciprocal temperature for different values of the work function change at a 60% Ni surface.



(a)



(b)



(c)

FIGURE 8. LEED patterns of ordered structures after adsorption of CO. (a) 1×2 structure (16% Ni) $u = 118 \text{ V}$. (b) 2×1 structure (45% Ni), $u = 120 \text{ V}$. (c) $c2 \times 2$ structure (77% Ni), $u = 110 \text{ V}$.

$\Delta\varphi = 350 \text{ mV}$ ($\cong 0.78 \Delta\varphi_{\text{max}}$) are parallel, which means that the surface is energetically homogeneous with respect to CO adsorption and ΔH_{ad} is independent on coverage within these limits. (For $\Delta\varphi < 25 \text{ mV}$ and $\Delta\varphi > 350 \text{ mV}$ the measurements are not exact enough for this type of evaluation.) The slope of the lines yields $\Delta H_{\text{ad}} = 23.5 \text{ kcal/mol}$.

Using a radiotracer method Klier *et al.*²⁰ derived a value of 25.3 kcal/mol for the binding energy of CO on a clean Ni (110) surface. The good agreement confirms the results of the flash desorption measurements. The uniformity of the surfaces towards CO adsorption is also supported by LEED observations: Adsorption of CO on the 16% Ni surface is at first accompanied by an increase of the background intensity. But at maximum coverage "extra" spots of a 1×2 structure appear in the diffraction pattern [Fig. 8(a)] which disappear quickly after evacuation as

desorption occurs. In contrast, a stable 2×1 structure is formed on the 45% Ni surface [Fig. 8(b)].

With the 60% Ni surface a 1×2 structure appears again like that of the 16% Ni sample. On the 77% Ni crystal a 1×2 structure also develops at low CO pressures which transforms at higher exposures into a $c(2 \times 2)$ structure [Fig. 8(c)].

In general the additional spots are rather sharp from which is concluded that large domains with periodic configuration of the adsorbed CO molecules exist. However, frequently an increase of the background intensity was also observed and therefore the existence of regions with disordered adsorption cannot be excluded.

Moreover, with the Ni rich samples the electron beam of the LEED optics was observed to interact with the adsorbed layers and destroyed the ordered arrangement within a few minutes. No extra spots were observed after CO adsorption on Ni (110) surfaces.^{17,21} Perhaps this was also due to the effect of the electron beam.

V. Discussion

The main results may be summarized as follows: After proper preparation of the clean surfaces no phase segregation could be detected; the surface composition agreed with that of the bulk as confirmed by Auger electron spectroscopy. Similar observations have been made by Hardy and Linnett²² for Cu/Ni foils annealed at 600°C on the basis of x-ray diffraction and electron-microprobe measurements.

The adsorption properties of the alloys are in general intermediate between those of the elements. Increasing the Ni content increases the work function change due to adsorption, i.e., the negative polarization of the adsorbed particles.

Somewhat surprisingly some ordered adsorbed structures appeared in the LEED pattern which are not observed with the elementary metals, and which are therefore specific to the alloys.

The adsorption energy of CO on the surfaces with 45%, 60%, and 77% Ni is similar to that found for CO adsorption on Ni (110). The bond is weaker on the 16% Ni surface. Detailed measurements with the 60% Ni alloy showed that the heat of adsorption for CO is virtually constant over a wide region of coverages, which means that the surface is energetically homogeneous towards CO adsorption and apparently no difference between Cu and Ni atoms exists. This is in particular a necessary condition for the production of the ordered adsorbed phases observed.

Since our knowledge of the electronic structure of metal surfaces is rather scant, any attempt to interpret these results must begin by using the bulk electronic properties of the Cu/Ni alloys. Formerly one assumed that copper and nickel form a common *d* band, in

which the holes at the Ni sites were gradually filled by the addition of Cu atoms.²³ More recent experimental work, in particular the photoemission studies of Seib and Spicer²⁴ suggest however that this "rigid band" model is not valid but must be replaced by a "virtual bound state" model.²⁵ According to this model the Ni 3*d* orbitals form localized levels between the Fermi level and the Cu *d*-band edge in the neighborhood of the Ni atoms, and which are broadened by resonance scattering with the other electrons. Long-range interactions between such states are called into play in order to explain the magnetic properties of the alloys. The enhanced electron density below the Fermi level could possibly explain the increase of the work function changes with increasing nickel content. However, the situation may be modified at the surface due to the existence of surface states.²⁶

Different binding conditions for adsorption at Ni and Cu atoms are thus to be expected *a priori*. However, the adsorption of a particle may induce a radical change of the electronic structure near the adsorption site, as been shown for example by Hagstrum with the Auger neutralization spectroscopy method.²⁷ This may cause long-range interactions between the adsorbed particles via the metal lattice.²⁸

Grimley²⁹ has suggested that the chemisorption bond is connected with a resonance in the electronic states. The broader these resonances are the more far reaching are the interactions and the less apt the concept of a "surface molecule" becomes. The appearance of ordered adsorbed phases in the LEED pattern is caused by the existence of interactions between adsorbed particles.³⁰ Obviously with adsorbed CO these interactions are sufficiently strong to smooth out the original variation in binding energy at Cu and Ni sites. It may be these interactions which are sensitive to the alloy composition and which are responsible for the existence of adsorbate structures peculiar to the alloyed metals.

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Application of Various Methods for the Determination of Adsorption Lifetime and Desorption Energy of Oxygen on Tungsten

H.-W. Wassmuth, H. Werner, and A. K. Mazumdar

Physikalisches Institut der Universität Marburg, 355 Marburg, Lahn, Renthof 5, West Germany
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The adsorption lifetime τ and the desorption energy Q of oxygen atoms on a polycrystalline tungsten surface have been determined as functions of the coverage θ by using a uhv mass spectrometer. A method based on contact potential and sticking probability measurements ($T=1200$ – 2500 K), a combined study of steady state and transient state desorption processes ($T=2000$ – 2600 K), and three different types of flash desorption measurements under single flight detection conditions ($T=1900$ – 2600 K) were employed. Satisfactory agreement of the results obtained from the different methods was observed. A compensation effect, depending on the coverage θ , was found between the pre-exponential factor of τ and the desorption energy Q which varies between 6.3 eV at $\theta=0$ to 3.4 eV at $\theta=1$. A further experiment employing a pulsed molecular beam method is in progress.

Introduction

With special reference to recent mass spectrometric investigations employing single flight detection of the desorbing products both under transient (flash filament)^{1–4} and steady state conditions,^{4,5} the dissociative adsorption of O₂ molecules on a hot tungsten surface is experimentally established. The surface species consist predominantly of atomic oxygen together with traces of tungsten oxides. At substrate temperatures $T \gtrsim 1800$ K the steady state desorption is principally that of atomic oxygen.

A fundamental requirement for an understanding of the kinetics of chemisorption involves the knowledge of the mean adsorption lifetime τ of the adparticles, the temperature dependence of which is given by the Frenkel equation

$$\tau = \tau_0 \exp(Q/kT). \quad (1)$$

Here, $1/\tau_0$ is a frequency factor and Q the desorption energy, both of which may depend on the coverage θ .

The following study describes the determination of τ for oxygen atoms on a polycrystalline tungsten