JOURNAL OF CATALYSIS 4, 654–664 (1965)

The Surface of Copper-Nickel Alloy Films*

I. Work Function and Phase Composition

W. M. H. SACHTLER AND G. J. H. DORGELO

From the Koninklijke/Shell-Laboratorium, Amsterdam, The Netherlands (Shell Research N.V.)

Received February 1, 1965

The work function and the phase composition have been measured for copper-nickel alloy films prepared by evaporation and subsequent annealing at 200°C under ultra-high vacuum. The photoelectric work functions of the alloys are found to be lower than those of the individual spec-pure metals sintered at the same temperature. Over a wide range of over-all composition the work function has a constant value of 4.61 eV. X-ray diffraction shows that in this range the sintered films consist of two phases: A copper-rich alloy coexists with an almost pure nickel phase. The data suggest a wide miscibility gap of the copper-nickel system at low temperatures. As the change in work function upon chemisorption of carbon monoxide is small, it is assumed that in the equilibrated two-phase systems the copper-rich alloy forms the adsorbing surface. Its composition is independent of the over-all composition.

I. INTRODUCTION

Metal alloys have aroused the interest of investigators of catalysis for various reasons. By systematic variation of the composition of an alloy being used as a catalyst it is possible to induce controlled variations in the collective properties of the catalyst and so to examine the significance of these properties in the catalytic process. Also it is possible to examine how, in multiphase systems, catalytic activity is affected by changes in crystalline structure, while all other parameters are kept constant.

Unfortunately, interpretation of results known so far has been severely hampered by lack of knowledge about alloys. For instance, we know next to nothing about the work functions of alloys. Authors advocating the "electronic factor" concept of catalysis generally assume that chemisorption is governed by electron transfer, either from the adsorbate to the metal (donor case) or in the opposite direction (acceptor case) (*1*). Obviously, if this is so, then the electron transfer in turn is essentially governed by the difference between the work function of the catalyst, on the one hand, and the ionization potential or the electron affinity of the adsorbate, on the other; in which case changes in catalytic activity with variations in alloy composition would necessarily be attributable to changes in work function.

In view of the wide propagation of the electronic factor concept it is surprising that the work functions of alloy catalysts have, in fact, never been measured. As a consequence, attempts to interpret the observed changes in catalytic activity using this concept have been, to say the least, highly hypothetical.

A second important gap in our existing knowledge of alloy catalysts concerns the composition and structure of the catalyzing surface, which, it can be argued, will often be very different from the composition and structure of the bulk of the alloy. In such cases it seems almost meaningless to interpret catalytic data in terms of the over-all composition and structure of the alloy. In

---

* A brief account of some of the results has appeared as a Letter to the Editor of this Journal [*J. Catalysis* 4, 100 (1965)].

this connection two points should be borne in mind.

(a) Many homogeneous alloys, prepared at high temperature, become thermodynamically unstable at the much lower temperatures at which catalytic reactions are studied, because the $T\Delta S$ term in the free energy equation is much smaller. Admittedly diffusion through the bulk of an alloy is slow, so that a metastable structure is maintained here. However, surface diffusion is much faster, particularly under catalytic conditions in which bonds are repeatedly formed and broken. As a consequence the surface atoms will rearrange. For instance, the surface of a homogeneous alloy A_xB_{1-x} might separate into a phase rich in A and another phase rich in B, while in the bulk the metastable structure persists.

(b) If thermodynamic equilibrium is eventually established throughout, the surface will tend to acquire a composition that has a minimum of surface energy. This means that if, for example, the surface energy of alloy A_xB_{1-x} is at a minimum when $x = x_m$, the composition of the surface will differ from that of the interior for all compositions, except when $x = 0$; $x = x_m$, and $x = 1$. Furthermore, the value of x_m would probably be largely dependent on the nature and amount of an adsorbate.

Large differences between surface and interior in copper-nickel alloys have already been postulated by Takeuchi *et al.* (*2*, *3*) in order to interpret their data on catalytic activity and heats of adsorption of hydrogen on these alloys.

The work described in the present paper was aimed at obtaining information on both the work functions and the surface composition of alloys, the copper-nickel system being chosen for particular study for three main reasons.

(a) At high temperatures the copper-nickel system forms a continuous series of alloys with almost statistical distribution of the atoms in the fcc crystal lattice. When the present work was started it was not known whether these alloys segregate at low temperature, although this seemed sensible on theoretical grounds.

(b) Nickel has an incompletely filled *d* band, which is gradually filled on addition of copper. The collective magnetic properties of copper-nickel alloys are therefore critically dependent on composition.

(c) Pure copper and nickel are strikingly different in their catalytic activity in, say, hydrogenation reactions or their chemisorption of hydrogen. The catalytic properties of copper-nickel alloys, therefore, have been studied by a number of authors. However, no satisfactory interpretation of the results has yet been advanced, most of them being in obvious disagreement with the prevailing theory which assumes that catalytic activity in hydrogenation reactions is governed by the number of holes in the d band.

All the measurements given in this paper were made on alloy films deposited under ultra-high vacuum. Such films have a number of important advantages over bulk samples. Not only are gaseous and adsorbed impurities rigorously excluded—a necessary prerequisite for any meaningful measurement of work functions—but the conditions for attaining equilibrium, even at low temperatures, are much more favorable. For, with their high specific surface area, films provide the full benefit of fast surface diffusion. Also, since films deposited at low temperature are known to be rich in lattice faults, diffusion within the bulk of each crystallite is enhanced as well. Yet even if the diffusion coefficient is small, equilibrium can be approached within a reasonable space of time, simply because the crystals are so very small (10^2–10^3 Å). Practical justification for this reasoning is amply supplied by literature data (*4*–*8*).

In the present investigation the work functions of the films were determined by a photoelectric method, using Fowler's theory, and the structure and composition of the alloys were determined by X-ray analysis. The composition of each phase was derived from the measured lattice parameters, using Végard's law.

II. EXPERIMENTAL TECHNIQUES

A. Methods of Preparing Alloy Films

All experiments were done under ultra-high vacuum, the pressure under normal conditions being equal to or below 10^{-10}

Torr. An extensive study was made of various methods of preparing alloy films, including: (1) evaporation of an alloy wire from a supporting tungsten, tantalum, or rhenium filament; (2) simultaneous evaporation of two pieces of the pure metals or of an alloy from a tungsten cup, heated by high-energy electron bombardment; (3) successive evaporation of the two metals from different sources, followed by heat treatment to homogenize the film.

At first glance method (1) appeared the most promising, since it was expected to produce a film of predetermined composition and homogeneous from the very beginning. This hope, however, turned out to be false. The composition of the vapor, it was found, approximately obeys Raoult's law, i.e., at the start it consists almost exclusively of the metal with the highest vapor pressure, namely copper. Only after most of the copper has been evaporated and the temperature has been further increased, does nickel come to prevail in the vapor. Consequently, by the time all the alloy has been evaporated, the metals have become neatly separated, so that essentially the film consists of a copper layer covered by a nickel layer. A serious disadvantage of this technique is that proper degassing of the metals prior to evaporation is impossible; since the temperature is highest at the end of the evaporation process, the amount of gas developed is intolerable by present-day ultra-high-vacuum standards. A second disadvantage is the strong tendency to form ternary alloys with the supporting metal. This causes the filament to burn through before evaporation is complete, and atoms of the supporting metal are then also incorporated in the film.

The second technique, we thought, would probably be better. Since the relative difference in vapor pressure between copper and nickel decreases with increasing temperature, we hoped that very rapid simultaneous evaporation of the two metals at high temperature would produce homogeneous films. First a tungsten or tantalum cup was degassed by electron bombardment; then pieces of copper and nickel of known weight were thrown into the cup by means of a lever system operated under ultra-high vacuum through flexible bellows. The cup was then quickly brought to incandescence by electron bombardment.

This technique was also discarded eventually, because again the pieces of copper and nickel could not be degassed prior to evaporation, and again alloys are formed between nickel and the cup material; sometimes the liquid alloy even melted a hole through the bottom of the cup and fell through. And as before, homogenization was not perfect and had to be completed by subsequent heat treatment. The direction of the atom beams could not be controlled, because the nickel and copper samples cannot be placed on exactly the same spot, and so the two beams leave the cup at different angles. The resulting film therefore has a lateral concentration gradient which cannot easily be predetermined, as it can in the third method we tried.

Since homogenization subsequent to deposition seems to be necessary with all three techniques, there is no reason to prefer either of the first two methods over the third technique, which in point of fact, has the advantages that each metal can be properly degassed prior to evaporation, and alloy formation with supporting wires can be prevented. The latter can be verified by inspection of the phase diagrams. The tendency to alloy with any of the wire metals used for support is strong in the case of nickel but almost negligible in the case of copper. Fortunately, though, nickel can easily be evaporated without support, while copper has too low a vapor pressure at temperatures below its melting point. Consequently, it was decided to evaporate copper from a tantalum filament and nickel from a nickel wire.

As the two sources are geometrically separated, the nickel/copper ratio varies over the lateral dimensions of the films. This feature is, however, not considered a disadvantage but can in fact be exploited, as is shown in the next section.

After deposition the films were homogenized by sintering at various temperatures and the resulting changes in work function registered.

B. The Phototube

After numerous development steps, we constructed the phototube shown in Fig. 1.

The body of this apparatus is a Pyrex tube, 300 mm long and 40 mm in diameter, closed at both ends. Through one end two parallel tungsten rods (A), 200 mm long and 2 mm in diameter, are fused. These serve as conducting rods for a 60 × 25-mm polished glass plate (B) which slides on four small tubes (C) attached to its back. A glass-clad iron bar (D) is also attached to the back of the glass plate, which can thus be moved magnetically from outside the tube. Both the plate and the sliding tubes are coated with electroconductive tin oxide, so that their surfaces have the same electric potential as the protruding ends of the tungsten rods. After a metal film has been deposited on its surface, the plate serves as a photocathode.

The anode is formed by a short tungsten bar fused in the upper wall of the tube (E) and carrying a small platinum wire pressed against the inside of the wall. The area round the anode is likewise coated with tin oxide.

A narrow glass strip (F) down the middle of the upper side of the photocathode serves as an X-ray probe. At the end of a run this probe is removed from the tube and the binary metal film deposited on it is subjected to X-ray analysis.

Two sidetubes, (G) and (H), are attached to the center of the main tube, forming an angle of 90° with it and with each other. One of these sidetubes (G) is closed by a plane-parallel quartz window (I). The other tube (H) carries two pairs of tungsten fuses, one pair connected by a nickel wire (J) and the other pair by a tantalum wire with a copper bead on it (K). This second sidetube is the evaporation tube. The axes of the evaporation and window tubes each form an angle of 45° with the surface of the photocathode.

Two further sidetubes, (L) and (M), serve to connect the cell to the vacuum pump or to introduce a gas.

While the metal filaments are being degassed the photocathode is accommodated on a third tungsten conducting rod (N) which is fused into the main-tube wall immediately opposite, and abutting one of the two other conducting rods (A). Here it is sheltered behind a semicircular glass screen (O), so that no impurities can reach it.

There are two semicircular glass screens, (O) and (P), fixed on either side of the

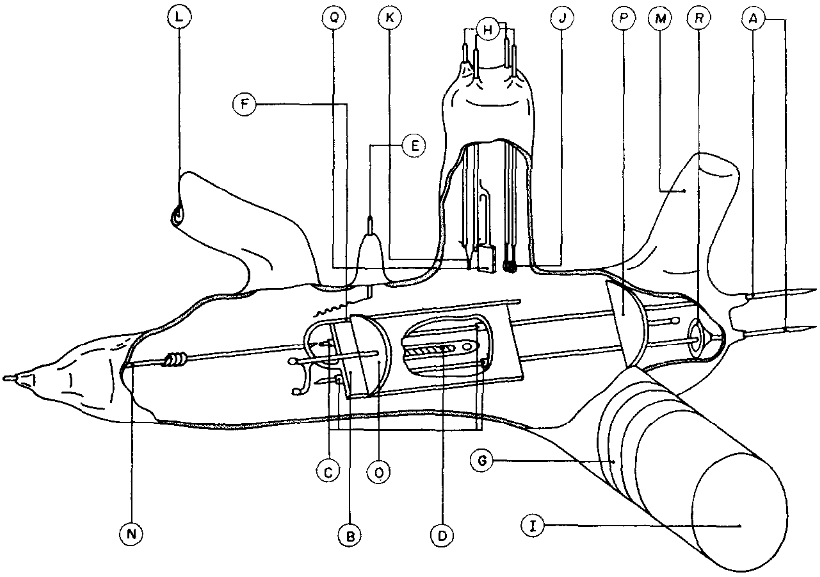

FIG. 1. Sliding-cathode phototube.

evaporation tube in such a way that they nearly touch the sliding photocathode. During evaporation only the part of the photocathode between these two screens is covered with a metal layer. A third screen (Q) inside the evaporation tube prevents the two metal sources from "seeing each other." A fourth screen (R) protects the area where the tungsten rods are fused through the glass, thus avoiding any short-circuiting due to evaporated metals between photocathode and anode.

Other cell types were used for films in which the Cu:Ni ratio was either extremely low or extremely high.

C. Procedure

Although numerous variations are possible, the operating cycle always contained the following steps.

First the glass body of the phototube had to be degassed. To do this the tube was baked in an (Balzers A.G.) oven, at a temperature of about 400°C. After about 16 hr, heating was stopped and the heating elements were removed. The pressure at this point was below 10^{-10} Torr. The photocathode was then brought to the left far end, beyond the evaporation area, and all the metal elements were degassed by a high-frequency eddy current provided by a 6-kW high-frequency generator (Philips). Finally, when the pressure had again dropped to below 10^{-10} Torr, the filaments in the tube and the ionization manometer were heated to incandescence, so that a thin metal film formed on the main tube wall just below the evaporation tube. Then the whole degassing cycle was repeated.

Subsequently the photocathode was moved back towards the middle of the tube so that 80% of its surface was below the evaporation tube, while the remaining 20% remained shielded by the left-hand screen. Then the first metal was evaporated and the work function of the resulting film was measured. After that the photocathode was again moved so that this time 20% of its opposite end was beyond the evaporation area, shielded by the right-hand screen (P). Then the second metal was deposited. For all experiments described in this paper, the pressure during the initial period of evaporation of either metal remained below 10^{-9} Torr.

As the thickness of the film formed in each evaporation step decreases by the square of its distance from the source, the ultimate composition of the metal layer along the axis of the photocathode (and of the X-ray probe) will be as shown graphically in Fig. 2.

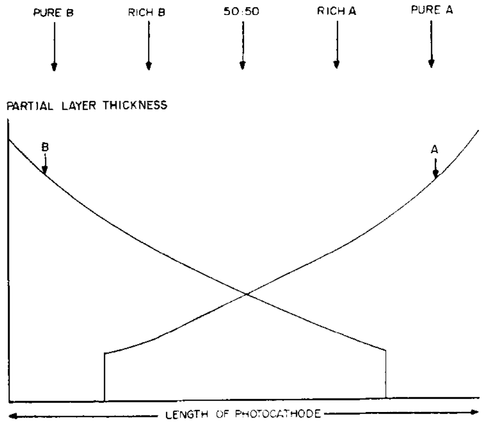

FIG. 2. Over-all concentration gradient of two metals A and B along axis of photocathode (schematically).

After both metals had been deposited, an ultraviolet light beam was focussed in the center of the main tube through the quartz window. The photocathode was then brought into a series of selected positions, and the photoelectric yield of the illuminated area in each position measured as a function of wavelength. In this way it was possible to measure work functions for a number of over-all compositions. The compositions themselves could be roughly estimated on a geometric basis as shown by Fig. 2, but were determined somewhat more precisely at the end of the run from the lattice constants derived by X-ray analysis.

The next step was usually heat treatment, whereby the tube was heated to, say, 200°C for a defined period to allow the metals to interdiffuse. The resulting changes in work functions were then measured both for the two pure metals and for the binary systems. Generally, this interdiffusion cycle was repeated several times until the work function acquired a stationary value.

Finally, a gas was sometimes admitted to the tube and the resulting change in work function measured for a number of over-all compositions.

D. X-ray Analysis

The structure of the copper-nickel alloy films deposited on the glass strip was determined by X-ray analysis after the end of a photoelectric measurement.

X-ray reflection photographs were made of well-defined segments of flat samples, mounted in the center of a cylindrical camera. The photographs were calibrated by reference to the diffraction lines of α quartz, which was applied in a thin layer on top of the specimen surface.

III. RESULTS AND DISCUSSION

A. Work Function of Pure Metals

All work functions were derived from the spectral distribution of the measured photoelectric yields (equal to the number of electrons emitted divided by the number of photons absorbed). Fowler's theory, in the approximation proposed by Anderson (*9*), was used to calculate the work functions from the yield distributions.

Work functions of metals are known to be affected by impurities and by the degree of sintering.

In order to minimize impurities, the present work was done under ultra-high vacuum conditions and with spectroscopically pure metals. As sintering causes a large increase in work function, it was felt essential to compare pure metals and alloys under identical conditions of sintering.

The work function of the fresh films depends on the local temperature of deposition. This temperature is higher than that of the environment; it depends on the distance between the photocathode and the evaporation source and on the heat conductivity of the photocathode and leads, as well as on the temperature of the evaporation source and the rate of deposition.

With the phototube described in the previous chapter, the work functions of unsintered films of the two spectroscopically pure metals, measured immediately after deposition were

Nickel	5.02 ± 0.02 eV
Copper	4.61 ± 0.02 eV

The figure for fresh nickel is higher than that reported by Suhrmann *et al.* (*10*) for nickel films deposited at −196°C and subsequently sintered at room temperature. From the dependence of work function on sintering temperature given by Suhrmann *et al.*, it would appear that in our apparatus the local temperature of the photocathode during film deposition was about 100°C. This seems reasonable.

B. Alloys of Medium Composition

A considerable number of preliminary experiments, with non-spectroscopically-pure grade metals, led to the following conclusions: (1) Stratified films of one metal deposited on top of the other readily interdiffuse at temperatures between 0° and 200°C. (2) The alloys have lower work functions than either of the metals, sintered at the same temperature.

Interdiffusion is effective even at room temperature. In the absence of diffusion the work function of a binary system should be equal to the work function of the metal deposited last. In fact it is found that the work functions of binary systems have lower values from the very beginning. It is even possible to observe interdiffusion visually at room temperature. For if a thin copper film is deposited on a glass slide and then covered by nickel, the back of the film first shows the typical red color of copper, but after 1 hr it has turned gray.

Whereas sintering for several hours at 200°C has the effect of increasing the work functions of the pure metals, it is found to reduce those of binary systems. However, there is a point beyond which further heating at the same temperature no longer affects the work functions.

These qualitative results were confirmed by experiments with spectroscopically pure metals. The results of two of these experiments are presented in Table 1 and Figs. 3 and 4. Here copper was deposited first and

TABLE 1

WORK FUNCTIONS (Φ) AND EMISSION CONSTANTS (α) OF COPPER-NICKEL ALLOYS[a]

Segment	Expt No.	Φ after evaporation, (eV)	α^b	Φ after sintering (eV)	α^b	Φ after CO admission (eV)	α^b
1 Pure Ni	I	5.03	6.0	>5.20	—	—	—
	II	5.04	7.1	>5.20	—	—	—
2 Ni-rich	I	4.86	3.0	4.61	3.2	4.71	4.0
	II	4.93	4.8	4.64	4.3	4.68	4.8
3 ~50/50	I	4.81	4.2	4.61	3.1	4.72	4.0
	II	4.84	7.4	4.61	4.3	4.67	4.8
4 Cu-rich	I	4.75	5.1	4.60	3.0	—	—
	II	4.80	11.2	4.62	4.2	4.66	3.8
5 Pure Cu	I	4.61	5.6	4.67	3.2	4.67	3.2
	II	4.60	4.7	4.65	3.7	4.66	3.6

[a] See also Figs. 1 and 2.

[b] Emission constant [Electrons photon^{-1} degree^{-2} $\times 10^{12}$].

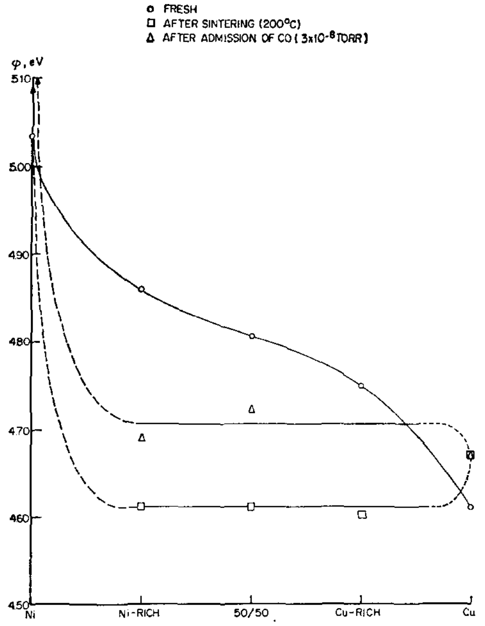

FIG. 3. Work functions of films prepared by evaporation of nickel on top of a copper film, followed by sintering and admission of carbon monoxide (Experiment I).

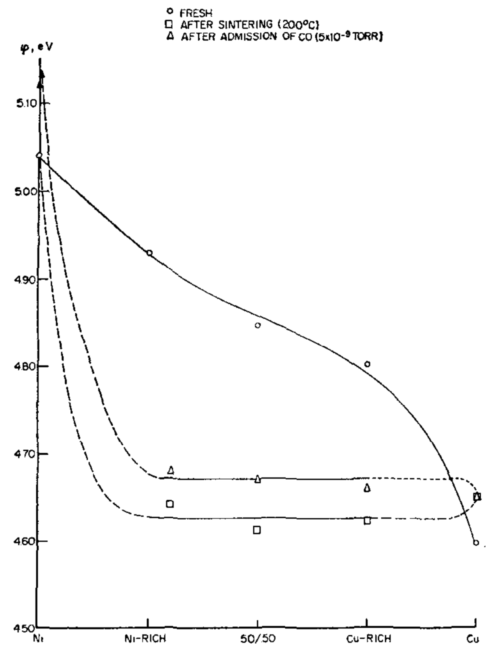

FIG. 4. Work functions of films prepared by evaporation of nickel on top of a copper film, followed by sintering and admission of carbon monoxide (Experiment II).

then nickel. It will be seen that the initial work functions of the binary systems are lower than that of pure nickel. After sintering, the work function of the pure nickel segments rose beyond the range of the quartz monochromator then being used, while the work function of the copper segments increased by 0.05 eV. The work functions of the binary systems, on the other hand, are considerably reduced. The most surprising result, however, is that the binary systems all have nearly the same work function of about 4.61 eV, despite the fact that the over-all copper-to-nickel ratio in the copper-rich system is about four times that of the nickel-rich system.

According to these results, therefore, there appears to be for copper-nickel films a wide range of over-all compositions for which sintering will always tend to produce a surface phase of roughly the same composition, with a work function of 4.61 eV.

More information is obtained from the X-ray diffraction results. A number of two-component film segments are found to consist of two phases after sintering. Each phase belongs to the fcc lattice type, but the lattice parameters are different. In Fig. 5 a photometric curve is given for the (111) and (200) diffraction lines which are found to be split up in doublets. A quartz line from the calibration sample is also included.

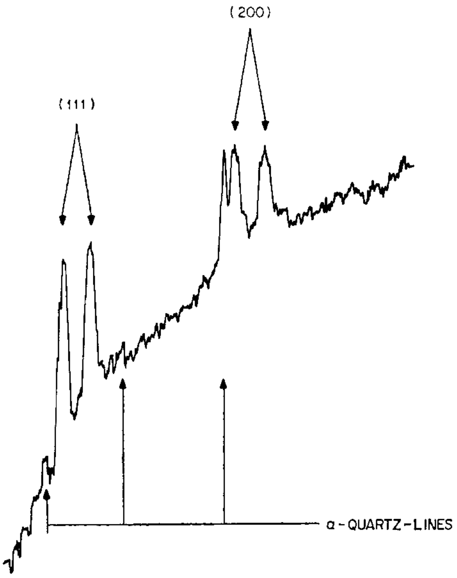

Fig. 5. Photometric curve of X-ray diffraction pattern (segment ~ 50:50, Expt. II).

The lattice constants are shown in Table 2, which refer to the same series of experiments as Table 1. The error in the lattice parameters is ±0.007 Å. As the lattice parameters of pure copper and of pure nickel differ only by 0.091 Å, the composition of either phase, as derived from Végard's law, is subject to an error of ±8%. In view of this, it does not seem useful to discuss minor differences between the various samples. The information obtained from the X-ray diffraction work then can be summarized as follows: (1) Alloys containing copper and nickel in a ratio near 1:1 are split up into two phases: a copper-rich alloy containing roughly 10% of nickel and a second phase of almost pure nickel, possibly containing 1% or 2% of copper. (2) On the copper-rich side of the film only the former phase is detected. (3) On the nickel-rich side, both phases are detected in Expt. I, but in Expt. II the

TABLE 2
PHASES AND LATTICE CONSTANTS IN BINARY FILMS

Segment	Expt No.	Number of phases detected	Lattice parameters (Å)	Description of phases
1 Pure Ni	I	1	3.524	Ni
	II	1	3.524	Ni
2 Ni-rich	I	2	1. 3.604	Cu-rich alloy
			2. 3.524	Ni or Ni-rich alloy
	II	1	3.525	Ni or Ni-rich alloy
3 ~ 50:50	I	2	1. 3.603	Cu-rich alloy
			2. 3.523	Ni or Ni-rich alloy
	II	2	1. 3.609	Cu-rich alloy
			2. 3.523	Ni or Ni-rich alloy
4 Cu-rich	I	1	3.615	Cu-rich alloy
	II	1	3.605	Cu-rich alloy
5 Pure Cu	I	1	3.615	Cu
	II	1	3.615	Cu

copper content was insufficient to detect the copper-rich alloy phase.

From the work function results it seems probable that the copper-rich alloy in the two-phase systems is located at the surface and the nickel-rich phase below the surface. To check this, carbon monoxide was admitted to the phototube at a pressure of the order of 10^{-8} Torr. The adsorption of this gas on metal films has often been investigated (*11*). It is, for instance, strongly chemisorbed on nickel, causing a rise in work function of 1.0 eV, but is not adsorbed on copper at such low pressures (*11*). (At much higher pressures a weak adsorption complex is formed, causing a decrease in work function.) It was therefore reasonable to expect the work function change caused by carbon monoxide adsorption to give a fair indication of which of the two phases formed the outer surface of the films.

The results are included in Table 1. It will be seen that, as expected, the work function of copper was not altered, but that the binary alloys showed an increase in work function of between 0.04 and 0.11 eV. Apparently, the adsorbing surface of the film belonged to the copper-rich phase.

It should be mentioned that after long exposure to carbon monoxide all work functions, even that of copper, increase. The reason for this is that nickel tetracarbonyl gas is formed at the pure-nickel end of the photocathode and subsequently decomposes on other parts of the surface where the thermodynamic potential of nickel is lower.

C. Alloys of Extreme Composition

Since it appeared that the two-component segments of the films described in the preceding section all acquired a surface layer of constant composition, we thought it would be interesting to examine films of extreme copper-nickel ratios. For this purpose we used a different type of phototube, with the two metal sources arranged so that very small amounts of one spec-pure metal could be deposited on top of a thick film of the other.

Two examples of these experiments are given in Tables 3 and 4. In the experiment summarized in Table 3 small portions of copper, each sufficient to form roughly one-third of a monolayer, were successively deposited on top of a nickel film. It will be seen that after 90-min sintering at 200°C the work function decreases to 4.62 eV. Within the experimental error this value is the same as found for the equilibrated copper-nickel films of relatively high copper content discussed in the previous section. However, after further sintering for 90 min at 275°C, the work function rises to 4.72 eV. Obviously, therefore, the equilibrium value for the work function of this film, containing only a very small amount of copper, is between the value for pure nickel, 5.02 eV, and the value of 4.61 eV, characteristic of films containing larger amounts of copper.

In our second example, presented in Table 4, small portions of nickel were deposited on top of a copper film. Again, a value of 4.61 eV was found after sintering. A second thick layer of copper was then deposited on the film, and a very small

TABLE 3
WORK FUNCTIONS OF FILMS WITH EXTREMELY LOW Cu:Ni RATIOS

Photocathode treatment	Φ (eV)
Ni layer	4.94
1st Portion of Cu	4.93
2nd Portion of Cu	4.88
3rd Portion of Cu	4.65
After sintering at 200°C, 90 min	4.62
After sintering at 275°C, 90 min	4.72
After 64 hours at 275°C	4.73

TABLE 4
WORK FUNCTIONS OF FILMS WITH EXTREMELY HIGH Cu:Ni RATIOS

Photocathode treatment	Φ (eV)
Cu layer	4.57
1st Portion of Ni	4.62
2nd Portion of Ni	4.70
3rd Portion of Ni	4.70
After sintering at 110°C, 16 hr	4.61
Large amount of Cu	4.67
Very small amount of Ni	4.76
After sintering at 110°C, 16 hr	4.67
After sintering at 160°C, 20 hr	4.68
CO admitted	4.70

amount of nickel on top of that. It will be seen that the work function of this system did not return to the value of 4.61 eV but stayed above it. After sintering for 20 hr at 160°C a final value of 4.68 eV was registered. Admission of carbon monoxide caused a rise in work function of only 0.02 eV, which shows that the nickel content of this surface after sintering was less than for the two-component segments described in the preceding section.

IV. Conclusion

The results reported for copper-nickel films of medium composition show that alloy formation at 200°C leads to a two-phase system. A copper-rich phase, containing roughly 10% nickel coexists with a second phase of almost pure nickel. It seems that the copper-rich phase forms the surface and is responsible for electron emission and adsorption of the binary system. The work function is found constant over a wide range of over-all compositions. The composition of either phase appears independent of the over-all composition, the latter only determining the relative amounts in which the two phases occur. These results suggest that the two-phase system reflects or nearly approaches the thermodynamic equilibrium of the two-component films at the temperature of sintering. This point will be considered in a subsequent article in connection with the thermodynamic data.

The work function of the alloy which forms the outer phase is lower than the work functions of pure nickel and pure copper, subjected to identical heat treatment. Alloying obviously has caused an increase in Fermi level. This result is at variance with the widespread opinion that the work function of alloys should be intermediate between the work functions of the two pure components (*1*).

The increase in Fermi level due to alloy formation seems not to be confined to the copper-nickel system. Massalski and King (*12*) in their discussion of spectroscopic results reported by Biondi and Rayne (*13*) conclude that also in this alloy the Fermi energy is higher than for each of the components.

Alloys that are either extremely rich or extremely poor in nickel form one phase only. The work function of such a phase appears to be intermediate between that of the pure metal of which it contains most and the ~10% nickel alloy which is presumed to be responsible for the electron emission of equilibrated films of medium composition.

Chemisorption of carbon monoxide at 10^{-8} Torr on copper-rich alloys leads to an increase of the work function. This finding might help to clarify our knowledge of the driving force in chemisorption on transition metals. It has long been known that carbon monoxide is strongly chemisorbed on nickel, leading to an increase in work function, whereas the same gas is only weakly adsorbed on copper, and causes a decrease in work function of that metal. It appeared reasonable to assume that this striking difference in chemisorption of carbon monoxide is related with holes in the *d* band, which are present in nickel, but absent in copper (*14*). If this view were correct, the first type of CO chemisorption (strong adsorption at very low pressures, causing an increase in work function) would only be expected for those copper-nickel alloys which possess holes in the *d* band. The fact that this complex has now been detected for alloys containing ~10% of nickel or less faces one with a new alternative: One must either assume that even these copper-rich alloys still have an uncompletely filled *d* band, or abandon the band model as a basis for discussing chemisorption phenomena. In the latter case the orbitals of individual atoms, serving as adsorption sites, rather than collective phenomena related to the crystal as a whole, would appear to provide a more suitable basis for a discussion of chemisorption and catalysis.

Once this view can be proven, it might even be exploited for a chemical analysis of the outermost surface. If the amount of carbon monoxide chemisorbed is assumed proportional to the number of nickel atoms in the surface and if, moreover, the increase in work function is taken proportional to the number of carbon monoxide molecules adsorbed per unit surface area, one may use this adsorption for a "photoelectric titration" of the nickel content of the outermost atomic layer. Indeed, the surfaces which contain roughly 10% nickel have been found to exhibit an increase in work function of 4–11% of the known value for chemisorption of carbon monoxide on pure nickel.

A number of questions arising from the present results are discussed in the following paper (*15*). There it will be shown that the two-phase systems obtained after heating at 200°C are indeed near equilibrium. Consideration of the mechanism of interdiffusion leads to a model of the two-phase alloys with the copper-rich alloy in the surface. Finally, the realization that the composition of the surface often deviates strongly from the over-all composition has prompted an attempt to reinterpret results on catalysis and chemisorption by copper-nickel alloys.

ACKNOWLEDGMENTS

The authors are indebted to Mr. W. Boog and Mr. L. N. A. ten Rouwelaar for recording and evaluating the X-ray diagrams, and to Mr. A. van den Broek for designing and constructing the phototubes.

REFERENCES

1. SCHWAB, G. M., *Angew. Chem.* **67**, 433–438 (1955).
2. TAKEUCHI, T., SAKAGUCHI, M., AND MIYOSHI, I., *Bull. Chem. Soc. Japan* **35**, 1390–1394 (1962).
3. TAKEUCHI, T. *et al.*, *Shokubai* 3, 144–147 (1961).
4. BELSER, R. B., *J. Appl. Phys.* **31**, 562–570 (1960).
5. HARRIS, L., AND SIEGEL, B., *J. Appl. Phys.* **19**, 739–741 (1948).
6. WEAVER, C., AND HILL, R. M., *Advan. Phys.* **8**, 375–437 (1959).
7. DUMOND, J., AND YOUTS, J. P., *J. Appl. Phys.* **11**, 357 (1940).
8. FUJUKI, Y., *J. Phys. Soc. Japan* **14**, 913–917 (1959).
9. ANDERSON, J. S., FAULKNER, E. A., AND KLEMPERER, D. F., *Australian J. Phys.* **12**, 469 (1959).
10. SUHRMANN, R., AND WEDLER, G., *Z. Angew. Phys.* **14**, 70–74 (1962).
11. SUHRMANN, R., OBER, H., AND WEDLER, G., *Z. Phys. Chem.* (*Frankfurt*) **29**, 305–316 (1961).
12. MASSALSKI, T. B., AND KING, H. W., Alloy phases of noble metals, *in* "Materials Science Progress" (Bruce Chalmers, ed.), Vol. 10. Pergamon Press, London, 1961.
13. BIONDI, M. A., AND RAYNE, J. A., *Phys. Rev.* **115**, 1522 (1959).
14. DOWDEN, D. A., AND REYNOLDS, P. W., *Discussions Faraday Soc.* **8**, 184–190 (1950).
15. SACHTLER, W. M. H., AND JONGEPIER, R., *J. Catalysis* **4**, 665 (1965) (following paper).