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The Surface of Copper-Nickel Alloy Films*

II. Phase Equilibrium and Distribution and Their Implications for Work Function, Chemisorption, and Catalysis

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Free energy calculations show that in the copper-nickel system there is a miscibility gap at low temperatures. The composition of the phases that are characterized by minima of the free energy agrees with experimental data on alloy films prepared at low temperatures by interdiffusion of the two components. From data on the diffusion it is inferred that for compositions within the miscibility gap, equilibrated films consist of crystallites each of which contains a kernel of almost pure nickel, enveloped in a skin of a copper-rich alloy. As the composition of either phase is independent of the over-all composition, the surface properties of these alloys are constant. This is confirmed by experimental data on the work function. The model also appears to be consistent with results on the catalytic activity and the heat of adsorption of hydrogen on granular alloy catalysts, as reported by various investigators.

I. INTRODUCTION

Most data on chemisorption and catalysis with copper-nickel alloys have been interpreted on the implicit assumption that the alloys are built up of one phase, viz. a fcc crystal lattice with random distribution of the nickel and copper atoms over the lattice sites. With one exception (*1*, *2*), all previous investigators seem to have neglected the possibility that the composition of the surface might differ strongly from that of the interior.

Random distribution of atoms has indeed often been confirmed experimentally for copper-nickel alloys prepared at high temperatures. This result is in agreement with thermodynamic expectation; at high temperature the free energy of alloy formation is governed by the entropy term which favors a solid solution with random distribution of atoms.

At low temperatures, however, the $T\Delta S$ term is much smaller and the free energy will eventually be determined by the enthalpy term ΔH. It has long been known, that for copper-nickel alloys, ΔH is positive; for a 1:1 alloy Kubaschewski (*3*) reports a value of ΔH = 460 cal/g atom. In other words, the formation of this copper-nickel alloy from the two components is an endothermic process. Consequently then, copper-nickel alloys should, in equilibrium, decompose into two phases. While this decomposition might be strongly inhibited in the interior of macroscopic crystals, it will more readily take place in a thin surface layer, in particular when the alloy is being used as a catalyst.

Owing to the low mobility of atoms in the solid state at low temperatures, direct experimental evidence for the existence of a miscibility gap in the copper-nickel system seems to be lacking. But numerous authors have obtained evidence for the nonrandomness of solid solutions of copper and nickel at low temperatures and copper-nickel ratios in the neighborhood of 1:1. The available evidence has been reviewed by Rapp and

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* Part of the results of this article have been mentioned in a Letter to the Editors of this Journal [*J. Catalysis* 4, 100 (1965)].

Maak (*4*). They draw attention to results by Ryan *et al.* (*5*), who found that copper-nickel alloys containing between 53% and 80% copper became superparamagnetic when subjected to neutron bombardment at 80°C. As this bombardment causes diffusivity to increase by a factor of 10^5, the alloys treated in this way might be assumed to be close to equilibrium. Ryan *et al.* suggest that a "Nahentmischung" in distinct phases is responsible for the observed superparamagnetism. They assume that there is a miscibility gap below 300°C, which is centered around the Ni:Cu = 1:1 ratio and extends farther to the nickel-rich than to the copper-rich side of the system.

New evidence for the possible existence of a miscibility gap was presented in the preceding article (*6*). Interdiffusion of copper and nickel in vacuum-deposited films led to the appearance of two phases, a copper-rich alloy, and a second phase of almost pure nickel. The suggestion was made that this two-phase system rather than the ideal solid solution may represent thermodynamic equilibrium of copper-nickel alloys of medium composition at a temperature of, say, 200°C. As the work function of the two-phase films had a constant low value, the hypothesis was advanced that the copper-rich alloy is located at the surface of these films.

In the present article both these suggestions are checked. Free energy calculations show that indeed the two-phase system corresponds to thermodynamic equilibrium at the temperature of preparation. Moreover, a model is given for the interdiffusion process. This model is based on the relative rates of diffusion of copper and nickel, both in the bulk and on the surface. From this model it follows that in the two-phase copper-nickel alloys, the copper-rich phase will be located at the surface. Finally, this model will be confronted with experimental evidence on the heats of adsorption and the catalytic properties of copper-nickel alloys prepared at low temperature.

II. Free Energy of Copper-Nickel Alloys

For the formulation of one gram atom of alloy,

$$x\,\mathrm{Cu} + (1 - x)\,\mathrm{Ni} = \mathrm{Cu}_x\mathrm{Ni}_{1-x} \quad (1)$$

the free energy, $\Delta G(x)$, at the temperature of formation, T, is given by

$$\Delta G(x) = \Delta H(x) - T\Delta S(x) \quad (2)$$

If the alloy is an ideal solid solution, the energy and entropy of formation are

$$\Delta H_{\mathrm{ideal}} = 0 \quad (3a)$$

and

$$\Delta S_{\mathrm{ideal}}(x) = -R[x \ln x + (1 - x) \ln (1 - x)] \quad (3b)$$

Deviations from ideality are conveniently described in terms of the excess functions

$$\Delta H^e(x) = \Delta H_{\mathrm{real}}(x) \quad (4a)$$

and

$$\Delta S^e(x) = \Delta S_{\mathrm{real}}(x) - S_{\mathrm{ideal}}(x) \quad (4b)$$

Complete determinations of the two excess functions in question have been published recently by Vecher and Gerasimov (*7*) and by Rapp and Maak (*6*). The data given by these two teams are in qualitative agreement inasmuch as they confirm that the excess energies are positive and the excess entropies negative. For a numerical evaluation of our experiments we shall use the data given by Vecher and Gerasimov.

These authors derived the thermodynamic properties of copper-nickel alloys at 1000°K from measurements of electromotive force and its temperature coefficient. For this purpose, the alloys were brought in contact with a molten salt containing copper iodide, and the emf's were measured with respect to a suitable reference electrode. Their results are compiled in Table 1; they show that the system deviates considerably from ideality.

Insertion of ΔS and ΔH in Eq. (2) gives the free energies. The ΔG values thus calculated for 200°C are given as a function of the composition of the alloys in Table 2, column 2, and graphically in Fig. 1.

Inspection of these data leads to the following conclusions. ΔG is positive in the case of alloys containing 50–90% nickel and negative in the case of copper-rich alloys. A minimum is located near $x = 0.82$. The existence of a second minimum at $x \ll 0.1$

TABLE 1

ENTHALPY AND ENTROPY FOR COPPER-NICKEL ALLOYS AT 1000°K[a]

x[b]	$\Delta H^e(x)$ (kcal/g at)	$\Delta S_{\mathrm{real}}(x)$ $\left(\frac{\mathrm{cal}}{\mathrm{degree\ g\ at}}\right)$	$\Delta S_{\mathrm{ideal}}(x)$ $\left(\frac{\mathrm{cal}}{\mathrm{degree\ g\ at}}\right)$	$\Delta S^e(x)$ $\left(\frac{\mathrm{cal}}{\mathrm{degree\ g\ at}}\right)$
0.0	—	—	0.0	—
0.1	0.31	0.46	0.6462	−0.19
0.2	0.50	0.75	0.9943	−0.24
0.3	0.52	0.86	1.2142	−0.35
0.4	0.48	0.90	1.3373	−0.44
0.5	0.45	0.90	1.3711	−0.47
0.6	0.38	0.89	1.3373	−0.45
0.7	0.26	0.75	1.2142	−0.46
0.8	0.13	0.57	0.9943	−0.42
0.9	0.03	0.30	0.6462	−0.35
1.0	—	—	0.0	—
Error	±30%	—	—	±15%

[a] Source: Vecher and Gerasimov, ref. (7).

[b] x = atomic fraction of copper in alloy.

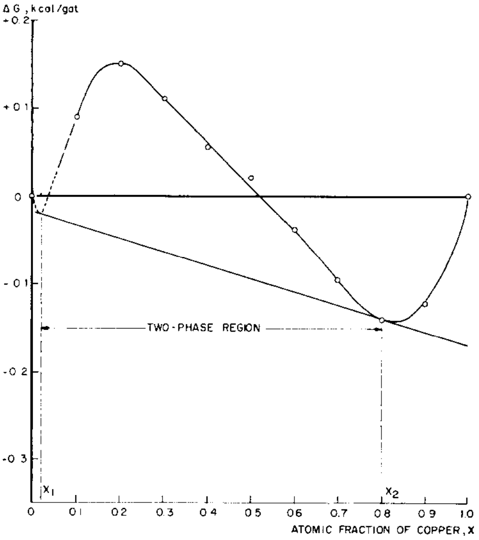


FIG. 1. $\Delta G_{200°\mathrm{C}}$ for copper-nickel alloys.

is probable for thermodynamic reasons, since it follows from Eqs. (2) and (3) that

$$\lim_{x \to 0} \frac{d(\Delta G)}{dx} = -\infty, \tag{5}$$

while the first measured point, at $x = 0.1$, has a positive value of ΔG. As no measurements are known for $x < 0.1$, this minimum has been indicated symbolically by a dotted curve.

A common tangent to the two negative portions of the curve has been drawn in Fig. 1. When in equilibrium, all alloys of compositions between the tangent points must consist of two distinct phases, one containing 18% nickel and 82% copper, the other phase being almost pure nickel.

In these calculations no allowance has been made for the possibility that $\Delta S(x)$ and $\Delta H(x)$ might also be temperature-dependent. In other words, the Neumann-Kopp rule

$$C_{p,\mathrm{alloy}} = xC_{p,\mathrm{Cu}} + (1 - x)C_{p,\mathrm{Ni}} \tag{6}$$

$$\Delta C_p = 0 \tag{7}$$

has been assumed to be valid. This might be a crude approximation, as the molar heat C_p of nickel has an anomaly at the Curie point, while such an anomaly will be absent for those alloys which are nonferromagnetic or have their Curie points far below 200°C. Therefore, a second calculation was made, in which the deviations from the Neumann-Kopp rules for nonferromagnetic alloys were estimated by breaking down the experimental $C_p(T)$ curve (8) of nickel into a "normal" curve and a saw-tooth-shaped anomaly and assuming that only the "normal" value contributes to the C_p value of the nonferromagnetic alloys in Eq. (6). The resulting $\Delta G(x)$ values are given in the third column of Table 2. It is seen that the position of the minima is not affected by this correction. As the accuracy of the absolute

TABLE 2
FREE ENERGY VALUES FOR COPPER-NICKEL ALLOYS[a]

x^b	$\Delta G_{200°C}$ (kcal/g at) Uncorrected	$\Delta G_{200°C}$ (kcal/g at) Corrected
0.0	0.0	0.0
0.1	0.09	0.09
0.2	0.15	(0.23)[c]
0.3	0.11	0.19
0.4	0.05	0.11
0.5	0.02	0.08
0.6	−0.04	0.01
0.7	−0.10	−0.06
0.8	−0.14	−0.11
0.9	−0.12	−0.10
1.0	0.0	0.0

[a] See also Fig. 1.
[b] x = atomic fraction of copper in alloy.
[c] Values presumably unreliable.

values of $\Delta G(x)$ is rather poor for both the corrected and the uncorrected values, we feel that the differences between the two sets of values are not physically significant. Therefore, only the uncorrected values are used in Fig. 1. For the present discussion, only the existence of the miscibility gap and the approximate location of the minima are of interest.

In the above calculation it has not been possible to make any allowance for specific effects due to surface energy, as there is a complete lack of data on the surface tension as a function of x.

III. MODEL: LOCATION OF PHASES IN COPPER-NICKEL FILMS

We cannot postulate the location of the various phases in the combined system unless we know the mechanism of interdiffusion. Both the effect of surface diffusion and the effect due to the difference in the diffusion rates of copper and nickel must be taken into account.

The rate of migration of the copper atoms is much higher than that of the nickel atoms. This has been demonstrated by Seith and Kottmann (*9*), who found that the interdiffusion of copper and nickel is accompanied by a pronounced Kirkendall effect. Before equilibrium is established three phases are present: copper/alloy/nickel. But while copper atoms diffuse through both interfaces, diffusion in the opposite direction is negligible, and as a consequence, holes are formed in both the copper and the alloy phases.

The mechanism of diffusion in a polycrystalline specimen has been studied in detail by Trønsdal and Sørum (*10*). They have shown that the diffusion of copper over the surface of nickel crystallites requires a lower activation energy than diffusion into the bulk of the crystallites. Consequently, the nickel crystallites are quickly enveloped in a skin of a copper-rich alloy, from which diffusion towards the center of each crystallite then takes place, as shown in Fig. 2.

We assume that this mechanism applies to all copper-nickel alloys prepared from the two metals by interdiffusion at low temperature. The equilibrium form depends on three parameters, namely the atomic fraction of copper x, and the values of x_1 and x_2 where the common tangent touches the $\Delta G(x)$ curve (Fig. 1). The values of x_1 and x_2 are, of course, dependent on the temperature at which equilibrium is established.

With the given mechanism and the known $\Delta G(x)$ curves, therefore, we can distinguish several distinct classes of alloy systems, characterized by their concentration ranges.

Range 1: $x_2 \leqq x \leqq 1$. Equilibrium will be established after all the nickel has been dissolved. A homogeneous alloy, rich in copper, is formed and the concentration of either metal at the surface is equal to the over-all concentration of the metal in the segment.

Range 2: $x_1 < x < x_2$. Equilibrium is

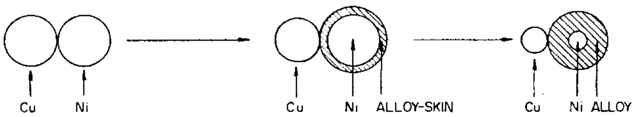


FIG. 2. Interdiffusion in copper-nickel films.

established after the copper has been consumed, resulting in a two-phase system. Each crystallite consists of a kernel of almost pure nickel ($x = x_1$), enveloped in a skin of alloy with $x = x_2$. The concentration of either metal in the surface phase will always be the same, irrespective of the over-all composition. Only the relative thicknesses of the skin and the kernel will reflect the over-all composition.

Range 3: $0 \leqq x \leqq x_1$. A homogeneous alloy is formed, containing more than 95% nickel. As no thermodynamic data are known in this region, the value of x_1 is purely hypothetical. Only the theoretical postulate Eq. (5) leads to the conclusion that $x_1 \neq 0$.

On closer inspection the existence of a fourth case must be inferred for the region where x is only slightly larger than x_1. As there is a minimum to the possible thickness of the alloy skin, it will be obvious that in the case of very low concentrations of copper the alloy skin will not completely surround the nickel crystallites. We therefore define:

Range 2a: $x_1 < x < (x_1 + \Delta x)$. Small patches of alloy with $x = x_2$ cover crystallites of almost pure nickel ($x = x_1$). This is the only case in which phase boundaries occur at the surface.

The four classes are summarized in Table 3.

It should be stressed that, while the phase equilibrium does not depend on the manner of preparation, the geometrical distribution does. The distribution may be quite different, for instance, for alloys which are originally prepared at very high temperatures and then equilibrated at low temperature. The model should be applicable to the films studied in our previous work (*6*).

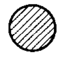
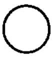
IV. Discussion

A. Model in Relation to Work Function

The experimental results described in the previous article (*6*) are in agreement with the model derived from independent data relating to the excess functions and the diffusion mechanism. The copper-nickel films of medium composition fall into Range 2. The work function of 4.61 eV was indeed found to be independent of the over-all composition ($0.2 < x < 0.8$) in this range. The X-ray analysis proved the existence of two phases. Their composition, as derived from the lattice parameters, agrees reasonably well with estimations deduced from the free energy curve for the temperature at which sintering was carried out.

TABLE 3

Location of Phases in Copper-Nickel Alloys

Range	x^a	Number of phases	Phase	x in outer phase
1	$x_2 < x < 1$	one		$x \geqq x_2$
2	$x_1 < x < x_2$	two		x_2
2a	$x_1 < x < x_1 + \Delta x$	two		x_1 and x_2
3	$0 < x < x_1$	one		$x \leqq x_1$

[a] x = atomic fraction of copper in alloy; x_1, x_2 minima in phase diagram (Fig. 1).

The results reported for alloys of extreme composition are also consistent with the model. Copper deposited on top of the nickel quickly diffuses through the top layer of nickel crystals, which are thus each covered by an alloy skin. The copper content of this skin is x_2 and its work function was again found to be 4.61 eV. However, there is not enough copper in this instance to completely envelop all the crystallites with an x_2-alloy skin and so, on further diffusion, the skin becomes thinner and finally breaks up into x_2 patches covering x_1 kernels (Range 2a). Since the x_1 and x_2 phases have different work functions, a contact potential is created between the surface patches, and the measured work function would be expected to be intermediate between that of pure nickel and that of the x_2 phase. This was indeed found to be the case.

For a copper-rich one-phase alloy (Range

1) the work function should be intermediate between those of the x_2 alloy and sintered copper. The final value obtained after prolonged sintering (4.68 eV) in fact bears this out. The nickel content of the surface here is less than that of an x_2 alloy, and consequently admission of carbon monoxide causes a smaller rise in work function than it does with x_2 alloy surfaces.

It seems that the results obtained with films prepared under ultra-high vacuum are in agreement with the model given. Thermodynamic equilibrium can be realized for films at considerably lower temperatures than in the case of macroscopic samples.*

B. Model in Relation to Catalysis

The model also helps to explain the results relating to the catalytic activity of copper-nickel alloys which have been reported by other authors and have hitherto not been amenable to straightforward interpretation.

Gharpurey and Emmett (*11*) have studied the hydrogenation of ethylene over copper-nickel alloy films sintered at 300°C. At this temperature $x_2 = 0.8$. They report that catalytic activity is poor with pure copper ($x = 1$), but that it rises sharply by two orders of magnitude on the addition of small amounts of nickel (Range 1) and finally reaches a rather high level at 20% of nickel ($x = 0.8 = x_2$). Between 20% and 75% of nickel ($x = 0.8$ and 0.25, respectively) the variations in catalytic activity, they found, remained constant within the experimental error, which is exactly what would be expected on the basis of the model given for Range 2.

When the nickel content was brought to 87.4%, Gharpurey and Emmett observed that the catalytic activity was again increased. This observation (only the one point is reported) might tentatively be ascribed to the occurrence of phase boundaries on the catalyzing surface, as this point presumably falls in Range 2a. No data are known for Range 3.

The activation energy of this reaction has been measured by Hall and Emmett (*12*). Using granular copper-nickel catalysts prepared by reduction at 350°C, these authors found the activation energy to be constant over the whole of Range 2. In the monophasic alloys of Range 1 the activation energy rises with increasing copper content as expected.

Takeuchi and co-workers (*1, 2*) have measured the heat of adsorption of hydrogen and the catalytic activity in the hydrogenation of ethylene and of benzene over granular copper-nickel alloys reduced at 200°C. Again it is possible to rationalize the results on the basis of our model. They report that the heat of adsorption of hydrogen is constant over a wide range of over-all compositions (Range 2) but rises with increasing nickel content at the two extremes, $x < 0.2$ (Ranges 3 and 2a) and $x > 0.9$ (Range 1), where according to the model the composition of the surface should vary with the over-all composition. And again, in these two hydrogenation reactions as in the others, constant catalytic activity was also found over a wide range of over-all compositions (Range 2), with variations occurring only at either edge of the phase diagram (Ranges 1, 2a, and 3, respectively). Like us, Takeuchi and co-workers came to the conclusion that the composition of the surface must be independent of the over-all composition in Range 2. Indeed, good support for this was provided by their electron diffraction analysis of similar catalysts treated with hydrogen chloride, which likewise indicated compositional differences between the surface and the bulk of the alloys.

Finally, the results of Shallcross and Russell (*13*) and Shield and Russell (*14*) should be mentioned. On measuring the catalytic activity of copper-nickel alloys in the ortho–para hydrogen conversion reaction, Shallcross and Russell also found it to be constant with Range 2 alloys ($0.05 < x < 0.9$) and to rise with increasing nickel content in the Ranges 1, 2a, and 3. Measurements of the heats of adsorption of hydrogen by Shield and Russell confirm the results obtained by Takeuchi *et al.*

Thus the model appears to provide a

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* This applies, however, only to the diffusion within each film segment where the diffusion paths are in the order 10^{-5} cm, while diffusion between various segments over distances in the order of centimeters remains negligible.

satisfactory basis for interpreting the experimental findings concerning copper-nickel catalysts prepared at low temperature.

In a way this might surprise, as an important aspect has been ignored in the previous discussion. The composition of the surface of an equilibrated alloy should, in general, depend on the ambient atmosphere. Accordingly, for alloys reduced with hydrogen or films equilibrated in a hydrogen atmosphere one might expect that the surface is enriched in nickel, as hydrogen is strongly chemisorbed on nickel, but only negligibly adsorbed on copper. This additional effect seems to be small, however. The films described in our previous article were prepared under ultra-high vacuum, whereas the films studied by Gharpurey and Emmett had been sintered in hydrogen, and the granular catalysts used by Takeuchi *et al.*, Hall *et al.*, and Russell *et al.* were prepared by reduction with hydrogen. The absence of a drastic effect of hydrogen becomes less surprising, if one considers the small amount of chemisorption of that gas at the temperatures (300° or 350°C) used by the authors mentioned.

V. Concluding Remarks

Although only the copper-nickel system has been treated in the present work, it is felt that part of the results are of more general validity. The solubility of one metal in the crystal lattice of another metal generally decreases with decreasing temperature, and many alloys studied at low temperature are therefore in a metastable state. When the alloy is used as a catalyst, however, the surface atoms will readily rearrange and then the phases responsible for the catalytic activity will be different from those detected by X-ray analysis of the bulk.

As a possible example we quote recent work by McKee and Norton (*15*) on the catalytic exchange of methane with deuterium on platinum-ruthenium alloys. These authors conclude from their X-ray analysis that ruthenium is soluble in platinum up to about 50%. The catalytic activity of this alloy system, however, shows a maximum at 20% Ru, while no anomaly is found for 50% Ru. It is not impossible that for these alloys too, the catalytic activity is a better indication of the actual phase composition on the surface than the X-ray analysis of the bulk is. The postulate that only 20% of ruthenium can be dissolved in platinum at the temperature of these experiments might provide a rational explanation for the results. It would imply that alloys containing more ruthenium exhibit a two-phase surface: besides the alloy with 20% Ru, pure ruthenium would be present in the surface. As ruthenium is a much poorer catalyst than the 20% Ru alloy, the catalytic activity should monotonously decrease with increasing ruthenium content between 20% and 100% Ru, and that is indeed what McKee and Norton find experimentally.

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