

LETTER TO THE EDITORS

Phase Composition and Work Function of Vacuum-Deposited Copper-Nickel Alloy Films

Published results on the catalytic activity of metal alloys are still often conflicting. Part of the difficulties stems from lack of knowledge of the composition of the alloy surfaces on which chemisorption takes place. At temperatures far below the melting point where chemisorption and catalysis are usually studied, the rate of phase transformation is very slow so that metastable states persist in the bulk. On the surface, however, atoms can rearrange much more easily and the phases formed there will be in thermodynamic equilibrium. This equilibrium, moreover, will depend on the nature of the ambient atmosphere.

If the phase composition of the surface differs from the bulk, it is obviously meaningless to correlate chemisorption phenomena with typical bulk properties such as the electron concentration (1) or the number of holes in the d band (2).

A particularly suspect example is the copper-nickel system. These alloys have often been investigated as catalysts, e.g. for hydrogenation reactions. With one exception (3), all authors make the tacit assumption that these alloys form an ideal statistical solution with random distribution of copper and nickel atoms. But thermodynamic data clearly show that up to several hundred degrees centigrade, most of these alloys are metastable; in equilibrium they should decompose into two distinct phases, viz., a copper-rich and a nickel-rich alloy. The excess energies and entropies of alloy formation have been determined for this system by Vecher and Gerasimov (4) and by Rapp and Maak (5). The free energies,

calculated from the data of the former group are plotted versus the copper content x for $T = 200^\circ\text{C}$ in Fig. 1. The curve shows two minima at x_1 and x_2 , respectively. No measured data are known for the minimum at x_1 , but its existence follows from the thermodynamic principle that for $x = 0$ the free-energy curve must have a negative slope, and the fact that the first experimental point has a positive value of ΔG . A common tangent is included to indicate the region where two coexistent phases are in equilibrium.

For large crystals, thermodynamic equilibrium at low temperatures will be established only after extremely long times. The conditions are much more favorable for thin films, prepared by evaporation under ultra-high vacuum. As the specific surface of these films is large, full advantage can be taken from rapid surface migration. Diffusion through the bulk is also rather fast, as films have a high concentration of lattice faults and as the path over which atoms must diffuse is only of the order of 10^2 or 10^3 Å.

We have therefore studied copper-nickel films prepared by successive deposition from the vapor of the two spectroscopically pure metals, followed by annealing at 200°C . Both the phase composition and the work functions of these films were determined by X-ray diffraction and photoelectric emission, respectively. Films were deposited on a sliding cathode in such a way that a concentration gradient was established over the cathode. One end was covered with pure copper, the other with pure

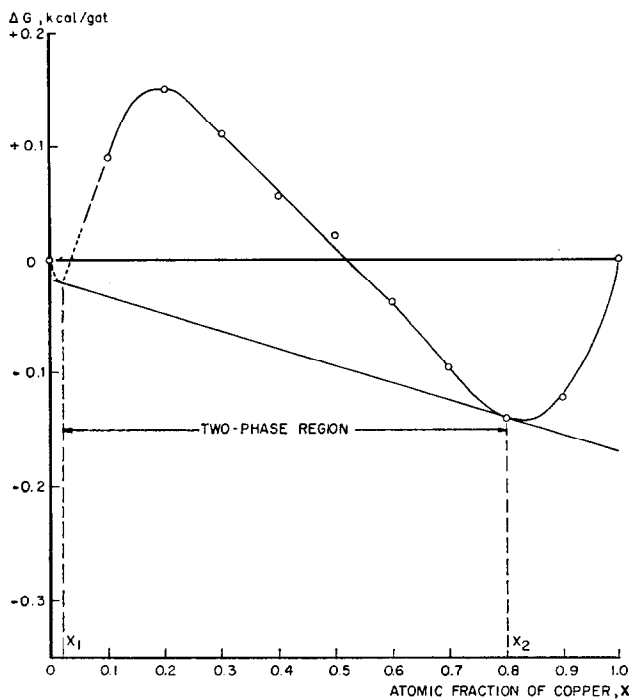


Fig. 1. Free energy of alloy formation at 200°C for copper-nickel alloys as a function of the atomic fraction of copper.

nickel; in the middle segments the nickel/copper ratio increased steadily from one end to the other. By shifting this cathode while an ultraviolet light beam was focused on the center of the phototube, the work function could be measured for a number of segments with different nickel/copper ratios under identical conditions of vacuum and heat treatment. The results of this work can be summarized as follows:

1. Annealing at 200° for several hours is sufficient to establish phase equilibrium in any segment. If the over-all composition is between x_1 and x_2 , a copper-rich alloy with $x_2 = 0.9$ coexists with a second phase of almost pure nickel. This is in satisfactory agreement with the phase composition expected for thermodynamic equilibrium.

2. Within the two-phase region—except at the edge on the nickel-rich side, where $x \approx x_1$ —the electronic work function has a constant value of 4.61 ev. This is lower than the work functions of spectroscopically pure nickel (5.3 ev) and of spectroscopically pure copper (4.66 ev) sintered at the same temperature.

3. The work functions of films with very low x or with $x > x_2$ are intermediate between the value of 4.61 ev and the work functions of pure nickel or pure copper, respectively.

A model has been worked out to describe the geometrical distribution of the phases in the two-phase region. It is consistent with the work function data and with literature results on the adsorption and catalytic activity of copper-nickel alloys.

The model makes use of the fact that copper diffuses more rapidly than nickel, and that surface migration is faster than diffusion through the bulk. It was shown by Trønsdal and Sørnum (6) that in polycrystalline samples the copper atoms quickly migrate over the nickel crystals, the latter being enveloped in a copper-rich alloy skin. We presume that further diffusion of copper takes place from the copper crystals into that skin and from the skin into the interior of the nickel crystals. For compositions between x_1 and x_2 equilibrium is established when the pure copper crystals are exhausted; the film then consists of a

conglomerate of crystals, each consisting of a kernel with $x = x_1$ and an envelope of $x = x_2$. The over-all composition determines the relative thicknesses of the kernel and of the envelope, but the composition of either phase is independent of the over-all composition.

As the work function and the catalytic and adsorption properties are governed by the outer phase only, they should be constant over the whole range between x_1 and x_2 , except very near x_1 , where the copper content is insufficient for the skin to envelop the kernel completely.

This model easily explains why the work function has been found constant over such a wide range of over-all compositions. It is, moreover in good agreement with the findings of Takeuchi *et al.* (3) and of Russell *et al.* (7, 8), who report that the heat of adsorption of hydrogen and the rate of a number of catalytic reactions (ortho-para hydrogen conversion, hydrogenation of benzene, etc.) remain constant in the range between x_1 and x_2 . It also seems possible to rationalize the results of Gharpurey and Emmett (9) with this model. These authors investigated the hydrogenation of ethylene films which, in contrast to the present work, were equilibrated under hydrogen rather than in ultra-high vacuum. Still, they observed a drastic increase, by two orders of magnitude, of catalytic activity with increasing nickel content in the monophasic region $x > x_2$, but in the wide region between x_1 and x_2 only slight and rather irregular variations of the activity were registered. Only at the edge of the two-phase region, near $x = x_1$, was an anomaly

found, which might tentatively be attributed to the appearance of two phases in the catalyzing surface.

It should be noted that the outer alloy phase, which is responsible for chemisorption of hydrogen and catalytic hydrogenation, contains much more copper than would be necessary to fill the holes in the d band. The observed phenomena are, therefore, in disagreement with the widespread notion that holes in the d band should be a prerequisite for these catalytic properties.

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