JOURNAL OF CATALYSIS 9, 166–171 (1967)

The Formation and Structure of Evaporated Copper-Nickel Alloy Films

J. J. BYRNE AND J. K. A. CLARKE

From the Department of Chemistry, University College, Belfield, Dublin, Ireland

Received, July 17, 1967

The preparation of homogeneous evaporated Cu-Ni alloy films has been investigated with a view to their use in catalytic studies. Special attention has been given to source design. Mixed films prepared by simultaneous evaporation followed by annealing, in both cases at a glass substrate temperature of about 500°, are single-phased and homogeneous irrespective of the composition. Disagreement between the present findings and those recently reported by Campbell and Emmett is discussed.

INTRODUCTION

Studies with well-characterized binary $VIII_3$–IB alloys are of special interest in seeking the fundamental bases of gas adsorption and catalysis. Vacuum-evaporated films have frequently been used in investigation of these properties for single metals because of their good reproducibility compared with other metallic forms. Extension of the method to alloys requires that binary films should be homogeneous and, ideally, for the production of clean surfaces that the method of preparation be capable of adaptation to ultra-high-vacuum conditions. Direct evaporation of massive alloy forms, either by direct resistive heating or by the "flash" method (*1*), suffers a number of disadvantages. In either method outgassing of the metal is difficult. Also, in the first, fractionation of the components generally occurs because of their different volatilities and this necessitates a subsequent severe heat treatment to achieve homogenization. As a first stage in the development of alloy films appropriate to extreme vacuums we felt it important to investigate the preparation of well-homogenized copper-nickel films by simultaneous evaporation from separate sources in conventional high vacuum.

Semiquantitative studies of alloy film preparation made by Belser (*2*) suggested that for Cu-Ni considerably lower homogenization temperatures were necessary for simultaneously evaporated films than for successive evaporation. Emmett, with Gharpurey (*3*), and recently with Campbell (*4*), has reported the preparation of mixed Cu-Ni films using mainly successive evaporation. Takeuchi and his group (*5*) have prepared mixed films by simultaneous evaporation at low temperatures but gave no information as to their homogeneity.

For the Pd-Ag system Moss and Thomas (*6*) have given procedures for the preparation of homogeneous films suitable for catalytic work and have discussed the processes involved.

EXPERIMENTAL

Source Design

Alloy films were prepared by simultaneous evaporation of spectrographically standardized Cu and Ni (Johnson, Matthey and Co.) onto the wall of a cylindrical Pyrex vessel at pressures of about 10^{-6} torr. A principal requirement in preparation of these mixed films is the attainment of an acceptable uniformity in composition over the area of the film. To this end a thorough investigation was made of possible arrangements of source filaments including: (a) those approximating to point sources, (b) coaxial spirals, and (c) hairpin filaments with mutually perpendicular planes. Method (a) proved impracticable because of the high current required to evaporate Ni from very short lengths of the wire either as such or wound on a tungsten support. While method (b) offered evaporation characteristics approximately equivalent to those of coaxial straight wires (*1*), the tendency of Ni spirals to deform at high temperatures precluded its use. Efforts to remedy this geometrical instability were made using Ni-plated tungsten wire but such filaments were difficult to outgas prior to evaporation due to the high content of occluded gas in the plated coating. Sources of type (c) were finally adopted (Fig. 1). The Ni was evaporated directly from a hairpin of 0.6-mm diameter Ni wire, and the Cu from beads on ledges of a specially shaped hairpin of 0.3-mm diameter tungsten (Tungsten Manufacturing Co.). Filaments were attached by stainless steel connectors to 2-mm tungsten rods sealed into the vessel. In order to ensure coincidence in vertical level of the centers of evaporation, conduction of heat to the heavy tungsten rods was offset by overwinding the lower end of each filament. Before evaporation both filaments were outgassed for 2 hr just below their evaporation temperatures. The vessel was at the same time baked at a temperature greater than or equal to that used in subsequent deposition of the film.

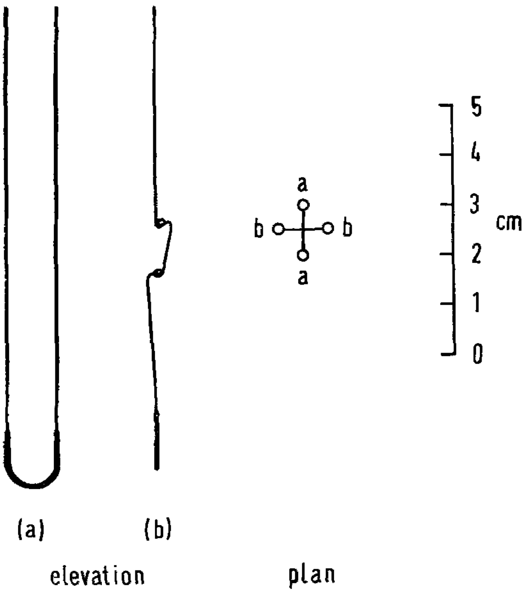

FIG. 1. Evaporation sources: (a) nickel; (b) copper (side-view of one limb).

Attention was also given to the problem of lateral source geometry and vessel design, since variation in composition of films may be expected due to directional nonuniformity of evaporation. Simple calculations based on the inverse square law give a general guide as to the influence on composition variation of vessel diameter, limb separation in the hairpins, and source eccentricity. There are two main conclusions: (i) large vessel diameters and small limb separation promote uniformity, this being vitiated somewhat by an increase in mutual shadowing of the sources, (ii) small relative movements of the axes of the hairpins cause serious variations in composition. Accordingly a vessel diameter of 10 cm and the smallest practicable limb separation of 1 cm were used, the overall geometry being stabilized by a glass spacer. The vessel had a cylindrical wall height of 9 cm.

Film Homogeneity

Alloy film compositions were determined by two methods: (a) electrochemical separation of the metals followed by spectrophotometric analysis (Ni) or weighing (Cu), and (b) analysis of lattice parameters measured by the Debye-Scherrer powder method. Analyses by (a) were accurate to better than ±0.5 atom % of each component. Method (b) gave analyses of similar accuracy when the procedure now to be outlined was followed.

Samples for X-ray diffraction studies were prepared by stripping the film from the glass substrate using, where necessary, 5% hydrofluoric acid to induce peeling. Diffraction measurements were carried out with a 114.6-mm Philips camera using Cu $K\alpha$ radiation on small sections (1–2 mm^2) of the film packed as a randomly oriented powder into a 0.2-mm diameter

Lindemann tube. Lattice parameters were derived by the Nelson-Riley extrapolation. These, in principle, yield alloy compositions by reference to published information for the copper-nickel system (*7, 8*). Caution must be exercised, however, in using this method in view of reported contractions in lattice parameters for very thin films (*9*). Heavier films (1000-Å nominal thickness) appear to show this effect to a very small degree or not at all (*10*). In the present work films of pure Cu and pure Ni of about this thickness, sintered at temperatures of 400°C or higher, gave lattice parameters in good agreement (± 0.0005 Å) with published values for the massive metals, indicating that measurement of composition in alloys should be reliable to $\pm 0.5\%$. In addition, however, this method is undependable for binary samples which have been incompletely homogenized. These give nonsymmetrical diffraction lines the centroids of which do not correspond to the actual composition. Nevertheless, for heavier well-homogenized alloy films the two methods of analysis give satisfactory agreement, typically to within ± 1 atom % for the same section of a film. The use of both these methods permitted a detailed mapping of the composition of the evaporated deposit over its area and hence made it possible to effect a further improvement in matching of source levels by careful adjustment of the vertical position and vertical separation of the Cu windings on the tungsten wire. Resultant films, containing in typical experiments approximately equal amounts of each metal, had horizontal and vertical variations in composition of less than about 3 and 5 atom %, respectively. Such variations are, of course, expected to decrease for films closer to the ends of the composition range. Mean compositions agreed, in general, to within ± 1 atom % with those calculated from loss in weight of the filaments.

A further important consideration in the preparation of alloy films is their detailed homogeneity. Simultaneous evaporation of the metals onto an unheated glass substrate does not yield a homogeneous solution, as is shown by the shapes and positions of the Debye-Scherrer lines. An estimate of the homogenization temperature required may be made from volume diffusion coefficients for the copper-nickel system. Mean and partial diffusion coefficients (D; D_{Ni}, D_{Cu}) obtained by extrapolation of high-temperature measurements (*11*) are such that in the temperature range 200–600°C all three coefficients are lowest at concentrations approaching 100% Ni. Root-mean-square displacements in Å [taken as $(2Dt)^{1/2}$, where t is time] at several temperatures calculated from values of D at 100% Ni and for a 2-hr heat treatment are 7×10^{-4} (200°), 0.2 (300°), 6.0 (400°), 94 (500°), and 830 (600°). The corresponding displacements calculated using values of the mean interdiffusion coefficient at 100% Cu (the composition at which interdiffusion takes place most rapidly) are 5 to 30 times greater depending on the temperature. It may be concluded that, while temperatures as low as 300–400° can cause considerable diffusion of Ni atoms into Cu-rich centers, complete mixing requires penetration of Ni-rich centers by Cu atoms and hence temperatures of about 500° are necessary.

Preliminary tests of homogeneity were made by visual inspection of X-ray diffraction photographs of powdered film samples. Poorly alloyed films show broadened Debye-Scherrer lines and consequently poor resolution of the $K\alpha$ doublet for reflections of large Bragg angle (331 and 420). While this approach does not allow for the particle-size broadening, comparison of results for alloys with those for pure metals prepared at the same temperature and following a standardized procedure gives useful qualitative information. Details of two series of experiments were as follows:

(1) A typical alloy film deposited at 430°C and annealed at that temperature for 2 hr gave diffuse 331 and 420 reflections whereas deposits of each pure metal similarly treated gave sharp lines with well resolved Cu $K\alpha$ doublets. (2) Films deposited at 500° and 520°C gave results more closely similar to those for the pure metals, and showed resolution to a greater or lesser

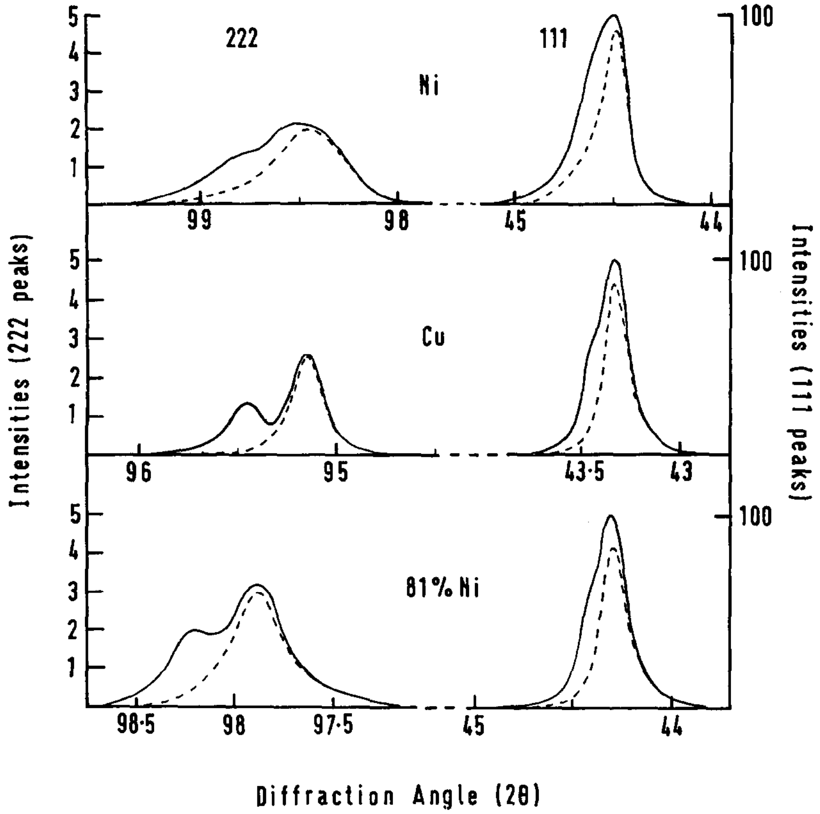

FIG. 2. X-Ray diffractometer profiles of 111 and 222 reflections for Cu $K\alpha$ radiation. Dashed line shows resolved α_1 components. Intensities are normalized so that the height of each 111 peak is 100.

degree depending on such factors as temperature of annealing and composition.

More detailed studies of the homogeneity of alloy films prepared at several substrate temperatures were made by X-ray diffractometry. For this work samples of metal films were mounted on flat glass slides and peak widths measured for the 111 and 222 reflections (Fig. 2) by means of a Philips PW 1050 diffractometer fitted with a sealed proportional counter and a Cu target. The analysis of results which follows is based on that described by Moss and Thomas (*6*).

The effects of crystallite size on peak widths may be separated from that of inhomogeneity of composition by the treatment of Barton and Carr-Brion (*12*) who adopted a method due to Jones (*13*). By making the assumptions that the diffraction peaks broadened by instrumental and particle-size effects are Cauchy in form and that the range da of lattice parameters present in the sample has a triangular distribution the following expression is obtained:

$$\left(\frac{da}{a}\right)^2 = \frac{3}{\pi^2}\left\{\frac{B_{222}^2\cos^2\theta_{222} - B_{111}^2\cos^2\theta_{111}}{\sin^2\theta_{222} - \sin^2\theta_{111}}\right\} \tag{1}$$

For a rectangular distribution of lattice parameters the numerical factor $3/\pi^2$ is replaced by $3/2\pi^2$. The symbols B_{111}, B_{222}, θ_{111}, and θ_{222} denote integral widths of the α_1 component and the Bragg angles, respectively, of the reflections indicated; a is the lattice parameter of the homogeneous alloy. In the application of (1) to measured peaks, the α_1 component of the Cu $K\alpha$ doublet was resolved by the graphical method of Rachinger (*14*). Results are summarized in Table 1. The degree of

TABLE 1
VALUES OF da/a FOR COPPER, NICKEL, AND COPPER-NICKEL ALLOY FILMS

Film composition (atom % Ni)	da/a*		Degree of alloying[a] = $100[1 - (da/\Delta a)]$	Film weight (μg/cm^2)	Annealing treatment (°C; hr)
	Triangular distribution	Rectangular distribution			
100	1.7×10^{-3}	1.2×10^{-3}	93.4	155	520°; 2
81	1.3×10^{-3}	9×10^{-4}	95.0	94	520°; 1.8
62	2.2×10^{-3}	1.5×10^{-3}	91.4	146	500°; 6
42	1.5×10^{-3}	1.1×10^{-3}	94.1	169	500°; 6
24	4.3×10^{-4}	3.0×10^{-4}	98.3	148	520°; 2
6	4.3×10^{-4}	3.0×10^{-4}	98.3	115	520°; 2
0	2.2×10^{-4}	1.5×10^{-4}	99.1	108	450°; 2

* Calculated using integral widths of the diffraction profiles.

[a] Assuming triangular distributions.

alloying is defined by the expression $100[1 - (da/\Delta a)]$ where da is the spread in lattice parameters calculated assuming a triangular distribution and Δa is the difference in lattice constant between pure Ni and pure Cu. While the method described is to be regarded as a comparative one (in view especially of the nonzero values of da/a calculated for pure Cu and pure Ni films) the results are taken as satisfactory evidence for the almost complete homogeneity of films deposited at 500–520° and subsequently annealed for 2 hr at the same temperature.

Film Orientation

The possibility of preferred orientation in the films was investigated by comparing the relative intensities of their principal diffractometer peaks with those of a standard powder specimen having random crystallite orientation (Table 2). Only crystal planes parallel to the substrate give rise to diffraction peaks at the appropriate glancing angle on the diffractometer. All films show some deviation from random orientation and this is most pronounced for pure Cu films, least for pure Ni. The Cu-Ni alloys are intermediate but, within experimental error, have a constant degree of preferred orientation independent of film composition.

DISCUSSION

The procedures described offer a means of preparing homogeneous polycrystalline Cu-Ni alloy films, as shown by both chemical analyses and evaluation of profile breadths from X-ray diffractometry. Further support for the homogeneity of films formed by simultaneous evaporation and annealing at a substrate temperature of

TABLE 2
RELATIVE INTENSITIES OF DEBYE-SCHERRER REFLECTIONS OF ALLOY FILMS

Composition (atom % Ni)	Film weight (μg/cm^2)	Annealing treatment (°C; hr)	Intensities[a]			
			111	200	220	311
100[b]	—	—	100	42	21	—
100	155	520°; 2	100	35	9	8
81	94	520°; 1.8	100	24	4	10
69	112	430°; 2.5	100	24	—	—
42	169	520°; 6	100	22	2	6
24	148	520°; 2	100	20	4	6
6	115	520°; 2	100	20	4	5
0	108	450°; 2	100	10	1	2

[a] Normalized so that intensity of each 111 reflection is 100.

[b] Randomly oriented powder—ref. (*18*).

500–520° lies in the highly symmetrical α_1 component profiles found (Fig. 2) and in the close agreement of measured lattice parameters with published values. These findings contrast with those of Campbell and Emmett, who have recently reported (*4*) that mixed films heated for several hours at 500° in a hydrogen atmosphere formed an alloy containing about 60% Cu, any excess of Ni or Cu present giving an X-ray diffraction pattern characteristic of that metal. There was no evidence for a second phase (*15*) in our alloy films, irrespective of their nominal composition and whether homogenization was carried out *in vacuo* or in a hydrogen atmosphere. A major point of difference between the experiments of Campbell and Emmett and the present work is that their substrate temperature during film deposition was 0°C whereas ours was the same as the temperature of subsequent homogenization. Atom movement would be promoted from the earliest stage in film growth in the latter technique and this may be decisive in achieving homogeneous solution.

The greater tendency towards preferred orientation in Cu compared to Ni films and to a randomly oriented powder agrees as to the influence of high substrate temperature during growth and of relative atom mobility of the two metals with previous results (*16, 17*). It is convenient, for the use of the evaporated alloy films in catalysis, that they have a constant orientation independent of film composition.

Results of catalytic studies with films prepared according to the procedure described here, and a further discussion of recent proposals relating to the Cu-Ni system, will be presented in a forthcoming publication.

ACKNOWLEDGMENT

One of us (J.J.B.) wishes to thank the Irish Department of Education for the award of a Research Studentship during the tenure of which (1963–66) this work was carried out.

REFERENCES

1. HOLLAND, L., "Vacuum Deposition of Thin Films." Chapman and Hall, London, 1956.
2. BELSER, R. B., *J. Appl. Phys.* **31,** 562 (1960).
3. GHARPUREY, M. K., AND EMMETT, P. H., *J. Phys. Chem.* **65,** 1182 (1961).
4. CAMPBELL, J. S., AND EMMETT, P. H., *J. Catalysis* **7,** 252 (1967).
5. TAKEUCHI, T., HONMA, N., AND IKUSHIMA, T., *Shokubai* (*Tokyo*) **6,** 352 (1964).
6. MOSS, R. L., AND THOMAS, D. H., *Trans. Faraday Soc.* **60,** 1110 (1964).
7. COLES, B. R., *J. Inst. Metals* **84,** 346 (1956).
8. OWEN, E. A., AND PICKUP, L., *Z. Krist.* **88,** 116 (1935).
9. SUHRMANN, R., WEDLER, G., WILKE, H. G., AND REUSMANN, G., *Z. Physik. Chem.* **26,** 85 (1960).
10. MOSS, R. L., DUELL, M. J., AND THOMAS, D. H., *Trans. Faraday Soc.* **59,** 216 (1963).
11. PINES, B. YA., AND SMUSHKOV, I. V., *Fiz. Tverd. Tela.* (*Engl. transl.*) **1,** 858 (1959).
12. BARTON, R., AND CARR-BRION, K. G., Warren Spring Laboratory Research Report RR/PCS/46, 1963.
13. JONES, F. W., *Proc. Roy. Soc.* (*London*) **A166,** 16 (1938).
14. RACHINGER, W. A., *J. Sci. Instr.* **25,** 254 (1948).
15. SACHTLER, W. M. H., AND DORGELO, G. J. H., *J. Catalysis* **4,** 654 (1965).
16. SACHTLER, W. M. H., DORGELO, G. J. H., AND VAN DER KNAAP, W., *J. Chim. Phys.* **51,** 491 (1959).
17. LEVINSTEIN, H., *J. Appl. Phys.* **20,** 306 (1949).
18. "X-Ray Powder Diffraction Index." Am. Soc. for Testing Materials, 1966.