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Effect of Preparation on the Apparent Surface Composition of Pd–Rh Alloy Films Used for CO Oxidation

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The Pd–Rh alloy films prepared by simultaneous deposition at 400°C and used for CO oxidation were shown by X-ray diffraction to consist of two phases in the range 30–90% Rh. Rates of CO oxidation were increased by small additions of Rh to Pd, but remained constant between 20 and 50% Rh; beyond 50% Rh, the rate increased sharply with increasing Rh content. If the surface composition is taken as being equal to the bulk composition for the homogeneous alloys at each end of the composition range, and otherwise equal to the observed composition of the Rh-deficient phase (for reasons discussed), the rate of CO oxidation increases linearly with apparent surface content of rhodium.

The CO oxidation rates were, therefore, used to estimate surface composition of Pd–Rh alloy films prepared by alternative methods, e.g., by annealing in H_2 successively deposited dual layers. These latter results show the importance of the order of deposition, film weight and composition in determining the surface composition in an alloy system where a miscibility gap can exist and interdiffusion rates are slow. Experiments to produce a range of metastable solid solutions are also discussed; apparent surface compositions are compared with overall (bulk) compositions.

INTRODUCTION

Methods of preparing sintered evaporated films of alloys which form random solid solutions, e.g., Pd–Ag, and their use in catalytic studies, have now been established (*1–3*). The preparation in ultrahigh vacuum of reasonably unsintered homogeneous Pd–Ag films has also been described (*4*). The present work extends recent interest in evaporated films of alloys which can exhibit a miscibility gap over a wide composition range, e.g., Cu–Ni (*5–8*) and Pd–Rh (*9*, *10*).

When ethylene was oxidized over Pd–Rh alloy films (*10*), the variation of activity with bulk composition was complex, as a consequence of hydrogen solubility in alloys with low Rh contents and phase separation between 30 and 80% Rh. It was proposed that the preferential nucleation of Rh in alloy films with >30% Rh, prepared by simultaneous evaporation, led to the formation of the Rh-rich phase as a kernel to the crystallites surrounded by a Rh-deficient solid solution of variable composition (phase I). It was noted that some apparently anomalous reaction rates fitted into place if the composition of phase I, given by X-ray data, was equated with the surface composition. Apart from the composition range where hydrogen is soluble in Pd–Rh alloys, there was some indication that ethylene oxidation rates would decrease linearly with increasing Rh content *in the surface layer.*

It seemed that this approach might be extended to another reaction, viz., CO oxidation, where the complication of hydrogen solubility is absent, for the following reasons: If the activity varied in a simple way with surface composition derived approximately from the composition of phase I, then this reaction might be used as a probe for surface composition in Pd–Rh alloy films prepared by other methods where physical techniques are inapplicable. In particular, the preparation of Pd–Rh alloy films by successive deposition of the component metals which are then annealed, might be examined as an alternative to simultaneous evaporation. Diffusion rates do not seem to have been measured for Pd or Rh atom movement in Pd–Rh alloys, but they appear to be extremely slow because prolonged periods of high-temperature annealing were required to bring out phase-separation in specimens quench-cooled from 1300°C (*11*). Hence successively deposited Pd–Rh films might usefully be compared with similarly prepared Cu–Ni films where one component diffuses readily.

EXPERIMENTAL

The Pd–Rh alloy films were formed on the inner surface of spherical Pyrex glass reaction vessels either by simultaneous evaporation from separate Pd and Rh sources or by successive deposition of layers of Pd and Rh, which were subsequently annealed in pure hydrogen. The evaporation sources were short concentric spirals of 0.5 mm diam Pd and Rh wire (Johnson Matthey, and Co. Ltd., "spectrographically standardized"). Films prepared by simultaneous evaporation were either deposited on the glass substrate at 400°C and then vacuum annealed for 1 hr at the same temperature or deposited at 0°C and annealed in 50 Torr H_2 at 400°C for 21 hr (1 Torr = 133.32 Nm^{-2}). The reaction vessel was sealed directly to a glass vacuum system incorporating greaseless stopcocks; the vessel and parts of the system were baked above 450°C and a vacuum of 10^{-6} Torr, measured with an ionization gauge, was usual. Before depositing a film, the Pd and Rh sources were outgassed for ~1 hr at temperatures close to the evaporation points of the metals, while the glassware was continuously heated.

The reaction mixture was prepared from "spectrographically pure" carbon monoxide and oxygen (British Oxygen Co. Ltd.), and when expanded through a trap at −78°C into the reaction vessel at ice temperature, gave 50 Torr (or 6.75×10^{20} molecules) of CO +25 Torr O_2. The reaction vessel was connected to the ion source of a mass spectrometer by means of a fine glass capillary leak; less than 2% of the gas mixture was removed per hour. The sensitivity of the mass spectrometer to CO and O_2 was redetermined at the start of each experiment, and the reaction rate derived from the rate of O_2 removal (cross-checked with the rates of CO removal and CO_2 formation).

At the end of each catalytic experiment the composition of the alloy film at 12 representative parts of the reaction vessel was determined by X-ray fluorescence analysis. As in previous work attention to the geometry and positioning of the evaporation sources ensured that the alloy films were reasonably uniform in composition over the 220 cm^2 area of the reaction vessel. The total film weight was found from the combined weight loss from the evaporation sources. Specimens for X-ray diffraction were obtained by stripping the film from fragments of the reaction vessel.

RESULTS AND DISCUSSION

Information on bulk Pd–Rh alloys and alloy films prepared by simultaneous evaporation of the component metals was previously reported in detail (*9*) and need only be summarized here. The existence of a wide miscibility gap has been demonstrated with bulk specimens annealed below 850°C although the establishment of equilibrium was extremely slow (*11*). Recent thermodynamic data (*12*) for Pd–Rh alloys confirm the experimental observations; the enthalpies of formation (10–90% Rh) are endothermic and only temperatures above ~860°C produce a sufficiently large $T\Delta S$ term to yield negative values of ΔG (assuming the temperature independence of ΔH and ΔS).

Alloy films, unused in catalytic reaction, prepared by simultaneous deposition of Pd and Rh on glass at 400°C exhibited apparently good bulk homogeneity at both ends of the compositions range, 0–30 and

80–100% Rh. However, over a wide range of intermediate composition there was evidence of phase separation, viz., asymmetrical X-ray diffraction line profiles, in which two maxima could sometimes be detected. Many examples of this behavior were also observed in films with intermediate compositions used to catalyze ethylene oxidation (*9*).

Simultaneous Deposition, Substrate 400°C

Table 1 records X-ray data for Pd–Rh alloys prepared by simultaneous evaporation (substrate at 400°C) and used in the present work to catalyze CO oxidation.

TABLE 1
LATTICE CONSTANTS IN Pd–Rh FILMS (SIMULTANEOUS DEPOSITION, 400°C)

Bulk composition[a] (at. % Rh)	Lattice constant (Å)
1.7	3.889
3.7	3.888
7.7	3.886
13.4	3.883
32.7	3.871
43.2	3.865
55.8	3.866; 3.823
61.8	3.856; 3.821
66.7	3.846; 3.812
77.6	3.848; 3.805
78.6	3.844; 3.810
91.3	3.824; 3.806
98.1	3.804

[a] X-Ray fluorescence analysis of sample previously examined by X-ray diffraction.

The lattice constant was derived from peak maxima, using the (111) and (222) reflections. Lattice constants from these reflections were identical or almost equal indicating that extrapolation to $\theta = 90°$ was unnecessary for present purposes. The X-ray data in Table 1 show clearly the tendency to phase separation in a number of the Pd–Rh alloy films with intermediate compositions, i.e., doubled diffraction maxima were observed from films with ~55–90% Rh. Although only a single peak maximum could be identified in samples with 32.7 and 43.2% Rh, the profiles were ill defined and may show the lower limit for phase separation. Thus Pd–Rh alloy films used for CO oxidation are probably subjected to phase separation in the range 30–90% Rh.

Lattice constants for arc-melted quenched Pd–Rh bulk alloys were reported by Raub (*11*), and when plotted against Rh content (*9*) show only a small deviation from Végard's law. From this information, the corresponding Rh contents of the phases observed in Pd–Rh films (Table 1) can be derived from the observed lattice constants. In Fig. 1, the composition derived from lattice constants is plotted against the composition of the sample obtained from X-ray fluorescence analysis. Where two phases were present in the films, the compositions of the Rh-deficient, phase I, and the Rh-rich, phase II, phases are shown by open triangles, upright and inverted, respectively. The composition of approximately homogenized alloy films (single X-ray peaks), also derived from X-ray diffraction shown by half-filled triangles, diverges from the expected composition at ~30–40% Rh, supporting the lower limit for phase separation suggested above. Homogeneous films at either end of the composition range are shown by filled triangles.

Rates of CO oxidation over these Pd–Rh alloy films, prepared by simultaneous deposition, were measured at 240°C and showed a convenient order of magnitude increase between 0 and 100% Rh. However, although some increase in rate occurred with additions of up to ~20% Rh, there was little further change up to ~50% Rh; beyond this composition the rate increased rapidly (Fig. 2). The films used varied in weight between 20 and 45 mg, but it was not thought necessary to make any correction to the observed rates for variation in surface area for the following reasons. Firstly, it has been found previously for sintered nickel films (*13*) that the surface area a is related to the film weight w by the expression $a = \mathrm{B} + \mathrm{D}w$ but the constant D for films sintered at 400°C was only 3.3 cm^2/mg (B was 490 cm^2). The relationship does not hold for light films, <5 mg, which were avoided in the present work. Secondly, in support of the

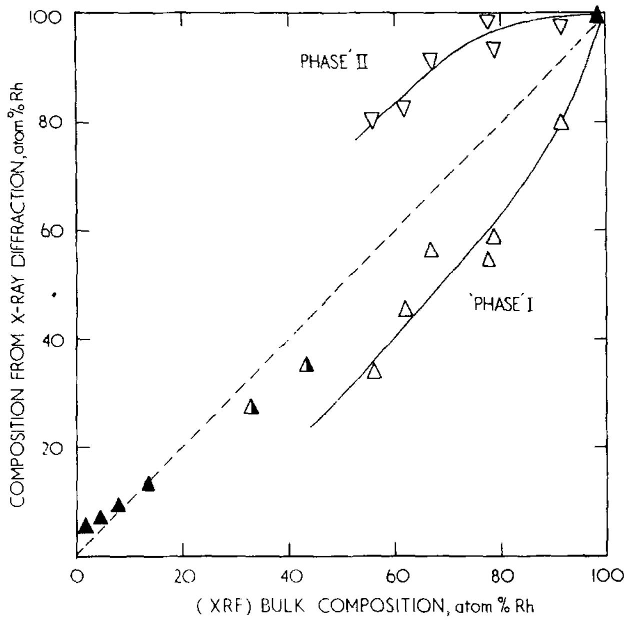

FIG. 1. Composition derived from lattice constants plotted against composition of sample analyzed by X-ray fluorescence; ▲, single-phase system; ▲, asymmetrical diffraction profiles observed; △, ▽, two-phase system.

assumption made, the observed CO oxidation rates on pure Rh films weighing 13.6 and 30.0 mg were 8.48 and 8.25 Torr/min, respectively.

In Fig. 2, the rate of CO oxidation is plotted against the average bulk composition of the film determined by X-ray fluorescence analysis of samples taken

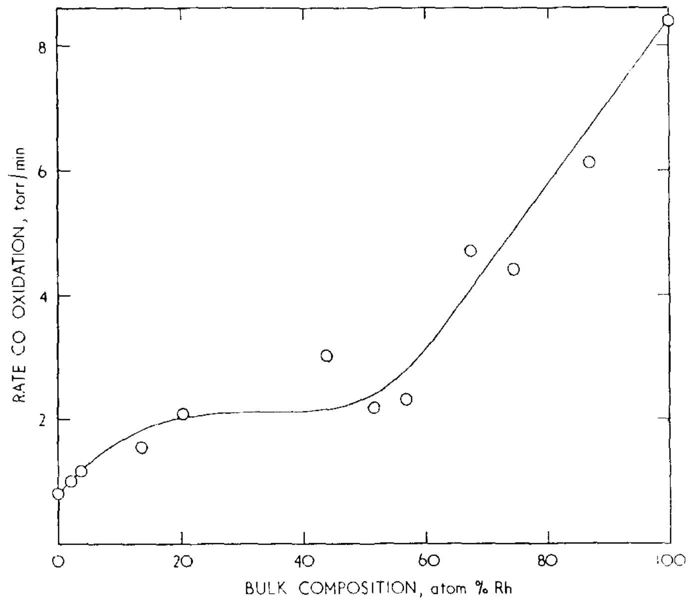

FIG. 2. Rate of CO oxidation (Torr/min) at 240°C as a function of average observed bulk film composition determined by X-ray fluorescence analysis.

from various parts of the reaction vessel as described above. The next step is to attempt to rationalize the activity pattern shown in Fig. 2 by replotting in terms of the apparent *surface* composition.

In the model proposed (*9*) for the structure of Pd–Rh alloy films prepared by simultaneous evaporation on to a substrate at 400°C, the preferential nucleation of Rh at composition beyond ~30% Rh was envisaged, arising as a consequence of the higher bulk heat of sublimation of Rh compared with Pd. [For discussion, see Ref. (9).] Hence, in the composition range 30% Rh upwards, the crystallites are composed of a Rh-rich kernel surrounded by a Rh-deficient solid solution (phase I), the Rh content of which increases with increasing Rh flux. However, above ~80–90% Rh, in the X-ray diffraction profile it becomes difficult to detect a difference in composition between the phase II kernel of the crystallite and the phase I outer layers, which are a little richer in Pd.

From Fig. 1, the composition of phase I can be read off for any particular bulk or overall composition of the alloy film. It is proposed that the composition of phase I is the surface composition of alloys showing phase separation. For alloys at each end of the composition range, and apparently homogeneous, the surface composition is taken to be equal to the bulk or overall composition of the film. The CO oxidation rates shown in Fig. 2 are replotted in Fig. 3 as a function of *surface* composition on the basis of the above assumptions. (Homogeneous alloys and the pure metals are shown by filled circles, and alloys with phase separation are shown by half-filled circles.) Treated in this way, the CO oxidation rates show a satisfactory linear relationship with Rh content.

It is proposed that CO oxidation rates can be used to estimate the surface composition in the following way: It is assumed that the rate of CO oxidation, r_{obs}, is related to the fraction of the alloy surface, θ, due to Rh atoms by

$$r_{obs} = r_1(1 - \theta) + r_2\theta,$$

where r_1 and r_2 are the rates of CO oxidation on pure Pd and Rh, respectively, for a given preparative method. If a Pd–Rh alloy film is formed at, say, a low sintering temperature and perhaps with a somewhat larger surface area, then experiments

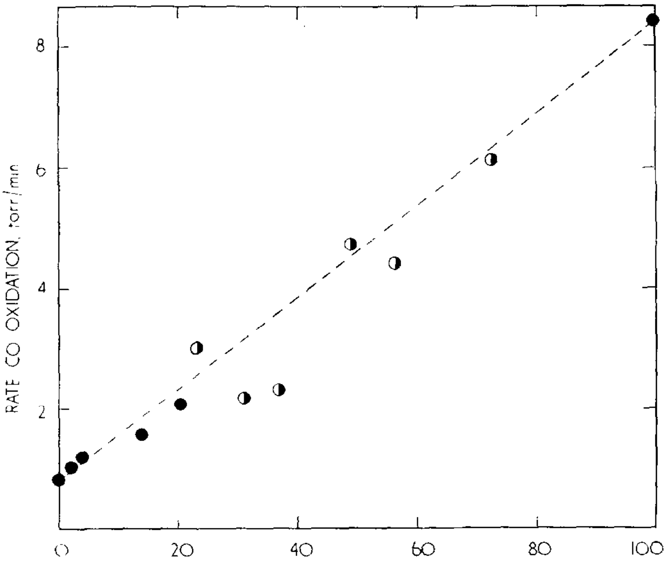

Fig. 3. Rate of CO oxidation (Torr/min) at 240°C as a function of apparent surface composition; ●, homogeneous alloys and pure metals; ◑, alloys showing phase separation.

with the pure metals at the same sintering temperature are required to derive new values of r_1 and r_2. Hence, for the alloy film in question, the surface composition is obtained from the observed rate of CO oxidation. The use of this equation is only strictly correct if the activation energies are equal for CO oxidation over the pure metals and their alloys; otherwise the apparent surface compositions derived could depend on the temperature at which rates were compared. Activation energies for CO oxidation over unsintered and sintered Pd films, over pure Rh films and over an 8% Rh–Pd alloy film were 29, 32, 25 and 30 kcal/mole, respectively. If the activation energies for other alloys remain within this range, as indicated, then the estimates of surface composition will be adequate to support the conclusions drawn in the following sections.

Dual Layers Annealed in Hydrogen

Alloy films were prepared by annealing successively deposited layers of Pd and Rh (deposited at 0°C), i.e., dual layer films in 50 Torr H_2 at 400°C for 21 hr. The surface composition of these films was evaluated using the approach described above. For this purpose CO oxidation rates were measured over pure Pd and Rh films similarly deposited and H_2 annealed. The activity of pure Pd for CO oxidation at 240°C (r_1) was 0.85 Torr/min, which is almost equal to the rate observed for Pd films deposited at 400°C, and briefly annealed in vacuum (previous section). The corresponding activity for pure Rh films, r_2 (deposited at 0°C and H_2 annealed at 400°C) was 7.5 Torr/min, and this rate is only a little less than the rate observed for pure Rh deposited and vacuum annealed at 400°C. From these values of r_1 and r_2, the apparent surface composition of H_2 annealed Pd–Rh dual layer films was obtained (Table 2). Table 2 also records information derived from X-ray diffraction measurements on the structure of these alloy films.

The first three films in Table 2 were prepared by depositing Rh first, keeping the Pd filament at a temperature below the evaporation point. Film 1 appeared to be reasonably homogeneous when examined by X-ray diffraction (single symmetrical diffraction peaks) and the composition derived from the lattice constant was approximately equal to the composition determined by X-ray fluorescence analysis of the sample, i.e., ~90% Rh. However, the CO oxidation rate indicated an apparent surface composition of only 62% Rh. The structural information appears to rule out an explanation envisaging Rh crystallites partially coated with Pd, and thereby reducing the activity compared with pure Rh. Instead it would seem that Pd has successfully penetrated the bottom Rh layer during the annealing period forming an alloy but that Rh migration upwards is inadequate through the thin top Pd layer. Thus, the surface content of the annealed film is Rh-deficient compared with the overall composition of the film.

TABLE 2

Structure and Activity of Dual-layer Films

Film no.	Order of deposition		Overall composition (at. % Rh)	Film weight (mg)	Film structure	Composition of XRD sample (atom % Rh)		Rate CO oxidation at 240°C (Torr/min)	Apparent surface composition (at. % Rh)
	Bottom layer	Top layer				XRF	XRD		
1	Rh	Pd	87.8	21.7	Homogeneous	88.3	91.4	4.96	62
2	Rh	Pd	73.5	20.7	Two-phase	74.7	21.6; 84.6	1.69	13
3	Rh	Pd	57.4	8.1	Two-phase	52.3	10.2; 78.8	1.46	10
4	Pd	Rh	89.2	30+	Homogeneous	88.9	91.4	7.2	95
5	Pd	Rh	67.6	37.6	Two-phase	66.8	5.2; 96.2	2.34	23
6	Pd	Rh	41.4	15.6	Two-phase	38.3	4.0; 81.6	2.69	28

The overall composition of film 2 (73.5% Rh) is such that a homogeneous alloy is not expected even after prolonged annealing at 400°C. Now a rather thicker layer of Pd has been deposited on the Rh compared with film 1. The structural information suggests that Pd atoms diffuse into the Rh layer, which has a limited solubility for Pd, and hence the outer layers remain very rich in Pd, i.e., the surface composition is apparently only 13% Rh. Prolonged annealing would eventually establish the equilibrium compositions of the two phases indicated by previous work (*11*) but it is also of interest to examine the situation for a rather thin dual layer film (film 3) where less interdiffusion through the bulk is required. After the standard annealing treatment (21 hr at 400°C in H_2), the X-ray diffraction indicates a phase containing 10% Rh, and the apparent surface composition is also 10% Rh suggesting that surface and grain boundary diffusion have enhanced the equilibration rate.

Dual layer films 4–6 (Table 2) were prepared by depositing Pd first, followed by Rh, and then annealing in H_2 at 400°C as usual. The overall composition of film 4 is almost equal to the composition of film 1 and again the homogeneous alloy expected is observed. X-Ray fluorescence analysis and X-ray diffraction from the same sample gave compositions of ~89 and 91% Rh, respectively, but, unlike film 1, the apparent surface Rh content was also high, i.e., 95% Rh. If the overall Rh content of the film is decreased (films 5 and 6), then the X-ray diffraction peaks are doubled showing phase separation, and now the apparent surface compositions are Pd-rich, i.e., 23 and 28% Rh, respectively.

For alloy films of Cu–Ni (*6*) where one component, copper, can migrate significantly faster than the other over surfaces, along grain boundaries etc., it is believed that the Group IB metal rapidly envelops the Group VIII metal crystallites as the dual layer film is sintered. Eventually, for compositions where the components are not completely miscible at the annealing temperature, the annealed film consists of crystallites with a Ni-rich kernel surrounded by a Cu-rich alloy. The apparent surface composition of films 5 and 6 suggests that in the Pd–Rh system, although diffusion rates are rather slow, nevertheless Pd, deposited under Rh, has migrated upwards to envelop the Rh crystallites at least partially. Unlike films 2 and 3, alloying is less developed (see XRD data), perhaps as a consequence of less atom movement when Rh arrives on a Pd substrate.

Film 4 also shows evidence that some Pd has reached the catalyst surface although initially deposited below a thick Rh film, but many discrete crystallites in the initial thin Pd deposit must be effectively encapsulated in the subsequently deposited Rh crystallites. During the subsequent annealing stage, Rh crystallites in film 4 do not have to take up a skin of pure Pd deposited on them, as in film 1, nor enveloping them in any great amount, as happens when a thicker Pd layer is deposited first (films 5 and 6). After annealing, the surface of film 4 is still slightly richer in Rh (95% Rh) than the overall film composition (89% Rh).

Simultaneous Deposition (0°C) Followed by H_2 Annealing

In the vapor phase the component metals suffer no miscibility restriction, and, in principle, a homogeneous alloy might be prepared by condensing the atoms at the point of impingement on a cold substrate. By this means, the range of mutual solubility of Pd and Rh might be extended. In practice, it is difficult to provide a sufficiently good heat sink to absorb the heat of condensation, and the substrate is also heated by radiation from the evaporation sources.

Alloys deposited at low temperatures will sinter extensively at the temperatures required for CO oxidation and for many other reactions, thereby complicating the observation of reaction rates. Thus, these films need to be stabilized by sintering before admitting the reaction mixture, but phase separation may be induced, especially at the surface. Therefore, alloy films were prepared by simultaneous deposition on the substrate at 0°C (instead of the 400°C used previously) and sintered in hydrogen at 400°C. It was then of interest to examine the alloys for phase separation and to measure the apparent surface composition. It is believed that progress towards establishing the separate phases must be limited compared with the two cases already treated, viz., deposition on a heated substrate (400°C) and interdiffusion of separately deposited layers, for the following reasons.

A process of continuous nucleation is envisaged, initially on a glass substrate, but for most of the film deposition time the substrate will be the alloy film itself. The concentration of critical nuclei, N^*, (polyatomic aggregates of minimum stability) is given by:

$$N^* = N_{\mathrm{ad}} \exp(-\Delta G^*/kT)$$

where N_{ad} is the adatom concentration on the substrate.

The interfacial (aggregate–substrate) free energy and substrate surface energy terms in ΔG^* are important for nucleation on a metal substrate, and there might not be an effective nucleation barrier (*14*) for either Pd or Rh at 0°C. In the case of simultaneous deposition on a substrate at 400°C, discussed above, it is believed that preferential nucleation of Rh occurs (*9*). In the case of dual layers, again Rh exists initially in pure form. Therefore only limited Pd atom diffusion is required to produce the Rh-rich phase in both cases. In contrast, Pd–Rh films deposited at 0°C might be nearly random solid solutions for the reasons given above, which subsequent sintering at 400°C may or may not separate out.

Table 3 shows X-ray data and the rate of CO oxidation over films deposited at 0°C and annealed in hydrogen overnight at 400°C. Symmetrical X-ray diffraction profiles were obtained, and the lattice constants measured agreed closely with those expected from the composition of the sample. Therefore as suggested above, this method of preparation can extend the range of mutual solubility; subsequent annealing appears to be insufficient to cause phase separation throughout the bulk of the crystallites composing the film. However, the apparent surface composition derived from CO oxidation rates, (last column, Table 3) shows considerable deviations in two out of three cases when compared with the overall film composition (first column). This is another example of desegregation at an alloy surface being in advance of changes in the bulk.

CONCLUSIONS

In preparing alloy films of metal pairs, e.g., Pd and Ag which form a continuous series of solid solutions, the objective seems relatively straightforward, namely, to find a method which will produce a homogeneous alloy with satisfactory surface area and surface cleanliness (*4*). The preparation of alloy films from metal pairs which are not completely miscible at typical film preparation temperatures raises some questions about the best tactics to employ. In some cases, one component can migrate readily over surfaces etc., for example, Cu in Cu–Ni, and it can be arranged (*6*) that the surface composition of the crystallites in the alloy film is the equilibrium composi-

TABLE 3
ANNEALED FILMS DEPOSITED SIMULTANEOUSLY AT 0°C

Overall composition (at. % Rh)	Film weight (mg)	Composition of X-ray sample (at. % Rh)	Lattice constant (Å)		Rate CO oxidation at 240°C (Torr/min)	Apparent surface composition (at. % Rh)
			expected	observed		
43.0	20.5	41.3	3.859	3.855	2.64	27.4
52.3	34.3	52.3	3.849	3.847	4.02	48.0
—	32.9	68.7	3.835	3.835	—	—
79.0	26.7	79.1	3.825	3.822	7.2	95.4

tion of the Cu-rich phase over much of the bulk composition range. As a result, only a very restricted number of significantly different surface compositions can be examined for adsorptive and catalytic behavior. The present work shows the variations in apparent surface composition which arise as a consequence of the general preparative method selected and the detail of its application for an alloy system, Pd–Rh, where a miscibility gap occurs and interdiffusion rates are slow. In such cases there is an alternative approach, viz., to attempt the preparation of a range of metastable solid solutions by the vapor-quenching method which would be assisted by low surface atom mobilities. The catalytic reactions studied over such films (and any stabilizing/sintering treatment) would have to be carried out at modest temperatures to prevent phase separation. Nevertheless many interesting series of alloy catalysts might be produced.

REFERENCES

1. Moss, R. L., and Thomas, D. H., *Trans. Faraday Soc.* **60**, 1110 (1964).
2. Moss, R. L., and Thomas, D. H., *J. Catal.* **8**, 151, 162 (1967).
3. Rossington, D. R., and Runk, R. B., *J. Catal.* **7**, 365 (1967).
4. Moss, R. L., Thomas, D. H., and Whalley, L., *Thin Solid Films* **5**, R19 (1970).
5. Sachtler, W. M. H., and Dorgelo, G. J. H., *J. Catal.* **4**, 654 (1965).
6. Sachtler, W. M. H., and Jongepier, R., *J. Catal.* **4**, 665 (1965).
7. Van der Plank, P., and Sachtler, W. M. H., *J. Catal.* **12**, 35 (1968).
8. Campbell, J. S., and Emmett, P. H., *J. Catal.* **7**, 252 (1967).
9. Moss, R. L., Gibbens, H. R., and Thomas, D. H., *J. Catal.* **16**, 117 (1970).
10. Moss, R. L., Gibbens, H. R., and Thomas, D. H., *J. Catal.* **16**, 181 (1970).
11. Raub, E., Beeskow, H., and Menzel, D., *Z. Metallk.* **50**, 428 (1959).
12. Myles, K. M., *Trans. Met. Soc. AIME* **242**, 1523 (1968).
13. Crawford, E., Roberts, M. W., and Kemball, C., *Trans. Faraday Soc.* **58**, 1761 (1962).
14. Neugebauer, C. A., *in* "Physics of Thin Films" (G. Haas and R. E. Thun, eds.), Vol. 2, p. 1. Academic Press, New York, 1964.