JOURNAL OF CATALYSIS 8, 151–161 (1967)

The Oxidation of Ethylene over Evaporated Palladium-Silver Alloy Films

I. Film Structure and Stability under Reaction Conditions

R. L. MOSS AND D. H. THOMAS

From the Warren Spring Laboratory, Stevenage, England

Received December 7, 1966; revised March 7, 1967

Palladium-silver alloy films were prepared by slow simultaneous evaporation in vacuum from separate sources onto the inner surface of a glass reaction vessel held at 400°C; with attention to source geometry an even composition was obtained. Electron micrographs showed extensive coalescence of the crystallites in silver-rich films changing to a compact mass of small crystallites at high palladium contents. Alloy films which were *not* used as catalysts showed good bulk homogeneity (symmetrical X-ray diffraction profiles, lattice constants in agreement with bulk values, etc.).

After use as catalysts for ethylene oxidation, silver-rich films were apparently still homogeneous but palladium-rich films reproduced the phenomena of Pd-Ag-H alloys (expanded lattices and double diffraction peaks in some cases, ascribed to α and β phases simultaneously present). The extent of the positive deviation in lattice constant from expected values correlated with the utilization of oxygen from the reaction mixture. However, pure palladium film catalysts always gave the bulk lattice constant in contrast to alloy films with as little as 1% silver which were apparently well charged with hydrogen after reaction. The ability of oxygen alone at reaction temperature, 250°C, to cause some separation of the alloy film towards its component metals was also demonstrated and discussed in relation to results using an alloy foil.

INTRODUCTION

Evaporated films of metals have been used extensively in the field of gas adsorption and catalysis and the present work is concerned with the extension of this technique to alloys, with particular reference to catalysis over palladium-silver alloys. The recent application of thin films to the copper-nickel system (*1*, *2*, *3*) has produced rewarding results. As a consequence of lattice faults and small crystallite size, equilibrium was approached and the coexistence at moderate temperatures of a copper-rich and an almost pure nickel phase over a wide composition range was demonstrated. In these circumstances, the copper-rich phase forms the adsorbing surface and a number of earlier results using copper-nickel catalysts can be rationalized. The palladium-silver system was chosen because these elements form a continuous series of solid solutions which have been selected for various investigations into the effect of electronic structure on magnetic (*4*) and electrical properties (*5*, *6*). The thermodynamic properties of the system have been studied thoroughly over a wide temperature range, 330–1200°K, showing large negative enthalpies of formation (*7–10*). While recent work suggests that instead of being a random solid solution short-range ordering may occur (*11*), clearly a miscibility gap is not expected.

The preparation of palladium-silver alloy films by simultaneous evaporation from separate sources and their characterization by various X-ray techniques has already been described (*12*); some of these films were used in a preliminary study of carbon monoxide oxidation. The work described here (Part I) is concerned with the structure and stability of palladium-silver alloy films used for the oxidation of ethylene, heated in oxygen, reduced, etc. Additional information on film structure obtained by electron microscopy/diffraction is also reported.

EXPERIMENTAL

Alloy films were formed on the inner surface of spherical Pyrex glass reaction vessels held at 400°C by slow (15 Å min^{-1}) simultaneous evaporation from separate palladium and silver sources, and then annealed in vacuum for 1 hr at the same temperature. For catalytic experiments 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 vacua of 10^{-6} torr measured with an ionization gauge were usual. A number of films were also prepared in an ultra-high-vacuum system. Before depositing a film, the palladium and silver sources were outgassed for ~1 hr at temperatures close to the evaporation points of the metals while the glassware was continuously evacuated and heated. The sources were short concentric spirals of wire (Johnson-Matthey, "spectrographically standardized") heated directly by passing a current through them. Only small changes in the deposition rate for a fixed current due to thinning of the wire were expected since the relative weight loss was small, e.g., less than 4% of the silver wire was usually evaporated.

After each catalytic experiment, the reaction vessel was carefully cut into pieces and the composition of 12 representative samples determined from the intensities of the Ag $K\alpha_{12}$ and Pd $K\alpha_{12}$ fluorescent X-ray emissions, calibrating with chemically deposited films of known composition. The silver and palladium sources were attached by small connectors to glass-coated tungsten rods and the weight and overall composition of the films deposited were estimated from the loss in weight of each source. Specimens for X-ray diffraction or for electron microscopy were usually obtained by stripping the film from fragments of the vessel itself. X-Ray diffraction measurements were made with a counter-diffractometer which provided information on the profile as well as the position of the diffraction peaks. Filtered copper radiation was used, taking for the wavelengths the values $K\alpha_1$, 1.54051 Å, $K\alpha_2$, 1.54430 Å, and resolving the $K\alpha$ doublet using a graphical method (*13*). The lattice constant a_0 was derived in most cases by extrapolating to $\theta = 90°$, using the Nelson-Riley function, the apparent lattice constants calculated from the centroid of individual diffraction peaks. Values of a_0 for silver films were found to be consistently small (*14*) compared with bulk silver but only by 0.05%. For alloy films a similar deviation would correspond to a variation of 1% in the composition of the alloy.

RESULTS AND DISCUSSION

Film Preparation

Evaporated Pd-Ag alloy films may be prepared either by simultaneous deposition of the component metals from separate sources or from an alloy, or alternatively, by successive deposition of palladium and silver followed by a homogenization procedure. On the basis of previous work (*12*), the preferred method was slow simultaneous deposition from separate sources onto the reaction vessel surface at 400°C, followed by a period of vacuum annealing at the same temperature. Films of Cu-Ni for catalytic use have been prepared by heating dual layers of the metals in hydrogen (*15*) but the large and variable capacity of palladium and its alloys with silver to absorb hydrogen raise doubts about making Pd-Ag alloy films by this method. Further it was found that while Pd-Ag dual layers interdiffuse to some extent during deposition, some hours of vacuum annealing above 500°C are required to produce even moderate bulk homogeneity. Since the alloy film can be prepared in a shorter time and at a lower substrate temperature by simultaneous deposition, surface contamination is somewhat reduced. Nevertheless it is still convenient that the alloy films were used to catalyze an oxidation reaction producing carbon dioxide and water vapor as the main products. For comparison, some films were also heated in a hydrogen atmosphere before use.

Uniformity of Composition

Evaporation from separate filaments is a convenient method of producing alloy film catalysts but requires attention to the position and geometry of the sources to obtain a uniform composition over the vessel surface. Different geometries have been tried including (a) two loops in vertical planes normal to each other and passing through the center of the vessel, and (b) two short concentric spirals of wire positioned about the center of the vessel. In each case the hottest part of the filament was placed at the center of the vessel to approach as closely as possible the ideal of a point source at the center of a sphere. Both geometries produced a reasonably uniform composition over the area of the reaction vessel (220 cm^2). However type (b) was used in the present work since it confers small advantages in ease of positioning the sources and in preparing moderately heavy films.

The compositions determined at representative parts of the reaction vessel by X-ray fluorescence analysis for some typical low, medium, and high palladium content films were as follows (mean composition in parentheses):

(12%)	14,	10,	13,	12,	11,	12,
	11,	11,	13,	13,	13,	12
(51%)	50,	54,	53,	55,	50,	51,
	51,	54,	53,	46,	50,	46
(84%)	88,	86,	88,	86,	83,	84,
	78,	83,	84,	83,	81,	84

The overall composition calculated from weight loss of the sources was not used since they can become alloyed during film evaporation; instead, the mean composition determined at 12 points on the reaction vessel surface was taken. The actual composition of specimens taken for X-ray diffraction was determined afterwards by X-ray fluorescence analysis.

Some films were prepared using an alloy wire source (short spiral) and the uniformity of the best film was comparable with that from separate sources, thus,

(26%)	22,	22,	22,	20,	28,	31,
	27,	27,	29,	31,	26,	32

However, silver and palladium have widely different vapor pressures at a given temperature so that silver volatilizes preferentially from the alloy wire at usual film deposition rates. The desired composition is not readily attained and the estimate of composition from weight loss is not available.

Electron Microscopy/Diffraction

Many of the alloy films prepared were examined by electron microscopy and electron diffraction for information on the state of crystallite aggregation, orientation, etc. Figures 1(a), (b), (d), and (e) show transmission micrographs from films of comparable weight which were used once to catalyze the oxidation of ethylene at 240°C; these films had been prepared and annealed at 400°C in the standard way. The structure of this series of alloy films varied consistently with composition. Silver-rich films [e.g., Fig. 1(a); ~13% Pd] showed extensive coalescence of the crystallites, while at the other end of the composition range [e.g., Fig. 1(e), ~94% Pd], the films were composed of a compact mass of small crystallites. In general, where the forces between condensed atoms and the substrate are weak, then the size of the crystallites (*16*) and their tendency to sinter together on annealing can be correlated with the melting point. The adhesion of silver and, probably, palladium to glass is low (*17*) and also the difference in melting point is substantial (Ag, 961°C; Pd, 1549°C), hence the change in composition from silver through to palladium leads to less sintering and the occurrence of a larger number of small crystallites. At the silver-rich end of the series, ~50% of the crystallites were oriented with the 110 direction normal to the glass substrate; the rest had orientations of almost all the other low integer planes. At the other end of the composition range, e.g., in Fig. 1(e), random orientation was found.

Figure 1(c), 51% Pd, fits neatly into the series, although the film was not used in catalytic reaction. This shows that the con-

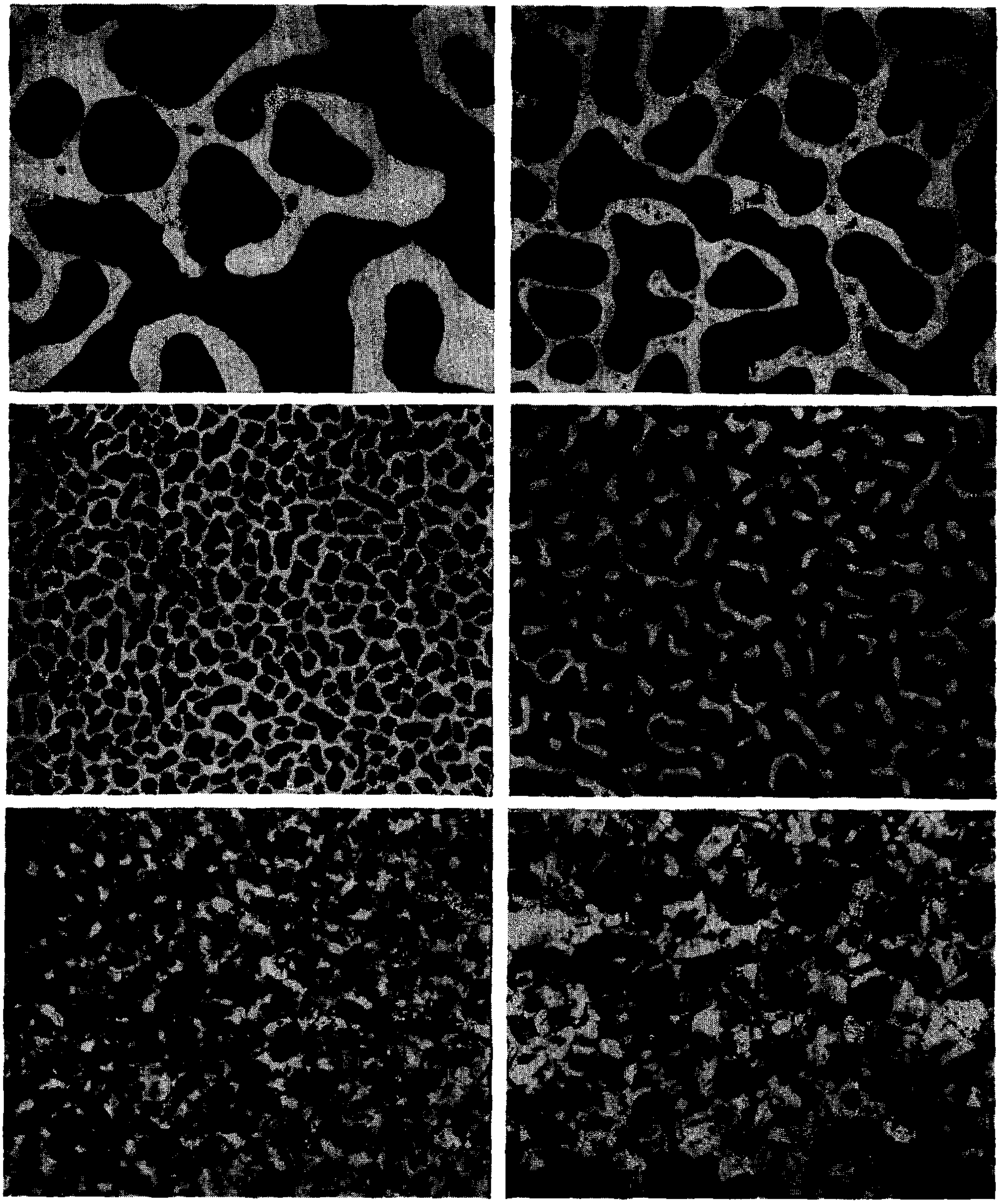

FIG. 1. Transmission electron micrographs of evaporated Pd-Ag alloy films: (a) 12.6% Pd, 24.5 mg, (b) 36.7% Pd, 25.6 mg; (c) 51% Pd, 15.6 mg; (d) 76% Pd, 20.7 mg; (e) 94% Pd, 22.1 mg; (f) 19.4% Pd, 35.4 mg. Films (a), (b), (d), and (e) deposited and annealed at 400°C, catalyzed C_2H_4 oxidation at 240°C; film (c) prepared similarly, not used in reaction; film (f) deposited at 400°C, not annealed, catalyzed C_2H_4 oxidation at 240°C. Magnification 20,000×.

ditions of film deposition or vacuum annealing were primarily responsible for the observed film structures. Figure 1(f) shows an electron micrograph of a film deposited at 400°C as usual, but not annealed before catalyzing the oxidation of ethylene. Although it possessed a low palladium content, ~19%, the film was unlike the corresponding annealed films and had suffered much less aggregation.

Bulk Homogeneity of Unreacted Films

Alloy films prepared by slow simultaneous evaporation with the substrate at 400°C *and not used in reaction* gave rise to approximately symmetrical X-ray diffraction line profiles. The corresponding lattice parameters, in Å (open circles) are shown in Fig. 2, which also records (broken line) lattice parameters for a series of Pd-Ag alloy wires (*18*). The homogeneity of these films, which showed only small random deviations in lattice parameter compared with the bulk values, therefore appears to have been reasonably satisfactory; the deviations probably arise from uncertainty in determining the composition by a separate method, i.e., X-ray fluorescence analysis. The structure of Pd-Ag films after being used to catalyze ethylene oxidation is discussed in the next section but it might be noted here that films of pure silver, pure palladium, and silver-rich alloy films also exhibited the expected lattice constant after reaction.

A closer analysis was made of the alloy films which appeared to have satisfactory bulk homogeneity, viz., all alloy films not used in reaction and silver-rich films after reaction. The X-ray line profiles may be broadened compared with the breadth observed for bulk specimens of pure metals due to the small size of the crystallites composing the films. This can mask any broadening of the profile about the expected 2θ value due to the occurrence of a range of lattice parameters arising from some degree of incomplete alloying. The broadening B_c due to crystallite size is given by the Scherrer expression

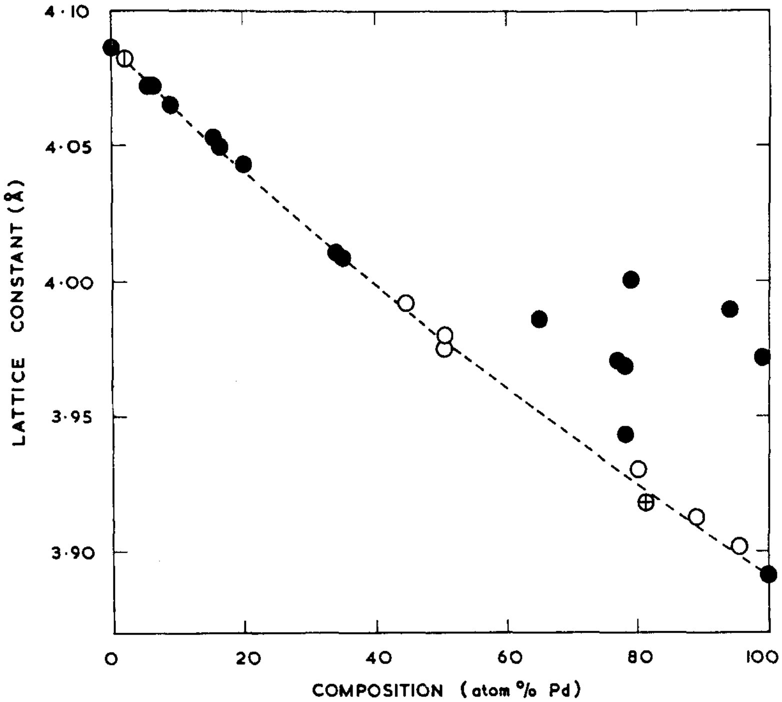

FIG. 2. Lattice constants for evaporated Pd-Ag alloy films, deposited and annealed at 400°C: ●, after catalyzing C_2H_4 oxidation (one standard reaction mixture) at 240°C; ○, unused in reaction (two evaporation sources); ⦶, unused in reaction, (alloy wire source); ⊕, unused in reaction (annealed in H_2 for 5 hr at 400°C). Lattice constants for Pd-Ag alloy wires, ref. (*18*), - - - - -.

$$B_c = K\lambda/L \cos \theta$$

where K is the Scherrer constant, λ is the radiation wavelength, L is the crystallite size normal to the substrate, and θ is the

Bragg angle. The broadening B_a due to any incomplete alloying is given by

$$B_a = 2 \tan \theta (da/a)$$

where da is the range of lattice parameter and a is the measured lattice parameter as derived from the angular position of the centroid of the diffraction line profile. By measuring the breadths of the 111 and 222 diffraction lines it is possible to separate the two effects and obtain a value for da/a. For greatest accuracy, Fourier analysis should be used, but a simpler treatment (*19*) based on Jones' method seems sufficient in the present case. Assuming a triangular distribution of lattice parameters and also that a diffraction line broadened only by instrumental and crystallite size effects has the Cauchy form, then

$$\left(\frac{da}{a}\right)^2 = \frac{3}{\pi^2} \frac{B_2^2 \cos^2 \theta_2 - B_1^2 \cos^2 \theta_1}{\sin^2 \theta_2 - \sin^2 \theta_1}$$

where the suffixes 1 and 2 denote the 111 and 222 lines having an observed breadth, B.

Values of (da/a) were determined where possible, i.e., where the 222 diffraction profile was present, in alloy films showing apparently satisfactory bulk homogeneity (symmetrical profiles and expected lattice constants) and used to catalyze ethylene oxidation at 240°C. The values of (da/a) were as follows with % Pd given in brackets:

1.4×10^{-3} (5.5%), 3.1×10^{-3} (6.2%),
1.7×10^{-3} (9.0%), 2.9×10^{-3} (15.5%),
2.3×10^{-3} (20%), 5.8×10^{-3} (34%) and
6.3×10^{-3} (35%)

As a comparison, films not used in reaction gave the following (da/a) values:

1.0×10^{-3} (2%), 8.2×10^{-3} (80%),
7.2×10^{-3} (89%), and 0.9×10^{-3} (99 + %)

Films made in vacuums of 5×10^{-8} torr (50.5%) and 5×10^{-9} torr (44.5%) and also unused in ethylene oxidation gave (da/a) values of 4.9×10^{-3} and 5.2×10^{-3}, respectively.

The conclusions to be drawn from this analysis of the X-ray data are (1) silver-rich alloy films after use in ethylene oxidation were still well-homogenized; (2) with increasing palladium content, both used and unused films may depart to some extent from good bulk homogeneity, i.e., (da/a) values increase, but decrease again so that the lowest value was found in a film with 1% or less silver, and (3) improved vacuum conditions during film preparation do not apparently improve bulk homogeneity.

The Structure of Alloy Films after C_2H_4 Oxidation

Silver, palladium, and silver-rich alloy films used to catalyze ethylene oxidation were found to have the same lattice constants as the bulk material (Fig. 2; filled circles). By contrast, the lattice constants of palladium-rich films (>60% Pd) used in reaction deviated markedly from the expected values. The following observations are relevant to interpreting the structure of these films:

(1) Four films exhibiting anomalous lattice constants in Fig. 2 had compositions of ~78% Pd; in each case the X-ray diffraction profiles were approximately symmetrical so that a meaningful lattice constant could be derived. Table 1 shows these lattice constants, the deviation, Δa_0, from the expected value, and the extent to which the oxygen present in the standard reaction mixture (10 mm C_2H_4 + 25 mm O_2) had been used up before the reaction was stopped. The deviation, Δa_0, was greatest when all the oxygen was used up (some ethylene remains when the reaction is to CO_2 and water). When ethylene was oxidized at 240°C with an oxygen-lean mixture (20 mm C_2H_4 +

TABLE 1

LATTICE CONSTANTS AND PERCENT OXYGEN USED IN C_2H_4 OXIDATION

Composition (% Pd):	80	78	78	77	79
Percent O_2 reacted:	No reaction	70	75	80	100
Lattice constant (Å):	3.930	3.944	3.969	3.971	4.001
Δa_0 (Å):	0.005	0.016	0.041	0.041	0.074

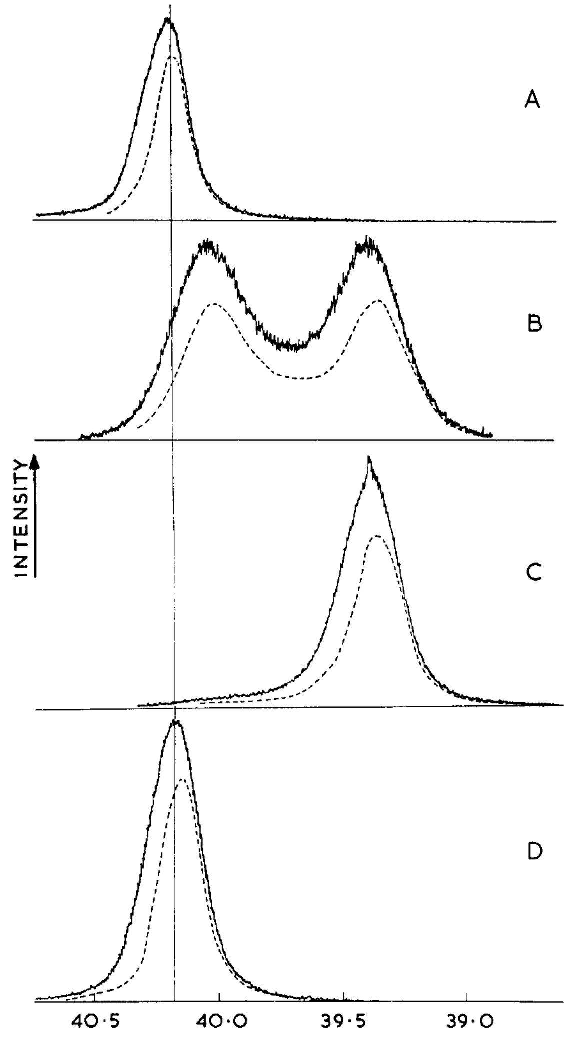

FIG. 3. X-Ray diffraction profiles from (111) planes of two 99% Pd/Ag alloy films: A, after preparation, isolated from reaction; B, after C_2H_4 oxidation at 240°C, 75% O_2 removed; C, second film after complete reaction of oxygen in C_2H_4/O_2 mixture; D, specimen of film from (C) after heating in vacuum at 400°C. Vertical line shows expected 2θ position of the diffraction peak; ———, unresolved trace; - - - - -, $K\alpha_1$ component.

25 mm O_2) over a 92.5% Pd/Ag film a maximum deviation of $\Delta a_0 = 0.10$ Å was found. Further, using an oxygen-rich mixture (5 mm C_2H_4 + 25 mm O_2) the reaction had little effect on an 85.5% Pd/Ag film ($\Delta a_0 =$ 0.015 Å).

(2) Figure 3 shows the (111) diffraction profiles observed in two films with 99% Pd; Fig. 3A was obtained from a centimeter square of Pyrex glass which had been removed in vacuum to a sidearm and isolated before admitting the C_2H_4/O_2 mixture. The lattice constant calculated from the centroids of this reflection and the (200), (311), and (222) reflections was 3.890 ± 0.002 Å, i.e., very close to the expected value. The (da/a) value was also as low as normally observed, 0.93×10^{-3}. After reaction (Fig. 3B), which removed 75% of the oxygen from the standard gas mixture, double peaks were observed from the (111), (200), and (222) planes [the (311) was weak and indefinite]. Lattice con-

stants calculated from the positions of the appropriate peaks of these doublets were 3.90_7 and 3.97_6 Å. After reaction, again over another alloy film containing 99% Pd, which completely removed oxygen from the standard C_2H_4/O_2 mixture, single peaks were observed (Fig. 3C) but, of course, shifted substantially from the expected 2θ position (a_0 observed = 3.972 Å compared with a_0 expected = 3.892 Å). When a piece of the reaction vessel with alloy film adhering was then kept in vacuum at 400°C for 24 hr and subsequently examined (Fig. 3D), the observed lattice parameter, a_0 = 3.895 Å was close to the expected value.

The possibility was considered that gross separation of the alloy towards its components, silver and palladium, is responsible for the anomalous lattice constants observed after ethylene oxidation. However, the X-ray beam can be expected to penetrate through the crystallites rather than only the outer layers of atoms. Particularly with 99% Pd/Ag alloys, the magnitude of the effect and, in general, the symmetry of the peaks contradict the idea of a substantial amount of de-alloying.

The anomalous lattice constants were found in the composition range where hydrogen is soluble in Pd-Ag alloys; outside this range, i.e., in the silver-rich films, only the expected lattice constants were observed. It is proposed that hydrogen, coming from adsorbed ethylene, dissolves in palladium-rich films during or towards the end of the reaction. The films were not examined *in situ* after reaction, but palladium is known to retain hydrogen in concentrations as high as H/Pd = 0.6 for periods up to one year when charged specimens are stored in the open air (*20*). The virtual excess hydrogen content of the system, when the standard C_2H_4/O_2 mixture reacts to produce CO_2 and water, corresponds to a modest hydrogen pressure but is sufficient to charge the small bulk of the alloy film.

The Pd-Ag-H system has been studied in some detail and the following observations are relevant to the present discussion. During hydrogen absorption into some Pd-Ag alloys from aqueous solution, potential plateaus are found and identified (*22*) with the occurrence of the $\alpha \rightarrow \beta$ transformation in the H-Pd system. Recent X-ray studies of alloys containing 80 and 89.6 atom % palladium (*22*) showed a continuous increase in lattice parameter up to the plateau potential, at which point the new phase appeared and diffraction lines for both the α and β phases were simultaneously present. Both phases are fcc but the β phase has a more expanded lattice (Table 2). As additional hydrogen absorbed the diffraction lines corresponding to the α phase disappeared; the lattice parameter of the β phase increases continuously as the potential at which the sample was removed became less positive.

The lattice parameter vs. potential plot for an alloy with more silver, 76.2% Pd/Ag, showed little evidence of a discontinuity but rather a steep increase in parameter; the coexistence of the α and β phases was not observed. A potential plateau was not observed at still higher silver content, 69.5% Pd/Ag, during hydrogen absorption, but instead a continuous expansion of the lat-

TABLE 2
LATTICE CONSTANTS OF Pd-Ag-H ALLOYS

	Lattice constant (Å)				
Atom % Pd	Uncharged	α Phase (max)	β Phase (min)	Charged[a]	Solubility, H/Me[a]
100	3.890	3.893	4.025	4.040	0.70
89.6	3.908	3.922	4.003	4.033	0.582
80.0	3.923	3.945	3.993	4.027	0.49
76.2	3.931	(3.991)	(3.996)	4.027	0.384
69.5	3.942	—	—	4.026	0.340

[a] P_{H_2} = 1 atm, 30°C.

tice. In early work Rosenhall (*23*) found that the $\alpha \rightarrow \beta$ transformation did not occur when the palladium content had fallen to 73% and recently Brodowsky and Poeschel (*24*) also placed this palladium content at ~75%. Finally, the hydrogen solubility increases with palladium content (*21*, *25*) from essentially zero at 30–40% palladium.

The observations reported in (1) above are examined first on the basis of this information on hydrogen absorption in Pd-Ag alloys. Only single symmetrical X-ray peaks were detected in alloy films with ~78% Pd (Table 1) and this composition is near the limit where separate α and β phases can coexist. Instead the lattice constant changes rapidly and probably continuously with hydrogen content and hence the wide range of lattice constants observed at this composition.

At palladium contents higher than 80%, both α and β phases might be expected under suitable conditions and Fig. 3B is interpreted on this basis. Here only 75% of the oxygen in the standard mixture had reacted. The peak at the higher diffraction angle corresponds with the maximum lattice constant expected for the α phase (cf. Table 2). The lattice constant from the lower angle peak in the doublet is somewhat less than the minimum for the β phase in Table 2 but without clear resolution of the doublet the accuracy is restricted. Alloy films with 80% or more palladium and thought to be well charged with hydrogen, produced lattice constants which were in general agreement with values observed in the β phase of Pd-Ag-H alloys (*22*, *23*).

Effect of Oxygen on Pd-Ag Films

Since the adsorption free energy of oxygen on silver is higher than on palladium, it is suggested that this difference should provide enough driving force to establish the diffusion of silver atoms from the bulk to the surface of Pd-Ag alloys at reaction temperatures (*26*, *27*). The extreme case which might show evidence of "de-alloying" was investigated, viz., the effect of oxygen alone on Pd-rich films.

Alloy films containing 68% Pd (Fig. 4) and 87% Pd were heated in 50 mm O_2 at 250°C for 1 hr, producing clearly asymmetric X-ray diffraction profiles. Usually after ethylene oxidation, reasonably symmetrical diffraction profiles were observed—ascribed at the higher palladium contents to the β phase of Pd-Ag-H alloys—but under suitable conditions double peaks due to both α and β phases were observed (Fig. 3B). Both diffraction peaks in the "doublet" show a shift in 2θ position in one direction towards higher lattice constants. However, Fig. 4 (effect of

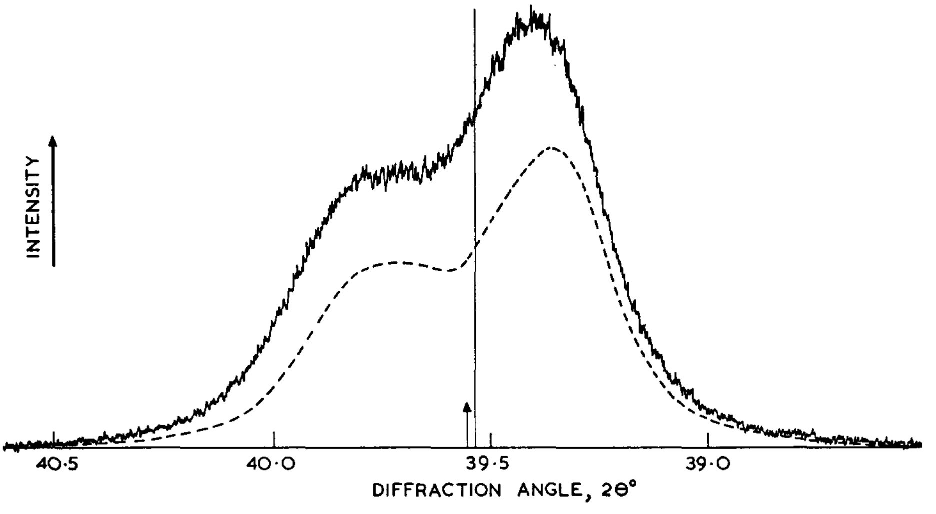

FIG. 4. X-Ray diffraction profile from (111) planes in 68% Pd-Ag alloy film after heating in 50 mm O_2 at 250°C for 1 hr. Vertical line shows expected 2θ position; arrow shows centroid of composite peak; - - - - -, $K\alpha_1$ component.

heating in O_2) is fundamentally different from Fig. 3B in that the X-ray profile has spread out from the expected position towards both lower and higher 2θ values. Further the lattice constant calculated from the position of the centroid, 3.946 Å, is in close agreement with the expected value for this alloy composition. The approximate lattice constants corresponding to the two peaks in the diffraction profile were 3.92 and 3.96 Å, i.e., richer in palladium and silver, respectively, than the overall composition but, of course, a range of solid solutions must have been present.

When another film of the same composition, 68% Pd/Ag, was subjected to an identical oxygen treatment but then heated in 50 mm hydrogen at 250°C for 1 hr before examination, the observed lattice constant was exactly as expected, 3.946 Å, and the profile was almost symmetrical. These observations suggest that oxygen at 250°C can cause a degree of inhomogeneity or "de-alloying." Whether this applied at any time during the ethylene oxidation reaction, particularly with respect to the immediate surface layers, is discussed again in Part II of this series (*29*, following paper).

An example of the advantages of alloy films compared with alloy foils for surface studies was afforded by an attempt to "de-alloy" a piece of Pd-Ag foil by heating in oxygen. From X-ray fluorescence analysis the palladium content was 58% and hence the expected lattice constant was 3.964 Å. The untreated foil gave many diffraction lines and $a_0 = 3.965 \pm 0.003$ Å was derived. Foil heated in 50 mm oxygen at 250°C for 1 hr gave $a_0 = 3.963 \pm 0.003$ Å and the diffraction profiles were entirely symmetrical. The absence of any evidence of de-alloying may be due in part to the reduced rate of diffusion in foil compared with films which have more defects, although the present alloy films were well annealed. Using alloy films, however, the outer layers of atoms in the crystallites are a significant fraction of the total depth of metal available to penetration by the X-ray beam. While changes in structure or composition of layers near the surface of the usual relatively thick foil must remain minutely represented in the diffraction profile, such changes show up with sensitive X-ray equipment, using evaporated alloy films.

Concluding Remarks

Slow simultaneous evaporation from carefully positioned separate sources onto the inner surface of a spherical glass reaction vessel at 400°C provides a convenient method for preparing reasonably well homogenized palladium-silver alloy films over an extended area.

These alloy films obviously have little internal pore structure (Fig. 1) and consequently a smaller surface area than films deposited at low substrate temperatures. However, in catalytic experiments the modest increase in temperature required to compensate for the reduced area is unlikely to require the use of an atypical temperature range for ethylene oxidation.

It is often argued that a small fraction of the surface of highly porous films can readily accommodate the residual gas molecules in conventional vacuum, but even if correct, it is unlikely to apply to the present low area films. In adsorption experiments and in certain catalytic experiments, stringent vacuum conditions would be necessary.

A second, and less emphasized effect of vacuum conditions during evaporated film preparation is change in the structure of the film, e.g., silver films showed marked structural differences when evaporated in vacuums ranging from 50 μtorr to 5 ntorr (*28*). The bulk homogeneity of Pd-Ag alloy films seems insensitive to vacuum conditions (see da/a values). A gross effect could be obtained by heating palladium-rich alloys in pure oxygen, which resulted in some "de-alloying."

Silver-rich alloy films, after catalyzing ethylene oxidation, were apparently still homogeneous [symmetrical X-ray diffraction profiles, "correct" lattice constants, and low (da/a) values]. Palladium-rich films reproduced the phenomena of Pd-Ag-H alloys (expanded lattices, Table 1, with the lattice constant changing rapidly but continuously around 78% Pd and evidence of double diffraction peaks ascribed to α and β phases above this composition).

Pure palladium films after catalyzing

ethylene oxidation always had the lattice constant of bulk palladium in striking contrast to alloy films with ~1% silver (Fig. 3) which were apparently well charged with hydrogen after the reaction. This result is discussed further in Part II (following paper) in relation to the catalytic results.

REFERENCES

1. SACHTLER, W. M. H., DORGELO, G. J. H., AND JONGEPIER, R., *J. Catalysis* **4,** 100 (1965).
2. SACHTLER, W. M. H., AND DORGELO, G. J. H., *J. Catalysis* **4,** 654 (1965).
3. SACHTLER, W. M. H., AND JONGEPIER, R., *J. Catalysis* **4,** 665 (1965).
4. HOARE, F. E., MATTHEWS, J. C., AND WALLING, J. C., *Proc. Roy. Soc.* (*London*) **A216,** 502 (1953).
5. TAYLOR, J. C., AND COLES, B. R., *Phys. Rev.* **102,** 27 (1956).
6. COLES, B. R., AND TAYLOR, J. C., *Proc. Roy. Soc.* (*London*) **A267,** 139 (1962).
7. CHAN, J. P., ANDERSON, P. D., ORR, R. L., AND HULTGREN, R., "The Heats of Formation of Silver-Palladium Alloys." 4th Tech. Rept., Ser. No. 126, Issue No. 4. Univ. of California, Berkeley, Oct. 1959.
8. PRATT, J. N., *Trans. Faraday Soc.* **56,** 975 (1960).
9. ORIANO, R., AND MURPHY, W. K., *Acta Met.* **10,** 879 (1962).
10. MYLES, K. M., *Acta Met.* **13,** 109 (1965).
11. WESTERLUND, R. W., AND NICHOLSON, M. E., *Acta Met.* **14,** 569 (1966).
12. MOSS, R. L., AND THOMAS, D. H., *Trans. Faraday Soc.* **60,** 1110 (1964).
13. RACHINGER, W. A., *J. Sci. Instr.* **25,** 254 (1948).
14. MOSS, R. L., DUELL, M. J., AND THOMAS, D. H., *Trans. Faraday Soc.* **59,** 216 (1963).
15. GHARPUREY, M. K., AND EMMETT, P. H., *J. Phys. Chem.* **65,** 1182 (1961).
16. LEVINSTEIN, H., *J. Appl. Phys.* **20,** 306 (1949).
17. BENJAMIN, P., AND WEAVER, C., *Proc. Roy. Soc.* (*London*) **A261,** 516 (1961).
18. COLES, B. R., *J. Inst. Metals* **84,** 346 (1955–56).
19. BARTON, G. H., AND CARR-BRION, K. G., "An X-ray Diffraction Method of Studying Trends in the Degree of Alloying of Nearly Alloyed Binary Mixtures." Unpubl. Rept. RR/PCS/46. Warren Spring Laboratory, Stevenage, England, 1963.
20. LEWIS, F. A., AND UBBELOHDE, A. R., *J. Chem. Soc.*, p. 1710 (1954).
21. LEWIS, F. A., AND SCHURTER, W. H., *Naturwissenschaften* **47,** 177 (1960).
22. AXELROD, S. D., AND MAKRIDES, A. C., *J. Phys. Chem.* **68,** 2154 (1964).
23. ROSENHALL, G., *Ann. Physik.* **24,** 297 (1935).
24. BRODOWSKY, H., AND POESCHEL, E., *Z. Physik. Chem.* **44,** 143 (1965).
25. VERT, ZH. L., AND TVERDOVSKY, I. P., *Zh. Fiz. Khim.* **28,** 317 (1954).
26. GONZALEZ, O. D., AND PARRAVANO, G., *J. Am. Chem. Soc.* **78,** 4533 (1956).
27. BORTNER, M. H., AND PARRAVANO, G., *Advan. Catalysis* **9,** 424 (1957).
28. MOSS, R. L., AND THOMAS, D. H., *Brit. J. Appl. Phys.* **15,** 673 (1964).
29. MOSS, R. L., AND THOMAS, D. H., *J. Catalysis* **8,** 162 (1967) (following paper).