Surface Potential Measurements of CO Chemisorption on Clean Palladium–Silver Alloy Films

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Surface potentials (S.P.) due to CO chemisorption at 0°C were measured for a series of evaporated Pd–Ag alloy films prepared in ultrahigh vacuum. The S.P. increased from zero (for pure Ag) with increasing Pd content but then increased sharply at ~60% Pd, remaining constant for higher Pd contents up to pure Pd (-0.62 V at 2×10^{-6} Torr CO). Results for Ag-rich films require a special explanation, e.g., electron activation, if the concept of relating chemisorption capacity to d-band vacancies, a collective property, is to be maintained but the concept of surface Pd atoms acting as individual adsorption centers in an Ag diluent is difficult to generalize across the whole composition range. It is suggested that the viewpoint from which the surface properties of an alloy system such as Pd–Ag are discussed, may depend on the concentration of the Group IB additive because, e.g., the band of surface electron states may not overlap the normal crystal band in Ag-rich alloys (unlike Pd-rich alloys), so that the surface properties need not relate to the electronic structure of the corresponding bulk alloy.

INTRODUCTION

There have been few studies of adsorption on alloys of Group VIII and Group IB metals, particularly where the surface has been prepared under very clean conditions, although such studies should help us to understand the catalytic activity of the transition metals. The preparation of alloy thin films in ultrahigh vacuum is an attractive method for obtaining suitable surfaces, and recently some valuable results were obtained for the Cu–Ni system (*1, 2*). However, the Cu–Ni system exhibits a wide miscibility gap at the substrate temperatures necessary to avoid extensively sintered films. Consequently the surface composition can be that for the Cu-rich phase and independent of the nominal film composition over most of the range, although other methods of preparation affect this result (*3*). Therefore, experiments with Cu–Ni films prepared in ultrahigh vacuum (*1, 2*) provide a comparison between the pure metals and alloys of essentially only one surface composition.

In contrast, Pd and Ag form a continuous series of solid solutions which have been selected for various investigations into the effect of electronic structure on thermal (*4–6*), magnetic (*5*), and electrical properties (*7, 8*). In previous work Pd–Ag films were prepared by simultaneous deposition of the component metals on a substrate at 400°C which is necessary in conventional vacuum to achieve satisfactory bulk homogeneity (*9*). Recently (*10*), we have shown that homogeneous Pd–Ag alloy films can be prepared without extensive sintering, by simultaneous deposition in ultrahigh vacuum with the substrate cooled to 0°C. The object of the present work was to use such films to measure the surface potentials (S.P.) which accompany the chemisorption of CO on Pd–Ag alloys and to discuss them in the light of present ideas about the electronic structure of these alloys.

EXPERIMENTAL

Palladium–silver alloy films were prepared by simultaneous evaporation from separate sources on to the surface of a spherical Pyrex vessel held at 0°C. The film was *not* subsequently annealed before admitting CO and measuring the S.P. change. The glass vessel was attached to a mainly stainless-steel ultrahigh-vacuum system incorporating a large, 100 l/s, and a subsidiary getter-ion pump, sorption trap, etc., with an easily obtainable base vacuum capability of 2×10^{-10} Torr. Initially the evaporation sources were beads of Pd and Ag on separate W heating loops using Specpure Pd and Ag (Johnson, Matthey and Co. Ltd.) and pure W (Tungsten Manufacturing Co. Ltd.). The Ag bead was formed from Ag wire (previously burnt out in O_2) wound around the W loop and melted in an atmosphere of H_2; the Pd bead was similarly formed in H_2. After prolonged outgassing, an alloy film could be deposited in a vacuum better than 1×10^{-9} Torr. Unfortunately these alloy films did not exhibit good uniformity of composition over the extended area of the S.P. vessel because of the impossibility of positioning both these nearly point sources close enough to the center of the same sphere. Therefore, the results described refer to alloy films prepared from short concentric spirals of Ag and Pd wire which had been shown to give a uniform composition in previous work in conventional vacuum (*11*). Table 1 shows typical X-ray fluorescence analyses of samples from alloy films taken at 12 representative points on the vessel surface. Alloy films prepared

from Pd and Ag spirals are clearly much more uniform than films prepared from beads on W heating loops.

It was not possible, however, to deposit alloy films from spirals of wire in the same good ultrahigh vacuum existing during evaporation from beads on W heating loops. With spirals, vacua of 5×10^{-9} to 2×10^{-8} Torr were measured, i.e., during evaporation a typical vacuum would be within this range. It was thought desirable to examine the composition of the residual gas, particularly with respect to gases such as O_2 which are adsorbed strongly. In some experiments, an omegatron was attached to the system close to the S.P. vessel. Figure 1 shows partial pressure analyses made during source outgassing and during the actual film deposition at 5×10^{-9} Torr. A little water vapor and oxygen were present during outgassing but subsequently disappeared. The inert gases, Kr and Xe, are not so readily removed by getter-ion pumping and probably usually occur. Otherwise the residual gases during film deposition were N_2 or CO and CO_2 which were not expected to be significant at these partial pressures.

Pure CO from break-seal flasks (British Oxygen Co. Ltd.) was admitted to the S.P. vessel through a metal uhv valve and a flow maintained by getter-ion pumping. Surface potentials were measured by the diode method using the circuit described by Pritchard and Tompkins (*12*) for determining I–V characteristics and maintaining a constant average cathode temperature. Electrical connection to the metal or alloy film was made by means of a Pt wire

TABLE 1
FILM COMPOSITION OVER SURFACE OF S.P. VESSEL

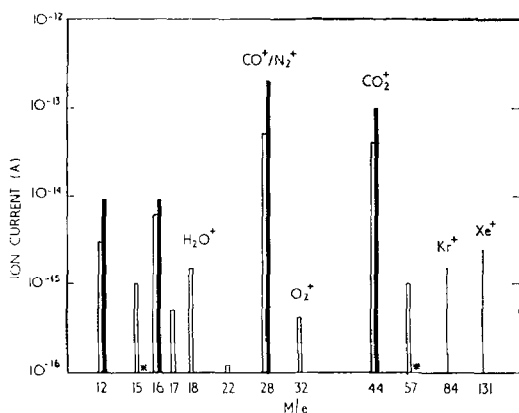| Source	Average film composition (wt % Pd)	X-ray fluorescence analysis of samples (wt % Pd)						Mean deviation
Pd and Ag spirals	21	19	25	24	21	22	20	2
		20	22	22	16	21	21	
Pd and Ag spirals	62	57	63	60	64	64	64	3
		66	65	62	58	64	68	
Beads on W heaters	42	28	32	47	38	57	30	8
		51	46	50	40	42	47	

FIG. 1. Omegatron analysis of residual vacuum during degassing of evaporation source (open vertical bars) and during actual film deposition at 5×10^{-9} Torr (solid vertical bars). Inert gases noted in vacuum shown by vertical lines; species remaining during film deposition but not analysed, shown by *.

partially embedded in the inner wall of the S.P. vessel. The W cathode was mounted above the Pd and Ag filaments which must be placed at about the center of the vessel. To eliminate grid action, the Pd and Ag filaments were connected to the cathode by a grid leak resistor of 100 MΩ and biased 12 V positive with respect to the cathode. The necessary criterion of parallel I–V characteristics when displaced along the V axis by a change in S.P. was fulfilled.

RESULTS

Film Structure

In view of the recent report (10) on the uhv preparation of homogeneous Pd–Ag alloy films suitable for adsorption studies, it only seems necessary here to establish that the adoption of alternative evaporation sources as discussed above, had not adversely affected the homogeneity or the degree of sintering.

After each S.P. experiment, samples of the alloy film were stripped from the vessel and examined by X-ray diffraction. The rather thin films used gave a limited number of weak diffraction peaks but these were symmetrical, and the observed lattice constants agreed well with those previously

observed for Pd–Ag alloy wires; the composition of the actual sample examined by X-ray diffraction was determined by X-ray fluorescence analysis.

Figure 2 a and b show electron micrographs of alloy films of approximately equal weight but containing 29 and 62 at. % Pd, respectively. Although the two electron micrographs are rather similar in appearance, it seems important to demonstrate this fact because the two alloys were markedly different with respect to the S.P. observed. These Pd–Ag alloy films are, therefore, very different from Pd–Ag films deposited at 400°C in conventional vacuum (see Fig. 1, Ref. 11) where the structure, as observed by electron microscopy, changed substantially with variation in composition. Apart from the increase in
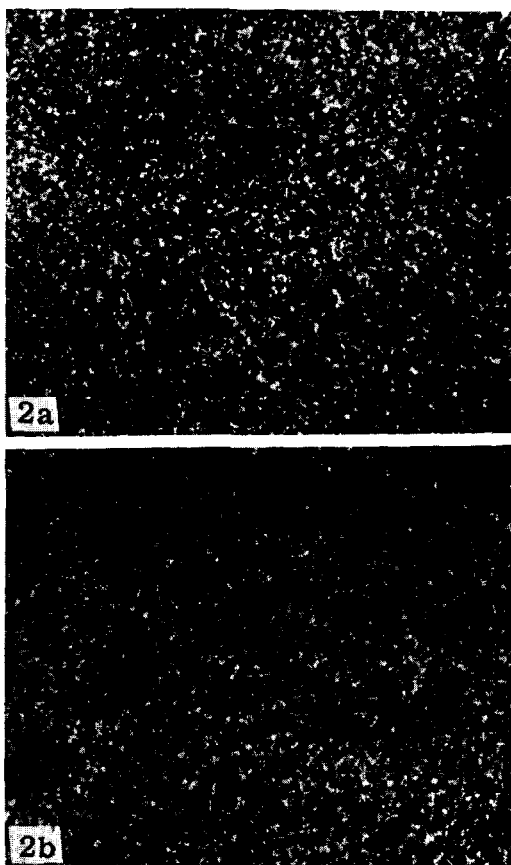

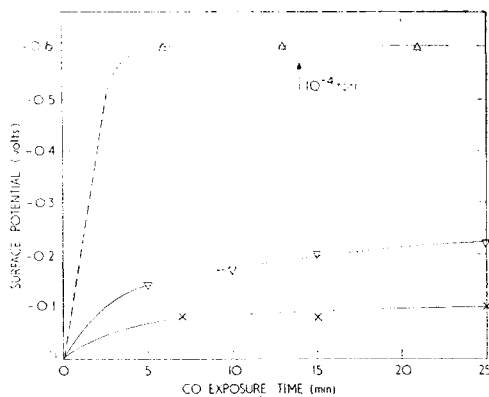FIG. 2. Electron micrographs of Pd–Ag alloy films: (a) 8.1 mg, 29% Pd; (b) 8.6 mg, 62% Pd. Magnification 50 000X.

FIG. 3. Variation in surface potential (S.P.) with length of exposure to CO at 2×10^{-6} Torr: $\triangle$, pure Pd film (pressure increased at time indicated); $\triangledown$, 29% Pd–Ag film; X, 7.6% Pd–Ag film.

surface area which arises as a consequence of the lower substrate temperature in the present work, i.e., 0°C compared with 400°C, the crystallite size should also be reduced by the improved vacuum (see discussion in Ref. 10).

S.P. vs Pressure and Time

The following experiments helped to establish the conditions for a valid comparison between alloys of various compositions and the pure metals.

Admission of CO to a freshly prepared Pd film at 0°C and at a series of pressures between 1×10^{-8} Torr and 1×10^{-4} Torr, showed that no appreciable S.P. developed below a pressure of 1×10^{-6} Torr. For example, the S.P. was only -0.05 V at 10^{-7} Torr CO compared with -0.60 V at 10^{-6} Torr CO. Additional CO pressure increases to 10^{-5} and 10^{-4} Torr had little effect. When using the diode, it is necessary to avoid cooling the cathode by the gas, and this generally limits its application to pressures below 10^{-4} Torr. It was considered that the comparison of surface potentials should be made at pressures well below 10^{-4} Torr CO and a pressure of $\sim 10^{-6}$ Torr was indicated as being sufficient to give satisfactory results.

Assuming that all the residual gas during film deposition was CO, then films might have been pre-exposed to a maximum CO

pressure of $\sim 10^{-8}$ Torr. Therefore, the above experiment also indicates that adsorption on the films during preparation cannot be significant.

Figure 3 shows the variation in S.P. with length of exposure to CO at 2×10^{-6} Torr for a pure Pd film and for two alloy films. The final S.P. was rapidly established over pure Pd in contrast with the Ag-rich alloys where there was a slow increase after the initial rise. The figure also illustrates that the S.P. for pure Pd was not further increased by raising the CO pressure to 10^{-4} Torr. On this basis, the criterion selected for comparing surface potentials for the alloys and pure metals was the value observed on exposure (at 0°C) to CO at a pressure of 2×10^{-6} Torr for 10 min (or equivalent, i.e., 1.2×10^{-3} Torr. sec).

S.P. vs Composition

Exposure of pure Ag films at 0°C to CO pressures up to $\sim 10^{-5}$ Torr did not produce a change which could not be ascribed to instrumental drift. An S.P. value of $+0.32$ V was reported (13) for Ag films exposed to 10^{-6} Torr CO at -196°C but a near zero value is likely at 0°C (14). It would appear that no value has been reported for pure Pd films at 0°C and so, in the present work, a number of measurements were made to establish a value and to test reproducibility. The S.P. observed on exposing pure Pd films at 0°C to 2×10^{-6} Torr CO for 10 min. was -0.62 ± 0.03 V (5 results).

Palladium-rich alloys with more than 60 at. % Pd adsorbed CO rapidly (like pure Pd) so that the S.P. was established almost immediately. In contrast the alloys with small Pd contents adsorbed CO less rapidly and as mentioned above, the S.P. continued to increase after the 10-min point (at 2×10^{-6} Torr), at which comparisons of S.P. were made. Nevertheless, the values for these latter alloys would not approach those for Pd-rich films.

Figure 4 shows the variation in S.P. with Pd content across the entire composition range. The essential features are (i) the S.P. for Ag-rich alloys (less than 50 at. %
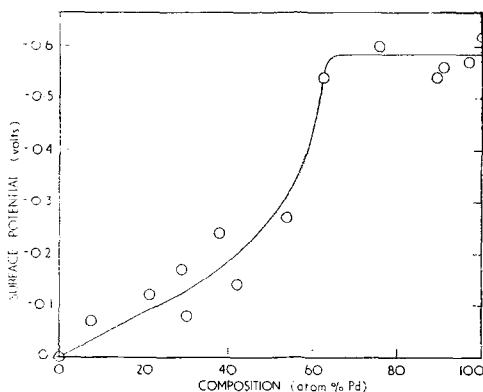
FIG. 4. Variation in surface potential (S.P.) on exposure to 2×10^{-6} Torr CO for 10 min (or equivalent) as a function of alloy composition.

Pd) was greater than 0, (ii) the S.P. for Ag-rich alloys increased with increasing Pd content (iii) the S.P. increased sharply at ~60 at. % Pd, and (iv) the S.P. was constant beyond 60 at. % Pd up to pure Pd.

DISCUSSION

The activity of the transition metals in adsorption and catalysis may be discussed either in terms of collective properties such as d-band vacancies or treated essentially as a chemical property of individual surface atoms. In this debate, chemisorption measurements or primitive catalytic reactions involving alloys of Group VIII and IB metals are particularly relevant. Experiments with Pd–Au or Pd–Ag alloys in the form of wires, foils, or thin films (15–20) as catalysts for parahydrogen conversion or for the recombination of hydrogen atoms show a qualitatively similar pattern. There is a characteristic sharp increase in activation energy or decrease in rate, perhaps starting when the Au or Ag content is more than ~40 at. %, but usually the change is only pronounced beyond 60% Au or Ag, i.e., the point at which d-band vacancies are just filled, according to magnetic susceptibility data.

As might be expected, less straightforward activity patterns are observed for more elaborate reactions over Pd–Au and Pd–Ag alloys and these require special discussion (21). Furthermore, some essentially

practical complications can arise, e.g., surface enrichment by silver in reactions involving oxygen and hydrogen solubility in Pd-rich alloys (11, 22) or, in certain other alloys, an unsuspected tendency to phase separation (1, 2). However the present discussion concerns the apparently innocent test of CO chemisorption on clean Pd–Ag alloy surfaces and the more fundamental objections to the simple d-band vacancy description have to be considered.

(i) The original conclusions from magnetic susceptibility measurements on alloys are not in accordance with modern measurements of the number of vacancies per atom in the d-band of palladium. For some time it has been realized that a simple deduction about the number of d-band vacancies (n_d) cannot be made from the composition at which paramagnetism disappears (23). With increasing concentration of the IB metal some electrons enter the $5s$-band of palladium and, in conjunction with new specific heat values, the rigid band analysis gives a value of $n_d = 0.48$ (6). Much more direct evidence on the value of n_d is available from de Haas–van Alphen measurements on pure palladium which yield a value of 0.36 (24) and suggests the rejection of the rigid band model, although it successfully explains the transport properties of Pd–Ag alloys (7) in terms of the density of states derived from specific heat measurements. The position can be maintained if it is assumed (8) that the s- and d-bands remain unchanged in shape by alloying but the s-band shifts its position linearly in energy relative to the d-band so that n_d varies from 0.36 for pure Pd to 0 for the 60% Ag alloy. However, a recent X-ray isochromat study (25) of the Pd–Ag system showed that 38 ± 5 at. % Ag was sufficient to fill the d-band, and the results could be described within a rigid band model. In summary, the number of d-band vacancies per atom of palladium may be nearer to 0.4 than the widely accepted value of 0.6, yet the latter value correlates rather better with the catalytic properties of the Pd–Au and Pd–Ag systems.

(ii) The band model is a theory of the

bulk properties of the metal (magnetism, electrical conductivity, specific heat, etc.) whereas chemisorption and catalysis depend upon the formation of bonds between *surface* metal atoms and the adsorbed species. Hence modern theories of chemisorption have tended to concentrate on the formation of bonds with localized orbitals on surface metal atoms. Recently the directional properties of the orbitals emerging at the surface, as discussed by Dowden (*26*) and Bond (*27*) on the basis of the Goodenough model, have been used to interpret the chemisorption behavior of different crystal faces (*28, 29*). A more elaborate theoretical treatment of the chemisorption process by Grimley (*30*) envisages the formation of a surface compound with localized metal orbitals and in this case a weak interaction is allowed with the electrons in the metal.

It has been proposed that studies by Sachtler *et al.* using Ni–Cu alloy films disprove the view that *d*-band vacancies are decisive for chemisorption (*31*). These Ni–Cu films consisted of two phases in equilibrium over a wide composition range and it was demonstrated that the *surface* composition was constant at ~80% Cu for alloys with compositions within the miscibility gap. Although *d*-band vacancies should not exist in such alloys, the capacity for hydrogen chemisorption was significantly greater than that for pure Cu and furthermore the Ni content of the surface could be titrated by chemisorbing hydrogen.

Now, it has been stated that the differences between the Ni–Cu and Pd–Ag systems (with respect to electronic structure) may be more impressive than their similarities (*6*) and this must be kept in mind both in making generalizations from one system, or in comparing H_2 chemisorption on Ni–Cu alloys with the present results for CO on Pd–Ag alloys. Nevertheless, the surface potentials observed when Ag-rich films were exposed to CO support the above conclusions from Ni–Cu alloys. However, we were able to study alloys of varying composition, and presumably varying surface composition, because there is no miscibility gap in the Pd–Ag system. The picture which emerges is more complex than results from a single Ni–Cu surface composition, i.e., ~80% Cu, would lead us to believe.

Suppose that work with Pd–Ag alloys was restricted to an alloy containing 80 at. % Ag/20 at. % Pd. Reference to Fig. 4 would then show a S.P. of approximately −0.1 V compared with 0 for pure Ag and −0.6 V for pure Pd when CO was adsorbed. One conclusion might be that Pd atoms in the surface are acting as individual chemisorption centers and that the Ag atoms are merely acting as a diluent. However, this implies that the surface potential is proportional to the number of CO molecules adsorbed per unit area which in turn is proportional to the surface Pd concentration. (It has inevitably to be accepted throughout that the latter is equal to the bulk Pd concentration, in the absence of evidence to the contrary.)

Now, clearly, the concept of individual Pd atoms in a silver diluent cannot be generalized for the whole composition range on the above basis; a more complex relationship between surface potential, coverage, and surface Pd concentration has to be invoked. For example, it has been found with pure metals that the surface potential rises sharply with coverage to a plateau value while bare surface remains (*12, 13*). If in addition, CO adsorption required pairs of Pd atoms so that the CO coverage initially increased rather slowly with increasing surface Pd concentration, then a combination of these effects might generate a curve such as Fig. 4. Nevertheless, the Pd-rich alloys all behaved exactly like pure Pd, and furthermore the break in the curve in Fig. 4 occurred at ~60% Pd which corresponds with the modern value of ~0.4 for the number of *d*-band vacancies. Therefore, we believe that it is not possible to reject the idea that *d*-band vacancies are important for CO chemisorption.

If *d*-band vacancies are relevant for CO chemisorption on Pd–Ag alloys, it is necessary to explain why the capacity to adsorb CO persisted almost up to 100% Ag, i.e.,

well beyond any estimate (see above discussion) for the maximum Ag content at which d-band vacancies can exist. It is not uncommon for activity in various reactions over Pd–Au and Pd–Ag to persist beyond 40% or even 60% Group IB metal, and one explanation is that d-band vacancies created by the excitation of electrons up to the Fermi surface exist even at small concentrations of the transition metal. Couper and Metcalfe (16) supported this idea by demonstrating the similarity between the activation energy for parahydrogen conversion and the Fermi energy of Pd–Ag alloys as a function of composition. About the same time Dugdale and Guénault (8) discussed the thermoelectric power in Ag-rich Pd–Ag alloys and explained the anomalously high value for the 1% Pd alloy on the basis that the palladium d-band moves in such a way that it remains just below the Fermi level. This suggests that electron promotion is energetically possible.

It might be that this electron activation model provides a feasible explanation for CO chemisorption on Ag-rich alloys and that d-band vacancies are relevant for this process. However, the following tentative explanation is advanced as an alternative because it might have some merit in reconciling the opposing viewpoints stated at the beginning of this section.

The existence of a band of surface-electron energy states caused by the termination of the periodic potential can be predicted by quantum mechanics. This band of surface states will overlap the normal crystal band if $|z|$ is not too large; z is given by

$$z = (\alpha - \alpha')/\beta,$$

where α is the Coulomb integral and α' is the Coulomb integral on the end atom in a chain of atoms (32). In a system of alloys, $|z|$ will depend mainly on β, the resonance integral, as the composition is varied. If the band of surface states overlaps the normal crystal band, the bulk properties of the metal will relate to the surface properties; in the transition metals d-band vacancies will be important in chemisorption and pre-

sumably this is also the case for the Pd-rich alloys.

It is suggested that increasing Ag content, and hence increasing separation of Pd atoms, will decrease the magnitude of β. Hence $|z|$ might become sufficiently large for the band of surface states to separate from the bulk d-band and Ag-rich alloys will behave like a two-dimensional atomic array. Unlike the Pd-rich alloys, the surface properties of these Ag-rich alloys need not relate to the electronic properties of the corresponding bulk alloy.

In summary, the viewpoint from which the surface properties of an alloy system such as Pd–Ag are discussed (practical complications apart) may depend on the concentration of the Group IB metal additive.

ACKNOWLEDGMENTS

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