

## The Surface Composition of Pd-Ag Alloys

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Palladium-silver alloys have been prepared by chemical reduction at 353 K and by equilibration in hydrogen at 673 K. They have then been investigated by Auger spectroscopy. The equation derived by Gallon has been used for the determination of the "monolayer intensity" and for the evaluation of data on the surface composition of alloys. The surface composition measured experimentally has been compared with the theoretical predictions. It appears that in compliance with the latter, the surface of equilibrated alloys is strongly enriched in silver. This silver enrichment is of the same order of magnitude as indicated earlier by other methods. The implications of this surface enrichment for chemisorption and catalysis are discussed.

### 1. INTRODUCTION

Palladium-silver alloys have been the subject of many studies in the field of surface science and catalysis. Pd and Ag form over the whole range of compositions a series of random solid solutions with interesting catalytic (1-5), chemisorptive (6-8), magnetic (9), and other properties (10-11). The complete solubility makes these alloys very attractive for studies on the surface composition of binary alloys.

Pd-Ag and the similar Pd-Au alloys have been repeatedly used to test various theories of catalysis by metals (1-5). It is known that when Pd is dissolved in Ag, the band of *d*-states becomes narrower and at a certain dilution its highest energy level falls below the Fermi level of the alloy (12). Due to this effect Pd-Ag alloys are then diamagnetic (in contrast to the strong paramagnetism of pure Pd) and their catalytic activity is found to be much lower than that of Pd. It is a highly intriguing question whether (and in which way) the changes in the occupation of the

*d*-band are related to the catalytic activity. However, before speculating on this problem, information on the surface composition is desirable. It is necessary to know which part of the decrease in the catalytic or chemisorptive properties is due to the decrease of the surface Pd content and which part of the decrease is possibly due to changes in the electronic structure.

Numerous attempts have already been made to determine the surface composition of Pd-Ag alloys, but no agreement has been achieved. Moss *et al.* (2) reported results which could be interpreted in terms of a surface enrichment in Pd. Christmann and Ertl (11) obtained results by Auger electron spectroscopy (AES) which led the authors to the conclusion that the surface composition is equal to that of the bulk. Wise and Wood (13) also applied AES and they interpreted their results as evidence for a marginal surface enrichment in Ag. In contrast to all this, Bouwman *et al.* (10) concluded that their measurements of the work function  $\Phi$  of alloys

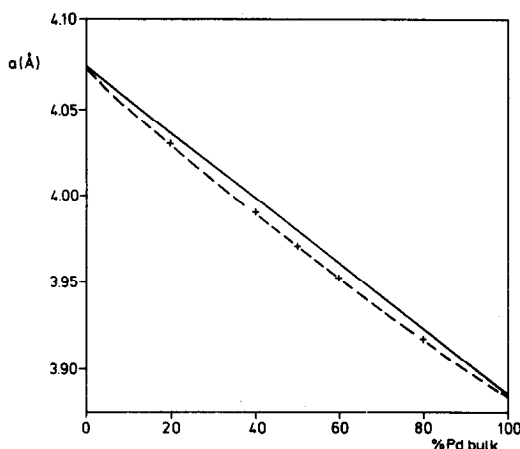


FIG. 1. Lattice constants ( $\times$ ) of Pd-Ag alloys as a function of the bulk percentage of Pd; ---, literature data (16); —, Vegard law.

and the work function changes  $\Delta\Phi$  upon CO chemisorption revealed a very pronounced surface enrichment in Ag. Stephan *et al.* (7), who measured the adsorption of CO volumetrically and also followed the thermal desorption of CO from a series of alloy films, confirmed the qualitative conclusions of Bouwman *et al.* (10). Such a disagreement on a rather simple system like Pd-Ag is a challenge to surface science. Which factors can be held responsible for the discrepancies—the corrosive character of CO adsorption (as is the case with Ni-Cu alloys (14), differences in the materials used by the various authors (polycrystalline films, epitaxial films, powders), or the methods of calibration, data evaluation, sensitivity of the measurements, etc.?

With these problems in mind we have undertaken a study of the surface composition of Pd-Ag alloy powders. The procedure of data evaluation and the determination of the necessary parameters is the same as in our previous papers (14, 15).

## 2. EXPERIMENTAL

### 2.1. Apparatus for Auger Electron Spectroscopy

The experiments were performed in a stainless-steel ultrahigh vacuum (UHV)

apparatus (Riber, France) equipped with a cylindrical mirror analyzer (CMA) (Physical Electronics). The UHV system offered the possibility to pretreat the alloys under atmospheric pressure using a commercial sample isolation valve (Riber). The sample holder was constructed of quartz and could be used either for evaporated metal films or for pressed powders. The evaporator from which the metal films were evaporated was oriented perpendicular to sample holder and consisted of a manipulative cylinder in which the two filaments were situated. In this way the internal surface of the UHV system and the CMA optics could be prevented from contamination by the evaporated metals. For further details of the experimental set up, see (14, 15).

### 2.2. Preparation of the Alloy Powders

The alloy powders were prepared from Pd sponge (purity 99.99%, Drijfhout, The Netherlands) and  $\text{AgNO}_3$  (p.a. quality). The Pd sponge was dissolved in p.a. aqua regia. After solution of the metal  $\text{NH}_4\text{OH}$  was added until a yellow solution was obtained (after the first addition a yellow precipitate is formed which dissolves after further addition of  $\text{NH}_4\text{OH}$ ). The  $\text{AgNO}_3$  is dissolved in water after which  $\text{NH}_4\text{OH}$  is added to obtain a silver/ammonia complex. The two solutions are mixed together and at  $80^\circ\text{C}$  are added under vigorous stirring to a solution of hydrazine hydrochloride in ammonia. After the chemical reduction is completed, the alloy powders are filtered off, washed and dried, and equilibrated in a hydrogen atmosphere at  $400^\circ\text{C}$ . The phase composition of the alloys was checked by X-ray diffraction. Only one-phase alloys were formed, the lattice constants of which were in excellent agreement with literature data (16) (see Fig. 1). To make the handling of the metal powders in the UHV system easier, pellets were pressed with a diameter of 0.7 cm, which

could be mounted on the sample holder. After evacuation cleaning was performed by sputtering with  $\text{Ar}^+$  ions. Equilibration following the sputtering was performed by heating the samples during 16 hr at  $400^\circ\text{C}$  in UHV.

### 2.3. Preparation of the Metal Films

The metals (specpure from Materials Research Company, USA) were evaporated from multihairpin W filaments onto a quartz holder. The pressure during evaporation was below  $1 \times 10^{-10}$  Torr. After thorough outgassing of the filaments the evaporated films were free of contamination. For more details, see (14, 15).

### 2.4. Experimental Conditions of Auger Spectroscopy

The Auger spectra were taken with a primary energy of 2000 eV and a beam current of  $10 \mu\text{A}$ . The modulation amplitude was 2 eV peak to peak.

### 2.5. Determination of the Escape Depth

To determine the escape depth of the Auger electrons of different energies, experiments were performed in which one metal was evaporated on top of the other (the temperature of the film was kept at 300 K).

First, a thick film of the first metal (Metal 1) is evaporated on the quartz holder and sintered. This film is then slowly covered by evaporation with the other alloy component whereupon the decrease of the Metal 1 Auger signal and the increase of the signal of the metal being evaporated are monitored and the variation of these two intensities is plotted against each other.

Analysis by means of the Gallon<sup>1</sup> equa-

<sup>1</sup> According to the Gallon model (15, 18) the total Auger signal is built up from discrete contributions of individual layers. A signal from  $n$  layers ( $n = 1, 2, \dots, \infty$ ) is given by

$$I(n) = I(\infty)[1 - (1 - I(1)/I(\infty))^n],$$

tion (14, 15) shows that such curves start to deviate from linearity when one monolayer of the material has been condensed on the underlying Metal 1 (15). The point where deviation from linearity sets in supplies the first approximate trial values. The values used for analysis (and shown below) are those checked by the best fit of the experimental points to the curve according to the Gallon equation.

Once the  $I(1)/I(\infty)$  value is known the mean escape depth can easily be determined from the same set of experimental data and the Gallon equation by finding the point on the above-mentioned curves where the relative signal intensity of 63% is reached (15). Actually, what we primarily obtain is the number  $n_\lambda$  of evaporated layers which are responsible for 63% of the signal. This number must be multiplied by the known (or assumed, when the orientation of the planes in, e.g., polycrystalline material is not known) distance  $d$  between the crystallographic layers. Since the acceptance angle of the CMA is  $\theta = 42.3^\circ$ , the real escape depth is

$$\lambda(\text{real}) = n_\lambda \cdot \frac{d}{\cos \theta} = 1.35 n_\lambda \cdot d.$$

When comparing this value with the literature data the following has to be realized. Seah (24) showed that the retarding potential method supplies us with a value

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where  $I(\infty)$  is determined by measurements on pure, bulk materials and  $I(1)/I(\infty)$  ( $= N_1$ ) by measurements where one metal is evaporated on another, as in (15) and in this paper.  $N_1$  can also be roughly estimated from the literature data on  $\lambda$ . The Gallon equation leads to almost the same numerical results as obtained by using the expressions for exponential attenuation of the signal;  $I(z) = I^0 \exp(-z/\lambda)$ , where  $z$  is the distance from the signal source of intensity  $I^0$ . However, it seems more logical to use an equation like the Gallon equation for a discontinuous problem (summing up contributions from a discrete layer), than a continuous exponential function. Also the difficulty of where to put zero for  $z$  is then avoided.

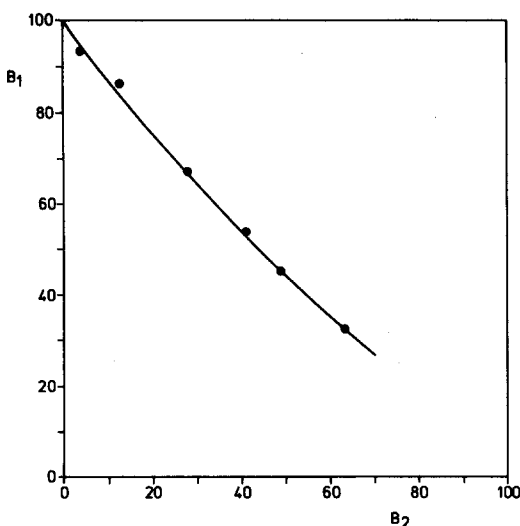


FIG. 2. The decrease of the Pd (330 eV) normalized relative signal ( $B_1 = I(t) 330 \text{ eV}/I(\infty) 330 \text{ eV}$ ) as a function of the normalized Ag (360 eV) peak ( $B_2 = I(t) 360 \text{ eV}/I(\infty) 360 \text{ eV}$ ) upon evaporating Ag on top of Pd.

of  $\lambda(\text{exp}) = \lambda(\text{real}) \cdot 0.74$ . However, not all authors took this correction into account, or they did not mention how  $\lambda$  was evaluated.

### 3. RESULTS

#### 3.1. Determination of the Parameters of the Gallon Equation, Mean Escape Depth

In some favorable cases it is possible to determine the relative signal intensity  $I(1)/I(\infty)$  of a monolayer of a given material by the procedure described in our previous paper (15). The procedure applied to Pd-Ag alloys is as follows. A film of Ag is slowly evaporated on top of a thick sintered film of Pd. Upon evaporation the decrease of the relative Pd (330 eV) signal is monitored and plotted in a graph as a function of the relative Ag (360 eV) signal which is monitored simultaneously. This plot is shown in Fig. 2. The curve drawn through the experimental points is the curve calculated by means of the Gallon equation (15, 18) with the following values of the relative monolayer intensi-

ties: Pd (330 eV) = 0.22, Ag (360 eV) = 0.20. It should be noted that Pd-Ag alloys are actually *not* best suited for the method applied. Because of the very small difference in Auger electron energies for both elements (i.e., the mean escape depth of Auger electrons differs for both elements only marginally), the curve in a graph as shown in Fig. 2 is almost linear and the error in determination of the  $I(1)/I(\infty)$  parameter is high. However, our estimate of the  $I(1)/I(\infty)$  parameter is supported by the results of other experiments where Pt was evaporated on top of a Pd film (15). It also leads to values of  $\lambda$  which are in agreement with the reliable data by Palmberg and Rhodin (23). Our values of  $\lambda$  or  $n_\lambda$  coincide with the averages of the values published in the literature (see (17)). Most of the literature values for  $n_\lambda$  vary between 3 and 5; our value is 4. At the worst, the determination of  $\lambda$  as we performed it can be considered as, at least, an additional support for the choice of a certain value from the literature.

It appeared to be impossible to reverse the procedure and to evaporate Pd on top of a Ag film. With this sequence of evaporation Ag diffused to the outer surface of the film even at low temperatures and made the measurements as described impossible. Similar behavior was observed when Ni was evaporated on top of a Cu film (14).

#### 3.2. Equilibrated Alloys

Pd-Ag alloy powders were equilibrated at 673 K after several sputter/anneal cycles. After 16 hr at 673 K no further change in Auger signal ratio was observed at room temperature and alloys were free of contaminants after this treatment. In Fig. 3 the ratio  $B_3$  is plotted as a function of the bulk Pd content (in %).  $B_3$  is defined as  $B_3 = I(\text{Pd } 330 \text{ eV})/[I(\text{Pd } 330 \text{ eV}) + jI(\text{Ag } 360 \text{ eV})]$ . If the whole

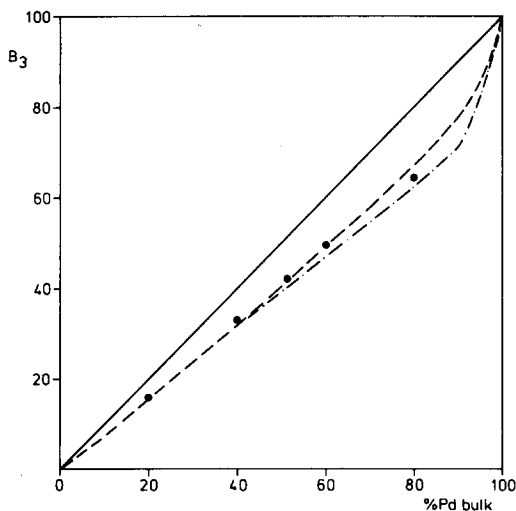


FIG. 3. Normalized peak ratio  $B_3$  ( $B_3 = I(\text{Pd } 330 \text{ eV})/I(\text{Pd } 330 \text{ eV}) + jI(\text{Ag } 360 \text{ eV})$ ;  $j = 0.93$ ) as a function of the bulk percentage of Pd. Comparison of experimental values (points) of the  $B_3$  ratio with the values calculated from the theoretical surface composition (—, ideal solution model; ---, regular solution model with varying  $\Omega$ ).

Auger signal originated in the first outmost layer this curve would represent the surface Pd concentration as a function of Pd bulk content. It can be seen that a Ag

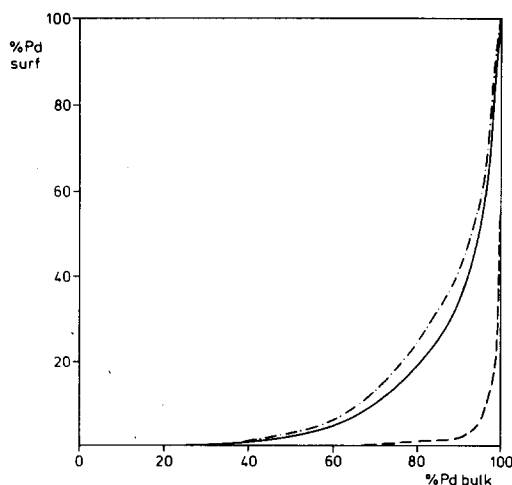


FIG. 4. Theoretical surface composition for three different models. (1) ---, ideal solution model; (2) —, regular solution model with  $\Omega = -4966$  cal/mole; (3) -·-, regular solution model with varying  $\Omega$ .

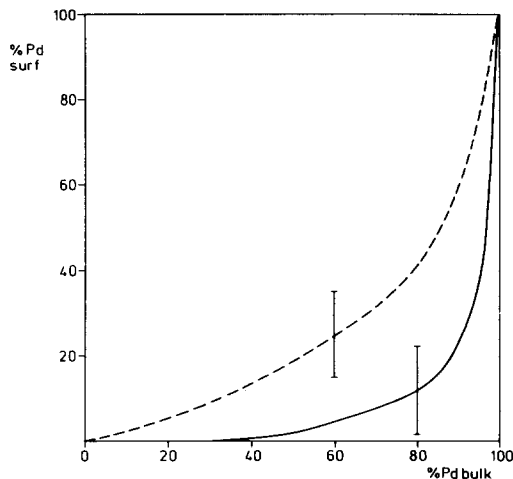


FIG. 5. The surface composition of Pd-Ag alloys equilibrated *in vacuo* (—) and after interaction with CO (---) as a function of bulk composition.

surface enrichment is indicated by these data. However, as we have already mentioned, with Auger electron energies of 330 to 360 eV only 20 to 22% of the total signal comes from the first layer and this means that the surface Ag enrichment is actually much more pronounced.

### 3.3. Interaction with Carbon Monoxide

The alloy powders were also treated with 0.1 Torr carbon monoxide at 670 K for 16 hr. After pumping away the gas at room temperature it appeared that a less pronounced Ag enrichment was observed (shown below, Fig. 5). It should be remarked that carbon was clearly detected during these experiments.

### 3.4. Theoretical Surface Comparison

It is possible to calculate the theoretical surface composition of alloys if several parameters are known. For the ideal solution model it is necessary to know the surface energies of the metals at a given temperature whereas for the regular solution model also the heat of mixing  $\Delta H_m$  is necessary (19, 20).

The surface energies of the pure metals

TABLE 1

Mean Escape Depth  $\lambda$ 

$E$ (eV)	$I(1)/I(\infty)$	$n_\lambda$ (atomic layers)	$\lambda$ (Å)		$\lambda$ lit. <sup>a</sup> (Å)
			For $d$ (110)	For $d$ (111)	
Pd (330)	0.22	~4	8	6	5-13
Ag (360)	0.20	~4	8	6	5-13

<sup>a</sup> Not all the literature data are corrected for the acceptance angle of the analyzer; most of the values vary between  $n_\lambda = 3$  and 5.

can be calculated at any temperature using the model of Tyson and Miller (21), so that the calculation of the surface composition of an ideal system is simple ( $\sigma_{Pd} = 1977$  dyn/cm,  $\sigma_{Ag} = 1182$  dyn/cm). The heat of mixing can also be obtained from the literature (22). However, one has to consider that the Pd-Ag alloy system shows no regular behavior ( $\Delta H_m/(X(1-X))$  is not constant, where  $X = \text{atom}\%$  Pd). Two cases are therefore considered below, both applied to the (111) face:

- (1) a constant regular solution parameter ( $\Omega = -4966$  cal/mole) and
- (2) a varying  $\Omega$  (calculated from the experimental values of  $\Delta H_m$ ).

In Fig. 4 the results of the various calculations are shown (only the first atomic layer enrichment is calculated). It can be seen immediately that a considerable enrichment of the surface in Ag is predicted by this simple theory.

#### 4. DISCUSSION

##### 4.1. The Surface Composition of Pd-Ag Alloys

As has been discussed in our previous paper (15), the primary Auger spectroscopic data (as in Fig. 2) can be evaluated in two ways. Either by using a proper theory and known parameters, such as the mean escape depth (or monolayer inten-

sity), the primary Auger data are converted into information on the surface composition which can be eventually checked by some other independent method, or the surface composition, determined by some other method or predicted theoretically, is converted into Auger peak intensities which are then compared with those experimentally found.

In Fig. 3 a comparison is made between the experimental data and the Auger signals calculated for surfaces with theoretically predicted surface compositions. It can be seen that a good agreement is obtained which means that quite a pronounced Ag enrichment is predicted and this prediction is experimentally confirmed.

In Fig. 5 the surface composition of Pd-Ag alloys equilibrated *in vacuo* and after interaction with CO is plotted as a function of the bulk composition. It is observed that carbon monoxide causes segregation of Pd to the surface which in effect counteracts and partially removes the Ag enrichment obtained after annealing *in vacuo*.

The validity of conclusions with regard to the surface composition is a.o. dependent on the accuracy with which the parameters for data evaluation are determined. In Table 1 our data (all corrected for the CMA acceptance angle) are compared with those in the literature. According to the literature, the mean free escape depth of electrons with an energy around 350 eV is about four atomic layers (23) (or about 8 Å, if no correction were made for the acceptance angle of the CMA, as in (24)). This value corresponds to a value for  $N_1 = I(1)/I(\infty)$  of 0.2 to 0.22 in agreement with the determination of the parameter in this paper.

The fact that only 20% of the total signal originates in the first layer makes Auger spectra rather insensitive to the surface (upmost layer) composition. Or, a rather pronounced surface enrichment is necessary to cause at least such a small

deviation from the diagonal line like the points in Fig. 3. This means that the surface composition as determined from Auger spectra is unavoidably accompanied by a considerable error. A rough estimate of the uncertainty in the surface composition is indicated in Fig. 5 for two concentrations.

#### 4.2. Surface Composition—Comparison with Literature Data

As already mentioned, Pd-Ag alloys have been studied by Christmann and Ertl (11). These authors have not detected any surface enrichment. The reason for the discrepancy between their data and ours is not known; the possible role of epitaxy should be checked. In contrast with (11), Wood and Wise (13) have observed an enrichment in Ag, though it was only marginal. However, the experimental procedure of Wood and Wise (13) differs from ours in two ways: (i) The authors (13) do not consider the signal built up from contributions of several layers but analyze the signal as if it were coming from the first layer only; (ii) the authors use the calibration factors according to the "Handbook" by Palmberg (25). The first point clearly yields an overestimate of Pd in the surface but it is interesting to note that the second point causes the same effect. The sensitivity factors derived from the Handbook are different from those we used and those published by Mathieu *et al.* (26). However, the primary data presented in the Handbook were obtained in a rather early stage of the development of Auger spectroscopy and the question is how clean the surfaces used for calibrations really were. The Handbook value for the Pd (330 eV)/Pd (270 eV) ratio is lower than in this and other papers and this could be because of the carbon peak contribution to the Pd (270 eV) peak. If this is the case, the Pd (330 eV) peak in the Handbook would be slightly too low and its use for calculations of sensi-

tivity factors would lead to an overestimate of the Pd concentrations in the alloys analyzed. With the sensitivity factor of this paper, the data of Wood and Wise (13) become similar to ours.

Data of the volumetric CO adsorption measurements [ $n(\text{CO})$ ] and the work function changes  $\Delta\Phi(\text{CO})$  also contain implicit information on the surface composition. Yet, it is difficult to convert these data in a quantitative way into surface composition data. Carbon monoxide is adsorbed in various forms, each having a different effect on the work function and requiring a different number of Pd sites. Nevertheless, we made the following rough estimate from the data in (6, 7, 10, 11). We took the number of CO molecules  $n(\text{CO})$  adsorbed per unit surface area or the total change of work function  $\Delta\Phi(\text{CO})$  as proportional to the concentration of Pd (in molar ratio) in the surface. By using the molar ratios of Pd in the surface determined in this way we calculated the relative Auger signal intensities as a function of the bulk composition and compared these with the measured ones. As can be seen from Fig. 6, all data indicate the same result: a surface enrichment in Ag.

#### 4.3. Implications for Chemisorption and Catalysis

CO adsorbed on Pd reveals two infrared bands which are usually associated with two modes of adsorption: single ("linear form")- and multiple ("bridged" form)-coordinated CO molecules. Soma-Noto and Sachtler (27) as well as Primet *et al.* (28) observed that the multiple-coordinated form of CO is strongly suppressed when Pd is alloyed with Ag. In contrast, the ir band of the single-coordinated CO is even stronger on some alloys than on Pd and it is in any case less suppressed by alloying than the other band. It is then interesting whether the whole decrease in the intensity  $I_m$  of the multiple-coordinated band

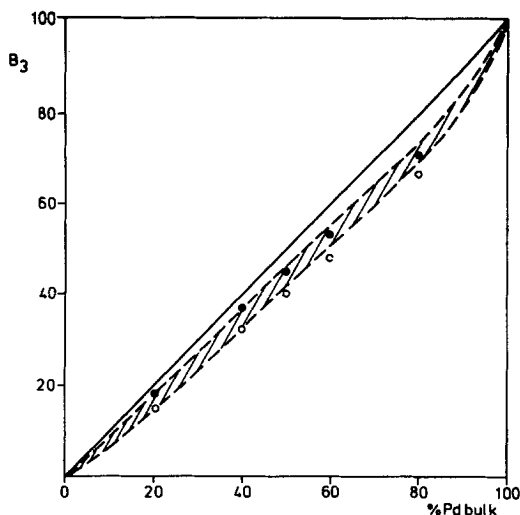


FIG. 6. Comparison of experimental values of the  $B_3$  ratio (O, sintered *in vacuo*; ●, after interaction with CO) with  $B_3$  ratios calculated using literature data on work function and results of the volumetric adsorption measurements (6, 7, 10, 11). The calculated values fall in the indicated band.

can be explained only by the decrease in the surface Pd concentration or whether additional assumptions, as for example about the role of the varying electronic structure of Pd atoms in alloys, are necessary.

Sachtler (29) calculated the normalized ratio of band intensities of the single ( $I_s$ )- and multiple ( $I_m$ )-coordinated species,  $q = I_s/(I_s + I_m)$ , as a function of the surface Pd concentration  $X_s(\text{Pd})$ . The formula for  $q(X_s)$  has been derived under the following assumptions: (1) On an isolated Pd atom, totally surrounded by Ag atoms, CO is adsorbed in the "linear" form; (2) on the Pd atom agglomerates, both forms are possible, a fraction  $\alpha$  of CO molecules is adsorbed in a "linear" form, a fraction  $(1 - \alpha)$  is multiple coordinated, the coefficient  $\alpha$  being independent of alloying. In other words, the decrease in the number of multiple-coordinated CO molecules is only due to the decrease in Pd concentration and not due to the changes in character of the Pd atoms (the

latter effect would lead a.o. to  $\alpha$  varying with  $X_s(\text{Pd})$ ).

The formula derived by Sachtler comprises one parameter  $\lambda$  which cannot be determined experimentally:  $\lambda = \epsilon_m \Theta_m / \epsilon_s \Theta_s$ , where  $\epsilon$  stands for specific absorbance and  $\Theta$  for coverage of given sites (at given pressure) for the single (s)- and multiple (m)-coordinated species. It is reasonable to estimate  $\lambda$  as being between, say 0.2 and 1 (estimates for Pt<sup>32</sup> give  $\epsilon_m/\epsilon_s \sim 0.2$ ).

The surface composition of the alloys on carrier used by Soma-Noto and Sachtler (27) is not known. However, if we assume that it was the same as that of our equilibrated alloys without carrier, the following comparison can be made.

The measured  $q(X_{\text{bulk}})$  function is taken from the paper by Soma-Noto and Sachtler (27) and compared with the  $q(X_s)$  curve calculated theoretically (29) with the assumptions (1) and (2) formulated above. This comparison can be, for example, performed in Fig. 5 of (29). From this, it is easily found which surface composition  $X_s$ ,  $X_s = f(X_{\text{bulk}})$  would lead to the  $q(X_{\text{bulk}})$  data as determined experimentally by Soma-Noto and Sachtler (27). The surface composition  $X_s = f(X_{\text{bulk}})$  found in the way just described, is compared in Fig. 7 with the analogous curve calculated from the Auger data of this paper. As can be seen, the agreement is satisfying. It means that if the surface composition of alloys in (27) were, indeed, the same as of our alloys, the calculation by Sachtler (29) and assumptions (1) and (2) can explain all data available. The strong decrease in the number of multiple-coordinated species can thus be explained by simple dilution of Pd in the surface of alloys.

It is very difficult to discuss the absolute values (i.e., not only the normalized ratios as we did above) of the two ir band intensities, as a function of alloy composition. There is always a danger that the particle size and, therefore, the band intensities



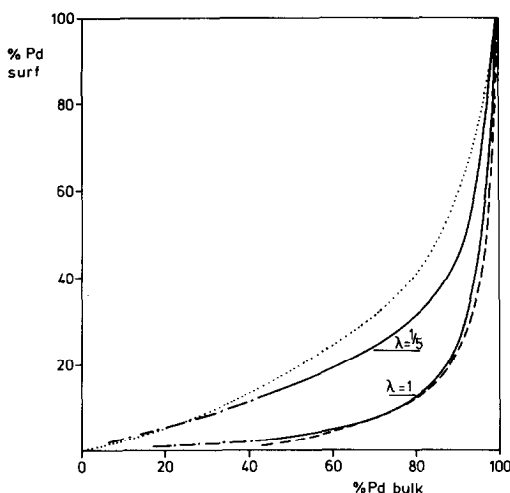


FIG. 7. Comparison of the surface composition of Pd-Ag alloys sintered *in vacuo* (---) and after interaction with CO (···) with the calculated surface composition according to infrared CO adsorption data (—) and the theoretical model by Sachtler (29) (see text for details).

vary when metals are alloyed. However, it seems interesting to note that when fraction  $\alpha$  of the linearly bound, single-coordinated molecules is low on pure Pd, a dilution by 50% of Ag atoms in the surface still leads to an increase in the absolute band intensity for this adsorption form. This is indeed found in (27).

It has already been pointed out (33) that an interesting difference exists between Ni-Cu and Pd-Ag alloys. The electronic structure of Ni does not change very much by alloying while the electronic structure of Pd atoms changes by alloying from about  $4d^{9.65}s^{0.4}$  into  $4d^{10}5s^0$  (the structure of a free Pd atom). It has also been observed that the catalytic reactivity in various reactions does not reveal any particularly abrupt change at a composition of 50 to 60% Cu in Ni, but it remained almost constant up to 70 to 85% of Cu. In contrast to it, the alloys of Pd-Ag (or Pd-Au alloys) frequently revealed almost negligible (Ag-like) activity at Ag (Au) bulk concentrations higher than 50 to 60%. Having no data on the

surface composition, one would be inclined to relate the two phenomena and say that a Pd  $4d^{10}5s^0$  structure is inactive for many (all) reactions. However, we have shown in this paper that the concentration of Pd is very low at Ag-bulk concentration of 50 to 60%. If the surface composition were predicted correctly by the simple theory of surface enrichment (see Fig. 4), the surface concentration of Pd at 60% Ag in bulk would be only 1 to 2%. This means that it would be a very difficult task to prove that the low activity of diluted Pd-Ag alloys is caused by changes in the electronic structure of Pd because in many reactions Ag itself does not have a low enough activity for it to be possible to measure quantitatively the contribution of that small percentage of Pd atoms in the surface.

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