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Auger Electron Spectroscopy Study of Chemisorption-Induced Segregation in a Pd–Au Alloy

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The chemisorption of oxygen has been studied by Auger electron spectroscopy at 500°C and pressures varying from 10^{-7} to 1 Torr on a 22 atom % Pd–Au alloy. A quantitative method has been used for calculating the Pd and Au surface concentrations. For the clean surface it agrees well with the bulk alloy composition even after ion bombardments and annealing. Significant Pd surface enrichment due to oxygen chemisorption has been observed. This result may provide an explanation for the influence of preoxidation treatments on the catalytic behavior of such alloys. Hydrogen chemisorption on the surface after oxygen treatment causes the oxygen and thus palladium surface concentrations to increase further.

INTRODUCTION

Deviation from the bulk composition is one of the most important phenomena governing the behavior of alloy surfaces. Since pioneering work by Takeuchi (*1*), the Cu–Ni system has been extensively studied and several examples of chemisorption-induced segregation or surface enrichment due to various treatments have been observed (*2–5*). Similar experiments were reported on other systems presenting continuous solid solutions (e.g., Pd–Ag) (*6*) and for intermetallic compounds (e.g., Pt–Sn) (*7*).

Surface enrichment, when it occurs, obeys in most cases a few simple rules which seem now well established (*8*): (i) an annealed surface becomes enriched in the constituent which has the lower heat of sublimation; (ii) ion bombardment lowers the surface concentration of the element which possesses the higher rate of sputtering; (iii) in chemisorption studies, the metal that forms the stronger bonds with the adsorbate segregates to the surface.

Quantitative studies of surface enrichment are still few. Auger electron spectroscopy is a unique tool for this purpose, provided two difficulties are overcome: (i) one must find a proper calibration method; (ii) the Auger transition which is considered must correspond to the minimum escape depth.

Pd–Au is an interesting system for it presents a continuous solid solution without miscibility gap in the whole range of concentration, at temperatures above 300°K.

In a previous paper, O'Cinneide and Gault (*9*) quoted a few preliminary Auger results which were obtained on a Pd–Au alloy. This paper is a more extensive study, somewhat different in its conclusions, of the same system with 22% Pd.

Recently Pd-surface segregation due to oxygen chemisorption was found by Wood and Wise (*10*) with a Pd-rich alloy. Samples with nearly equivalent Au and Pd

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concentration exhibited only small effects and no experiments with Au-rich alloys were reported.

EXPERIMENTAL

Apparatus

The experiments were performed in a Varian LEED chamber with 4-grid optics. A sample isolation valve allowed exposure of the alloy to gases up to atmospheric pressure with the rest of the chamber remaining in ultrahigh vacuum.

The Auger detector was a retarding field analyzer (referred to as RFA). The energy of primary electrons was about 2 kV and they struck the sample at normal incidence. The beam current was about 20μA. A 140 l/s ion pump and a titanium sublimation pump allowed us to reach ultimate pressures in the low 10^{-10} Torr range after baking. After adsorption experiments, the Auger spectra were always recorded at room temperature with the residual gases evacuated.

Sample

A 22 atom % Pd–Au alloy wire (specpure, Johnson-Matthey) was melted four times in a crucible under ultrahigh vacuum (10^{-8} Torr at a temperature near the melting point), pressed in air into the form of a disk, and then spotwelded on a pure Au frame which was mounted within the experimental chamber. Impurities in both alloy and Au frame, as detected with AES, were mainly S, C, O, and traces of Ca, K, and Cl.

The alloy surface was decontaminated by several cycles of ion bombardments followed by annealing at moderate temperature (500°C maximum). Traces of K and Cl were quite easily removed; 4 cycles were necessary to remove the other impurities.

The actual alloy was checked by X-ray diffraction and found to be 22 ± 3 atom % Pd.

Auger Transitions

The main Auger peak in the Pd spectrum is a $M_5N_{4,5}N_{4,5}$ transition which appears near 327 eV. If the resolution of the analyzer is good enough a shoulder can be detected at 326 eV. We have been able to observe this shoulder with our RFA in the spectrum of pure Pd sample but not in the alloy spectrum.

Au displays a well-resolved peak at 238 eV but its intensity is too small and the signal-to-noise ratio too large in this area for using it in an accurate measurement. This is the reason why we have preferred to compare the 327 eV Pd peak to the large $N_7O_{4,5}O_{4,5}$ transition of gold (69 eV).

Although the energy gap between these two peaks is quite large it does not seem that the corresponding escape depths differ very much. Brundle (*11*) has summarized the values of escape depths calculated or estimated by various authors for more than 10 elements. As pointed out by Tracy (*12*), these findings suggest a nearly universal curve (within a factor of 2). From values given in Brundle's paper, it may be concluded that the 69 eV Au peak and the 327 eV Pd peak arise from depths not exceeding 4 and 8 Å, respectively. Therefore, the phenomena which we have observed take place in the uppermost layers of the alloy surface. The C peak at 270 eV and the small Pd peak at 274 eV could not be resolved. The C peak to peak heights could easily be deduced after comparison between the 274 and 327 eV Pd peaks in pure Pd and alloy spectra.

Calibration Method

It is now well established (*13*) that the peak-to-peak heights of the Auger transitions are a direct measure of the concentration of the elements at the surface. This implies, among other things, that no effects due to surface roughness are considered. We have recorded Auger spectra from several regions of the sample and no significant differences were observed.

For a quantitative calculation, one must find the relative sensitivities of both alloy constituents. Let us call I_{Pd} and I_{Au} the peak-to-peak heights for the 327 eV Pd and 69 eV Au transitions in the alloy spectra. The concentration C_{Pd} at the surface is then:

$$C_{\mathrm{Pd}} = \frac{I_{\mathrm{Pd}}}{I_{\mathrm{Pd}} + \sigma_{\mathrm{Pd,Au}} I_{\mathrm{Au}}}.$$

The relative sensitivity $\sigma_{\mathrm{Pd,Au}} = I_{\mathrm{Pd}}/I_{\mathrm{Au}}$ may be calculated from the same transitions in pure Pd and Au spectra, recorded under identical experimental conditions. We found in this way $\sigma_{\mathrm{Pd,Au}} = 0.168$. One must point out that it is most important to make the measurements on well-decontaminated surfaces. This is especially true for Au since the height of the 69 eV transition is dramatically affected when large amounts of contaminants, especially carbon, are present on the surface.

To check the validity of this method, we have compared our spectra to those published in the "Handbook of Auger Electron Spectroscopy" (*14*). The ratio $I_{\mathrm{Pd}}{}^{\mathrm{H}}/I_{\mathrm{Au}}{}^{\mathrm{H}}$ (H standing for Handbook) is then 1.73. We believe that the discrepancy comes from the use of the 69 eV Au transition. All the spectra given in the Handbook were obtained with a cylindrical mirror analyzer (CMA). As already observed in this laboratory with Pt (*15*), the RFA gives for low energy transitions (<100 eV) and relatively to high energy transitions much higher peaks than a CMA.

To calculate the actual relative sensitivity we have recorded the 69 eV Au transition in our apparatus for pure Au and compared it to the same transition in the Handbook. It turns out that for this transition our RFA gives peaks 8.89 times higher than the CMA. Thus, we find $\sigma_{\mathrm{Pd,Au}} = 1.73/8.89 = 0.195$.

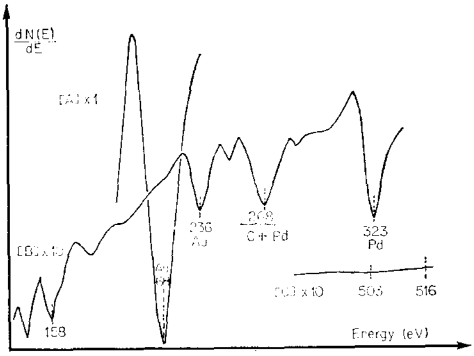

Fig. 1. Auger spectrum of a Pd–Au alloy surface with traces of carbon. Primary beam: 2000 eV, 50 μA. Modulating amplitude (peak-to-peak): 10 V.

Both values agree well within experimental errors and the mean value $\sigma = 0.182$ was taken in the following.

RESULTS AND DISCUSSION

Clean Alloy Sample

No quantitative measurement could be made during the cleaning procedure, i.e., successive bombardment and annealing cycles. As mentioned above, the 69 eV peak is masked when important amounts of impurities stay on the surface and at first, before any treatment, the transition was not detectable at all. The peak increased progressively during the cleaning procedure and after 4 cycles all impurities had disappeared except a small amount of C (Fig. 1) which does not affect the height of the 69 eV Au transition, as checked on pure Au spectra.

The calculated value of the Pd concentration was then 17.7% and the surface was considered clean. Note that the extreme values calculated from $\sigma = 0.195$ and $\sigma = 0.168$ give Pd surface concentrations equal to 16.7 and 18.9%, respectively. If we compare these results with the X-ray diffraction test which gives 22 ± 3 atom % Pd, we can say that the agreement between the original alloy composition and our calculations is reasonably good.

TABLE 1

Comparison of a Few Physical Parameters for Pd and Au

	Pd	Au
Heat of vaporization (kcal/mole)	90	88
Surface tension (erg/cm^2)	1430	1340
Atom size (Å)	2.74	2.88
Sputtering yield (500 eV A^+) (atoms/ion)	2.1	2.4

As mentioned above, the 69 eV Au and 327 eV Pd transitions arise from about 4 and 8 Å, respectively. Thus, strictly speaking, we have not calculated the concentration at the surface (the first layer) but the mean composition of a "selvedge" composed of the first uppermost layers. This distinction is fundamental since theoretical calculations by Williams and Nason (*16*), based on an ideal solution model, predict enrichment of only the first monolayer.

Accurate calculations of the composition of this topmost layer are somewhat uneasy. For example a solution was given by Stoddart *et al.* (*17*) from a comparison between high and low energy Ni transitions in a Pd–Ni alloy. Unfortunately we cannot use this method in our particular case since high energy transitions are not available in the Pd spectrum and are too weak for Au (except a 2024 eV peak which cannot be detected with our 2 kV electron gun).

As a matter of fact, this type of calculation seems unnecessary with Pd–Au. Williams and Nason's theory is based for a great part on the differences in heats of vaporization and surface tension between the two constituents of the alloy (*16*). For Pd–Au, as seen in Table 1, the differences are very small. The same conclusion applies for the differences in atom sizes (less than 10%), an important parameter in McLean's strain theory (*18*) which has been invoked by McDavid and Fain (*19*) for explaining some unexpected results in Cu–Au alloys.

Concerning a possible surface enrichment due to argon ion bombardment, the sputtering rates for Pd and Au, as taken from Wehner's compilation (*20*) are not very different either (Table 1). Preferential sputtering is thus unexpected. We have been able to confirm this statement after depth profiling experiments which we have done in a different Auger apparatus with Pd–Au alloys of various compositions (*21*).

We can then safely conclude that the different existing theories predict no or very little surface enrichment for a Pd–Au alloy. Such a system seems to be rather insensitive to the surface treatments used

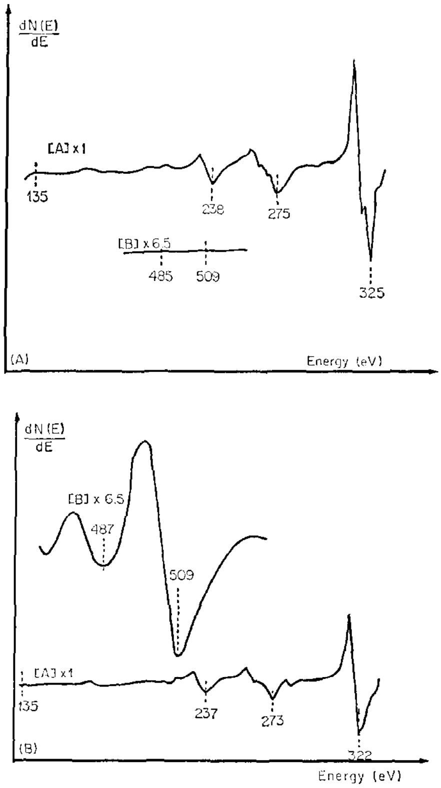

FIG. 2. Adsorption of oxygen on pure Pd. (a) Auger spectrum of a pure Pd surface. Primary beam: 2000 eV, 20 μA. Modulating amplitude: (A) 5 V; (B) 20 V. (b) The same surface after O_2 adsorption (P_{O_2} = 5 Torr, 500°C, 1 hr); same conditions as in (a).

in the cleaning procedure (ion bombardment and annealing). The reasonable agreement between our calculated value, 17.7%, and the original alloy composition, 22%, validates our calibration method, and we have used it in oxygen adsorption experiments.

O_2 Adsorption on Pure Metals

Preliminary experiments were done on pure Pd and Au samples. Adsorption of 5 Torr O_2 on Pd at 500°C for 1 hr resulted in the appearance of a very important oxygen peak at 509 eV (Fig. 2). Meanwhile the 327 eV Pd peak faded away and the sample turned violet. A single flash at 700°C was sufficient to restore the previous situation, i.e., no oxygen peak, strong palladium peak, and grey sample.

A similar experiment was done with a pure Au sample (350°C, 1 hr, $P_{O_2} = 0.5$ Torr). A small oxygen peak at 504 eV could be detected, but it was much more difficult to remove than on Pd.

Quite clearly, Pd and Au behave in a very different way. Pd adsorbs O_2 easily at 500°C but desorbs it with a small temperature increase; Au adsorbs O_2 with difficulty but it is not easy to get rid of the adsorbed O_2. In this respect Au seems to behave like Pt where dissolution of O_2 into the bulk occurs (*22*) so that several ion bombardments and annealing cycles are necessary to restore a clean surface.

O_2 Adsorption on Pd–Au Alloy

Several O_2 doses were introduced onto the clean alloy surface at 500°C, with pressures varying from 3×10^{-7} to 1 Torr and for approximately 1 hr.

On Fig. 3 we have plotted, as a function of oxygen peak-to-peak height, the relative amounts α and β in percentages of Au and Pd, respectively, calculated as explained above. These quantities are not actual concentrations since part of the surface is now covered with oxygen. They are not surface concentrations either, since, as already pointed out, A.E.S. samples several layers, between 2 and 4 in our particular case. We have not attempted to reach the exact composition of the first layer.

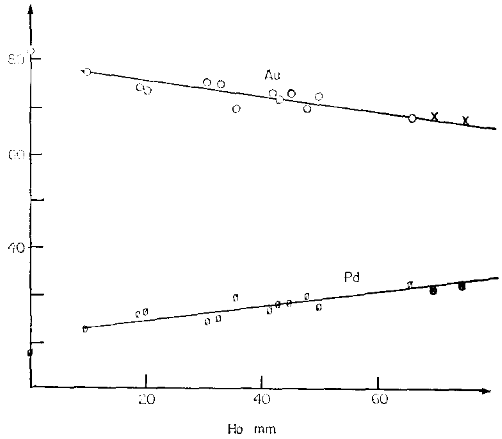

FIG. 3. Relative amounts α and β in percentages of Au and Pd, respectively, versus oxygen peak-to-peak height in the Auger spectra.

$$\text{O}, \ \alpha = \frac{\sigma_{\text{Pd,Au}} I_{\text{Au}}}{I_{\text{Pd}} + \sigma_{\text{Pd,Au}} \cdot I_{\text{Au}}} \times 100;$$

$$\varnothing, \ \beta = \frac{I_{\text{Pd}}}{I_{\text{Pd}} + \sigma_{\text{Pd,Au}} \cdot I_{\text{Au}}} \times 100;$$

X, ⊗: α and β after H_2 adsorption.

In any case, in spite of some scatter of the experimental points, it is quite clear from Fig. 3 that the presence of oxygen on the surface results in increasing the Pd/Au ratio. This is especially true for 1 Torr O_2 adsorption where β reaches 32.2%. As the Pd–O bond is stronger than the Au–O bond (*23*), it is not surprising that Pd and not Au segregates to the surface, in view of the rules given in the Introduction.

A typical Auger spectrum (1 Torr, 500°C, 1 hr) is given in Fig. 4. As in all other alloy spectra, the peak in the 270–275 eV region (C + Pd) is not higher than in the pure alloy spectrum; the C peak is thus very small so that, as already pointed out, it does not affect the height of the 69 eV Au transition. The situation

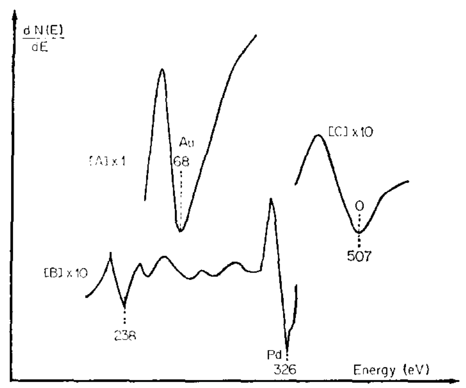

FIG. 4. Pd–Au alloy surface after O_2 adsorption ($P_{O_2} = 1$ Torr, 500°C, 1 hr). Primary beam: 2000 eV, 50 μA. Modulating amplitude: 10 V.

is somewhat different with the 330 eV Pd peak. As mentioned above, large amounts of O_2 on the surface caused the Pd peaks to decrease. However, this phenomenon is not easy to quantify with a sufficient accuracy. Thus, the observed effect, that is increase of the Pd surface concentration due to O_2 adsorption, is certainly underestimated. From a crude calculation we believe that the error may reach a few percentages for the highest values of β.

In a recent paper, O'Cinneide and Gault (*9*) reported a catalytic study of the isomerization and hydrocracking of hexanes on Pd–Au and Pt–Au supported alloys. They observed that the activity of these catalysts could be dramatically affected if pretreatment included oxidation. This was especially true of a 15 atom % Pt–Au alloy which displayed activity for the first time and a 35 atom % Pd–Au alloy which was much more active than before oxidation.

Our results seem to indicate that this "abnormal" behavior of the Pd–Au alloy might be explained, at least partly, by a Pd surface-enrichment effect. Since Au is inactive for these catalytic reactions, preoxidation treatment may increase the concentration of active sites on the surface and thus the catalytic reactivity will be changed. However, the statement that the inactive constituent of the alloy surface acts merely as a diluent should be regarded with some caution.

Another interesting feature of this study is the position of the O transition in our Auger spectra. Values given in Fig. 3 refer to the oxygen KLL transition which is expected at 516 eV. In all our spectra, this transition appears at 504–509 eV. This strong chemical shift means that oxygen is tightly bonded. This finding and its relevance to catalysis have been discussed in ref. *9*.

H_2 Adsorption on Pd–Au Alloy

In two experiments, 2 Torr hydrogen were admitted in the chamber at 500°C for 1 hr, just after an O_2 experiment (1 Torr O_2, 500°C, 1 hr). This resulted in increasing the O peak at 506 eV and a corresponding Pd segregation to the surface occurred, as can be seen in Fig. 3. The effect of H_2 seems therefore to "pump" O_2 from under the surface (dissolved in Au) with a corresponding Pd segregation to the surface.

We plan to support our conclusions with additional studies of O_2 adsorption on Pd–Au and Pt–Au alloy with different Pd and Pt concentrations.

REFERENCES

1. Takeuchi, T., *Shokubai* **3**, 144 (1961).
2. Sachtler, W. M. H., and Dorgelo, G. J. H., *J. Catal.* **4**, 654 (1965).
3. Quinto, D. T., Sundaram, V. S., and Robertson, W. D., *Surface Sci.* **28**, 504 (1971).
4. Takasu, Y., and Shimizu, H., *J. Catal.* **29**, 479 (1973).
5. Helms, C. R., and Yu, K. Y., *J. Vacuum Sci. Technol.* **12**, 276 (1975).
6. Mathieu, J. R., and Landolt, D., *Surface Sci.* **53**, 228 (1975).
7. Bouwman, R., and Biloen, P., *Surface Sci.* **41**, 348 (1974).
8. Bouwman, R., Toneman, L. M., and Holscher, A. D., *Surface Sci.* **35**, 8 (1973).
9. O'Cinneide, A., and Gault, F. G., *J. Catal.* **37**, 311 (1975).

10. Wood, B. J., and Wise, H., *Surface Sci.* **52**, 151 (1975).

11. Brundle, C. R., *J. Vacuum Sci. Technol.* **11**, 212 (1974).

12. Tracy, J. C., *J. Vacuum Sci. Technol.* **11**, 280 (1974).

13. Ertl, G., and Küppers, J., *Surface Sci.* **24**, 104 (1971).

14. Palmberg, P. W., *in* "Handbook of Auger Electron spectroscopy." Physical Electronics, Minnesota, 1972.

15. Legare, P., Lindauer, G., and Maire, G., unpublished.

16. Williams, F. L., and Nason, D., *Surface Sci.* **44**, 377 (1974).

17. Stoddart, C. T. H., Moss, R. L., and Pope, D., *Surface Sci.* **53**, 241 (1975).

18. McLean, D., *in* "Grain Boundaries in Metals." Clarendon, Oxford, 1957.

19. McDavid, J. M., and Fain, S. C., *Surface Sci.* **52**, 161 (1975).

20. Wehner, G. K., *in* "Methods of Surface Analysis," (A. W. Czanderna, ed.), p. 10. Elsevier, Amsterdam, 1957.

21. Hilaire, L., Legare, P., and Maire, G., unpublished.

22. Legare, P., and Maire, G., unpublished.

23. Trapnell, B. M. W., and Hayward, D. O., *in* "Chemisorption," Chap. VI. Butterworths, London, 1964.