

SURFACE COMPOSITION AND OXYGEN CHEMISORPTION ON Ag–Pd ALLOYS

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Ag–Pd alloys prepared by room temperature coprecipitation from solutions of the corresponding nitrates have been subjected to surface analysis by Auger electron spectroscopy. Previous work on the adsorption of O₂ on the same alloys showed that except for very high Pd concentration the adsorption heat was independent of alloy composition. On untreated and Ar ion sputtered alloys Pd enrichment in the surface layers was found, while on thermally annealed alloys (<0.1 Torr or 1 atm of H₂ or O₂), surface segregation of Ag took place. This is the expected result from surface tension and/or atomic size considerations. The relation of these findings with the earlier data on the chemisorption heat of oxygen is discussed. The implications of these conclusions upon present models of metallic alloys is pointed out.

1. Introduction

Several years ago heats of oxygen chemisorption were measured on Ag–Pd alloys which were prepared by room temperature coprecipitation from a solution of their nitrates [1]. Heats of oxygen chemisorption in the temperature range 500–700 K were deduced from measurements of the reaction equilibrium: $\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{O}(\text{s})$ (1), where g and s refer to gaseous and adsorbed phases respectively. Conditions were adjusted such that less than a monolayer of oxygen was chemisorbed by means of reaction equilibrium (1), the fraction of surface covered with adsorbed oxygen varying between 1×10^{-4} to 0.7. The experiments showed that the adsorption heat retained a value close to that corresponding to pure Ag (–54 kcal/mole) as the bulk alloy composition changed from 1 wt% to 100 wt% Ag. The heat of adsorption for oxygen on pure Pd was found to be –24.6 kcal/mole. From these results it was inferred that, in contrast to Pd, Ag figured preponderantly in the

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composition of the alloy surface. This suggestion was strengthened by the observation of the functional relationship between the adsorption equilibrium constant for reaction (1) and oxygen surface coverage: for the Ag-Pd alloys and pure Ag the function decreased with increasing oxygen surface coverage, while it was independent of coverage for Pd.

It may also be argued that the similarity of the behavior of oxygen adsorption between alloys and pure Ag resulted from the details of the adsorption itself and not by surface enrichment of Ag. This contention may be justified by the relatively large difference in adsorption heat between the two metals, and by the assumption that the electronic properties of Ag, which contribute to the Ag-O binding energy, are not substantially modified by the presence of Pd. According to this suggestion Pd acted simply as a diluent for Ag. There was much interest in the resolution of the problem for the understanding of the surface reactivity of these alloys but because of the difficulty in performing an independent analysis of surface composition, the matter could not be resolved at that time.

By means of Auger spectroscopy it is now possible to determine the surface composition of these alloys and to resolve between the two alternatives. Presently, we have subjected the same alloy samples which were employed in the original adsorption-equilibrium reaction (1) to Auger analysis and, consequently, provided for a more definitive interpretation of the earlier experiments.

2. Experimental

Details on alloy preparation and characterization may be found in earlier publications [1,2]. Briefly, aliquots of chloride free Ag and Pd nitrates were dissolved in distilled water. Concentrated HNO_3 , saturated with KNO_3 , was added. The solution was cooled to $0^\circ C$ and while stirring vigorously, HCHO and NaOH were added to a constant excess. The precipitate was decanted, washed and extracted in a Soxhlet extractor for 24 h, dried at $110^\circ C$. Clear separation of the α_1 - α_2 X-ray diffraction lines were obtained, thus permitting an accurate computation of the lattice constant [3]. The fact that Vegard's law was closely followed was taken as an indication of alloy formation [1]. Electron microscopic examination of Ag rich alloys showed extensive coalescence of the particles and a large amount of dendritic morphology with considerable internal structure (fig. 1) while Pd rich alloys appeared as a more compact, cellular aggregation of smaller crystallites (fig. 2). The morphology-composition interdependence of this alloy system was noted earlier on films evaporated on Pyrex glass [4]. The effect was correlated with the large difference in melting point of the metals.

Auger analysis was carried out with standard equipment (Physical Electronics Mod 540) employing a cylindrical mirror analyzer. Alloy samples were "supported" on In metal (99.999%) [5]. The experimental conditions were as follows: operating pressure 1.3×10^{-9} Torr, incident electron beam energy 3 keV, beam current



Fig. 1. Electron micrograph of Ag-Pd alloy, 70 at% Ag.



Fig. 2. Electron micrograph of Ag-Pd alloy, 10 at% Ag.

50 μ A, peak-to-peak modulation 3 V, time constant 0.001 sec, and normal incidence of the primary beam. Compositions, C_x (% atom fraction), were calculated by means of the equation [6]:

$$C_x = \frac{H_x/f_x}{(H_x/f_x) + (H_y/f_y)} \times 100, \quad (2)$$

where x, y correspond to Ag and Pd respectively, H is the Auger peak height, f the sensitivity factor. The validity of eq. (2) rests on the assumption that peak intensity is proportional to the molar fraction of a given alloy component. For the Pd–Ag system this assumption was found to be valid [7,8]. The $M_5N_{4,5}N_{4,5}$ transitions of Pd at 300 eV and that of Ag at 351–356 eV and sensitivity factors of 1 and 1.4, respectively, were employed [9]. Their relative amplitude could be reproduced to better than $\pm 3\%$. No overlapping of Auger peaks of the alloy components occurred. Each alloy was analyzed at various locations; variation in composition was found to be within ± 1 at%. Considering the reported Auger sampling depth of ~ 8 Å for Ag, 350 eV [10], we estimate about a similar sampling depth for the Ag–Pd alloys.

3. Results

The results obtained are reported in fig. 3. All alloy samples displayed a surface richer in Pd than their bulk. There was an almost constant compositional difference between surface and bulk for alloys with Ag content down to 37at%. The only detectable surface impurity was found to be carbon ($\sim 5\%$) whose level, however, did not vary appreciably among the alloys and as a result of the various gas and thermal treatments. A few sputtering experiments were carried out using Ar ions,

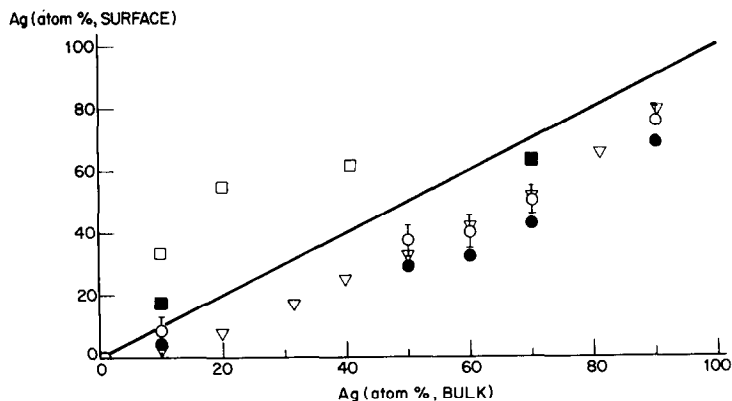


Fig. 3. Surface versus bulk composition of Ag–Pd alloys; (○) this work, no pretreatment; (●) this work, 10 min sputtering; (■) this work, 8 h, O₂, 1 atm; (▽) from ref. [8]; (□) from ref. [11].

Table 1

Effect of sputtering on surface composition of Ag–Pd alloys, Ar ions, 950 eV, 10 μ A, 5×10^{-5} Torr, 10 min

Bulk composition (Ag at%)	Treatment	Surface composition (Ag at%)
90	None	75
	Sputtering	70
70	None	50
	Sputtering	47
60	None	40
	Sputtering	35
50	None	37
	Sputtering	29
10	None	8
	Sputtering	5

950 eV, 10 μ A, 5×10^{-5} Torr, 2 and 10 min periods. Subsequent to sputtering the surface Ag content decreased (table 1). This is most likely attributable to the higher sputtering rate of Ag in relation to that of Pd [8].

The present results are consistent with previous Auger observations on polished Ag–Pd alloy tablets which had undergone sputtering experiments [8] (fig. 3), while the surface of epitaxially grown Ag–Pd alloy films (<1000 Å thick) showed no enrichment in either metal [7]. On vacuum fractured alloys, the surface composition reproduced very closely that of the bulk [8]. On Ag–Pd particles embedded on a support of an undisclosed nature surface Ag enrichment was detected [11] (fig. 3).

Table 2

Effect of thermal anneal and gas atmosphere on surface composition of Ag–Pd alloys

Bulk composition (Ag at%)	Treatment	Surface composition (Ag at%)
70	None	50
	H ₂ , 1 atm, 400°C, 3 h	73
	O ₂ , 1 atm, 300°C, 8 h	64
	Air, 0.5 Torr, 300°C, 7 h	67
50	None	37
	H ₂ , 1 atm, 400°C, 3 h	50
	Air, 0.5 Torr, 300°C, 7 h	53
10	None	9
	O ₂ , 1 atm, 300°C, 8 h	17

Because of the interest in investigating the effect of thermal anneal under different gas atmospheres on surface composition, experiments were carried out on alloys which had been annealed in H_2 (400°C, 1 atm, 3 h), in O_2 (300°C, 1 atm, 8 h), and at low residual pressure (300°C, 0.1 Torr, 7 h). Cooling to room temperature was carried out in a gas atmosphere similar to that prevailing during the high temperature anneal. The results are collected in table 2.

4. Discussion

In the temperature range of interest Ag and Pd form a continuous series of disordered solid solutions [12]. Ag has a lower surface tension and a smaller atomic radius than Pd. Consequently, it is to be expected that Pd atoms at the surface of Ag–Pd alloys have a tendency to exchange with Ag atoms from the interior, leading to a surface enrichment of Ag. Quantitative predictions on the amount of enrichment are dependent upon various assumptions – possible role of short-range order [13] and/or of non-nearest neighbors interchange – which are difficult to define with precision. Experimental measurements of surface composition agree with this simple model. Using photoelectron emission [14] and CO adsorption [15] on alloy films, Ag enrichment was found, while the composition of surface (100) and (111) planes of epitaxially grown alloy films (250–1000 Å thick) was found by Auger spectroscopy to be similar to that of the bulk [7]. Thus, under some conditions size and/or surface tension effects may not be sufficient to produce preferential segregation of Ag at the surface. In the latter studies Ag enrichment was present in non-equilibrated films only. Inspection of fig. 3 shows that in the present investigation, with the exception of the 1 and 10 Ag at% alloys, the latter were enriched in Pd. This was a consequence of the preparation method employed and the resulting conditions of growth of alloy nuclei during precipitation. If the reduction rate of $Ag(NO_3)$ in solution was faster than that of $Pd(NO_3)_2$, local depletion of the Ag salt may have taken place, even under vigorous stirring, and an increasingly higher amount of Pd may be accumulated in layers closer to the surface. This effect may be supported by the observation that for low Ag content, the bulk composition was very nearly equal to the surface composition while Pd enrichment set in and increased with increasing Ag bulk content. At high Ag, the excess over Pd was sufficient to overcome any local depletion which may have been generated by a faster precipitation rate (fig. 3). Further support for the existence of different precipitation conditions between alloys with low and high Ag content is derived from the observation of the drastically different morphology of the 10 and 70 Ag at% alloys (figs. 1 and 2). Surface composition and morphology of the alloys were controlled by local conditions during precipitation.

Two important conclusions may be drawn from the experiments on thermal anneal, namely: (a) surface Ag segregation increased, irrespective of the conditions prevailing in the surrounding gas phase, (b) at the relatively high temperature of

400°C ($\sim 0.55 T_m$ for Ag) surface–bulk equilibrium was not achieved even after 3 h treatment. In contrast to this relatively slow equilibration, on alloy films equilibrium was found to set in rapidly at 250°C [4]. Sputtering with Ar ions was found to increase the surface content in Pd. This is an expected result in view of the faster sputtering rate of Ag [8].

The results of the earlier study on the heats of adsorption of oxygen have been replotted using the surface compositions observed in the present work (fig. 4). It should be noted that some caution must be exercised in comparing a typical monolayer effect (chemisorption) to a multilayer phenomenon (Auger electron emission). In fact, it may happen that by converting the Auger signals to atomic layer compositions, through a knowledge of the electron attenuation length, differences in the first layer from the values averaged over the few topmost layers may be found [16]. Assuming that these differences are not significant for the present alloys, some important conclusions may be drawn from the characteristic correlation shown in fig. 4. It should be noted that surface compositions of the untreated alloys have been used in fig. 4 (instead of the H₂ annealed used in the study of the reaction equilibrium (1) [1], since the H₂ treatment did not produce a significant surface composition change (table 2). Fig. 4 shows that the value of the adsorption heat of oxygen is almost independent of the surface composition of the alloys and very near to that for pure Ag. This observation, together with the realization that the alloy surface of all samples except the 1 and 10% Ag alloys, contained Pd in excess to the equilibrium composition, indicates that the behavior represented in fig. 4 was the result of the nature of the adsorption itself and not of excess Ag segregation at the surface. This conclusion raises two questions regarding the electronic nature of (a) the Ag–oxygen bond, and of (b) the Ag–Pd alloys. Although a detailed analysis of both of these questions is not possible here, we shall endeavour to indicate a few relevant points. Clearly the almost constant value of the oxygen adsorption heat on a surface containing large amounts of Pd cannot be easily reconciled with an alloy model which assumes that Ag and Pd form common bonds and

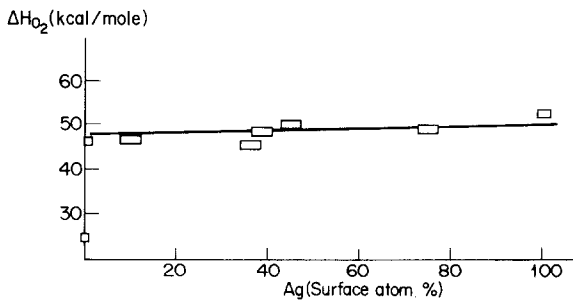


Fig. 4. Surface composition of Ag–Pd alloys versus heat of O₂ chemisorption, ΔH_{O_2} (from ref. [1]).

that Ag s-electrons lead to filling of the Pd d-states until the 60 wt% Ag composition is reached. Since oxygen–Ag bonding involves s-electrons from Ag and p-electrons from oxygen, it is difficult to visualize how with increasing Ag concentrations, the energy of the bond remains practically constant while the availability of s-electrons increases. A different model for metallic alloys assumes that each component is well screened from the other and has the same electronic structure as the pure phase [17]. Additions of Pd simply dilute Ag leaving its adsorption characteristics unchanged and the overall adsorption behavior of the alloy is a superposition of those of the two metals. Because of the relatively large difference between Ag and Pd in the adsorption heat for oxygen, it is most likely that Ag atoms only were covered with oxygen. Thus, the present results are more consistent with this latter alloy model, even though it appears that some changes in the s-electron population of Ag upon alloying with Pd must be allowed for [18]. Other effects, including the possibility of formation of Ag surface clusters, sharing in the chemisorption bond and giving an adsorption heat essentially similar to that of Ag, may also be invoked, but a realistic quantification of this idea is hard to achieve. The conclusion seems inescapable that dilution of Ag with Pd did not influence the chemisorption bond energy of O₂ on Ag; and one is essentially confronted with a dilution effect. Interestingly, a similar picture has emerged from studies on CO chemisorption on Pd and Ag–Pd [19]. In this instance, the frequency of IR bands of CO adsorbed on Pd sites remained almost constant with varying alloy composition. Also, the activation energy for CO desorption was found to be insensitive to alloy composition. The Authors conclude for a decisive effect of Ag dilution upon the geometry of the Pd adsorption site, the latter being important for the various adsorption modes of CO.

5. Conclusions

Ag–Pd alloys, prepared by low temperature precipitation from solutions of the corresponding nitrate, follow closely Vegard's law, but show Pd enrichment at the surface in contrast with the Ag enrichment which may be expected from surface tension and/or atomic size considerations. It is suggested that the compositional inhomogeneity between surface and bulk is the result of nucleation and growth rate differences between Pd and Ag. The thermodynamic affinity of Ag in oxygen chemisorption was not influenced by Pd alloying, which acted as an almost inert diluent to Ag. Interestingly, this behavior is reminiscent of that observed earlier in CO chemisorption, whose initial heat was found to be largely independent of alloy composition [7]. We conclude that electronic interactions responsible for metal–metal bonding in the alloy did not have a primary role in the metal–oxygen bonding at the surface.

Surface composition in the Ag–Pd system is controlled by conditions employed in the preparation and treatment of the alloy. Depending upon the temperature–time–atmosphere chosen, a surface enriched in either Ag or Pd may be obtained and retained even at moderate temperatures.

Finally, oxygen chemisorption seems to indicate a surface whose structure and composition are controlled by a simple dilution of Ag atoms by Pd in a disordered fashion rather than by atomic ensembles of fixed composition and structure [20].

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References

- [1] M.H. Bortner and G. Parravano, in: *Advances in Catalysis and Related Subjects*, Vol. 9 (Academic Press, New York, 1957) p. 424.
- [2] F. Hund and E. Tragner, *Naturwissenschaften* 39 (1952) 63.
- [3] M. Straumanis and A. Ievins, *Die Präzisionsbestimmung der Gitterkonstanten nach Asymmetrischen Methode* (Springer, Berlin, 1940).
- [4] R.L. Moss and D.H. Thomas, *J. Catalysis* 8 (1967) 151.
- [5] G.A. Theriault, T.L. Barry and M.J.B. Thomas, *Anal. Chem.* 47 (1975) 1492.
- [6] P.W. Palmberg, *Anal. Chem.* 45 (1973) 549A.
- [7] K. Christman and G. Ertl, *Surface Sci.* 33 (1972) 254.
- [8] H.J. Mathieu and D. Landolt, *Surface Sci.* 53 (1975) 228.
- [9] P.W. Palmberg, G.E. Riach, R.E. Weber and N.C. McDonald, *Handbook of Auger Electron Spectroscopy* (Physical Electronics Industries, 1972).
- [10] P.W. Palmberg and T.N. Rhodin, *J. Appl. Phys.* 39 (1968) 2425.
- [11] B.J. Wood and H. Wise, *Surface Sci.* 52 (1975) 151.
- [12] M. Hansen, *The Constitution of Binary Alloys* (McGraw-Hill, New York, 1958);
J.N. Pratt, *Trans. Faraday Soc.* 56 (1960) 975;
R. Oriani and W.K. Murphy, *Acta Met.* 1 (1962) 879;
J.P. Chan and R. Hultgren, *J. Chem. Thermodynamics* 1 (1969) 45.
- [13] R.W. Westerland and M.E. Nicholson, *Acta Met.* 14 (1966) 569.
- [14] R. Bouwman, G.J.M. Lippits and W.M.H. Sachtler, *J. Catalysis* 25 (1972) 350.
- [15] J.J. Stephan, P.L. Franke and V. Ponec, *J. Catalysis* 44 (1976) 359.
- [16] J.M. McDavid and S.C. Fain, *Surface Sci.* 52 (1975) 161
- [17] N.D. Lang and H. Ehrenreich, *Phys. Rev* 168 (1968) 605.
- [18] C. Norris and H.P. Myers, *J. Phys. F1* (1971) 62;
E.A. Stern, *Physics* 1 (1965) 255.
- [19] Y. Soma-Noto and W.M.H. Sachtler, *J. Catalysis* 32 (1974) 315.
- [20] D.A. Dowden, in: *Catalysis, Proc. 5th Intern. Congr. on Catalysis, Miami Beach, 1972*, Ed. J.W. Hightower (North-Holland, Amsterdam, 1973) Vol. 1, p. 621.