



# Surface characterisation of cobalt–palladium alloys

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## Abstract

Bimetallic alloy surfaces exhibit quite different adsorption properties from properties of the elemental metal surfaces. The differences in the behaviour can be explained in terms of electronic (ligand effects) and structural (ensemble composition effects) concepts.

In this work, Auger electron spectroscopy-thermal desorption spectroscopy measurements were used to characterise the surface of two polycrystalline  $\text{Co}_{50}\text{Pd}_{50}$  and  $\text{Co}_{37}\text{Pd}_{63}$  (at.%) alloys exposed to some oxygen-containing probe molecules, i.e. CO,  $\text{O}_2$  and  $\text{N}_2\text{O}$  at 300 K. In addition, X-ray photoelectron spectroscopy was used to elucidate the variation of electronic properties of Co and Pd upon alloying. The studied alloy surfaces proved to be active in dissociative chemisorption of  $\text{O}_2$  and  $\text{N}_2\text{O}$  as well as in the chemisorption of molecular CO. The desorption measurements revealed that CO molecules were less tightly bound to these surfaces than to the individual metals. This observation suggests an electronic interaction between Co and Pd atoms in the alloy, as evidenced by X-ray photoelectron spectroscopy measurements for core and valence bands.  $\text{N}_2\text{O}$  decomposition process resulted only in molecular  $\text{N}_2$ , which promptly desorbed, and O atoms, which remained at the surface, poisoning further  $\text{N}_2\text{O}$  adsorption by a site blocking mechanism. Amount of desorbing oxygen molecules significantly depended on the exposure of both  $\text{O}_2$  and  $\text{N}_2\text{O}$  adsorbates and the Co surface concentration (an ensemble composition effect).

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## 1. Introduction

The effect of adding a metal to another one has historically been argued to be geometric or electronic. The geometric effect refers to the creation of an optimal ensemble of the active metal atoms upon coordination with a second metal. The electronic or ligand effects refer to a change in the local electronic

structure upon addition of a second metal due to charge transfer, orbital rehybridization or other changes in the electronic structure. Coq and Figueras [1] recently published an excellent review of both the electronic and geometric effects of alloying Pd with a second metal.

Both the geometric and the electronic effects alter chemical properties of bimetallic alloy surfaces with respect to properties of the elemental metal surfaces [2]. It is difficult, however, to completely distinguish between the two effects. In addition to the strict electronic and geometric effects, the unique effects of mixed sites are also known [1].

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Nowadays, surface characterisation of the Co–Pd alloy system by electron spectroscopies and gas adsorption is still very scarce. In this alloy system, a tendency to Pd surface segregation has been found previously [3]. In addition, when oxygen was adsorbed on polycrystalline  $\text{Co}_{50}\text{Pd}_{50}$  surface, the surface segregation of cobalt and its reaction with oxygen were evidenced [4]. Beyond bulk alloys, Co–Pd layer systems have also been studied [5,6]. The alloying effect at the interface of Co/Pd in such systems with different stoichiometry were clearly visualized in the photoelectron spectra [5,6]. In order to study changes in reactivity, induced by the alloying, Matolinova et al. [6] investigated CO adsorption properties of the alloys. A significant weakening of the CO bond to Co–Pd alloy surface compared to pure Pd was observed [6].

In this paper the interaction of bulk  $\text{Co}_{50}\text{Pd}_{50}$  and  $\text{Co}_{37}\text{Pd}_{63}$  (at.%) alloys with CO,  $\text{O}_2$  and  $\text{N}_2\text{O}$  molecules at 300 K is reported. Part of the  $\text{O}_2$  and  $\text{N}_2\text{O}$  results obtained by the combined use of Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS) were published in previous papers [4,7]. In the present paper more details concerning  $\text{O}_2$  and  $\text{N}_2\text{O}$  adsorption are presented, the TDS measurements have been extended to CO and, in addition, the XPS results of the Co–Pd alloys with respect to the pure metals are added.

## 2. Experimental

A polycrystalline Co–Pd alloy sample with the bulk composition  $\text{Co}_{50}\text{Pd}_{50}$  (at.%) was used in the gas adsorption study. Details concerning the preparation of this sample has been reported previously [3]. Its surface and the  $\text{Co}_{37}\text{Pd}_{63}$  (at.%) alloy surface, prepared by annealing ( $T = 773$  K,  $t = 5$  min) of the  $\text{Co}_{50}\text{Pd}_{50}$  alloy sample under UHV conditions [3] were studied. Two Co–Pd alloy samples with bulk compositions (at.%)  $\text{Co}_{30}\text{Pd}_{70}$  and  $\text{Co}_{70}\text{Pd}_{30}$ , and two pure metal samples of 4N cobalt (Johnson Matthey, UK) and 4N palladium (Mennica Panstwowa, Poland) were used in the XPS study.

Gas adsorption experiments have been performed in an UHV chamber ( $p \leq 1 \times 10^{-7}$  Pa) equipped with three-grid retarding field analyser (VG, UK) for the AES-LEED studies and a quadrupole mass spectro-

meter (QMS 7B, VG, UK) for the TDS measurements. Prior to adsorption studies, the alloy sample was carefully cleaned by cycles of  $\text{Ar}^+$  ion bombardment (300 eV,  $1 \mu\text{A}/\text{cm}^2$ , 1 h) and annealing (973–1073 K) until the carbon and sulphur peaks corresponding to contamination disappeared. The Auger derivative spectra were recorded at 300 K using a modulation voltage of 10 V rms and a primary electron beam energy of 1.3 keV. Surface composition of the samples was investigated by AES and XPS using earlier quantitative studies on Co–Pd alloys [3].

Carbon monoxide (C.P. grade, Matheson, USA), oxygen (spec.pure, VEB Techn.G.W., Germany) and nitrous oxide (99.6% purity, Matheson, USA) were introduced into the chamber by its backfilling to  $1 \times 10^{-6}$  Pa. The gases were adsorbed on the Co–Pd surface at 300 K. Gas exposures are given in langmuirs ( $1 L = 1.33 \times 10^{-4}$  Pa s) uncorrected for

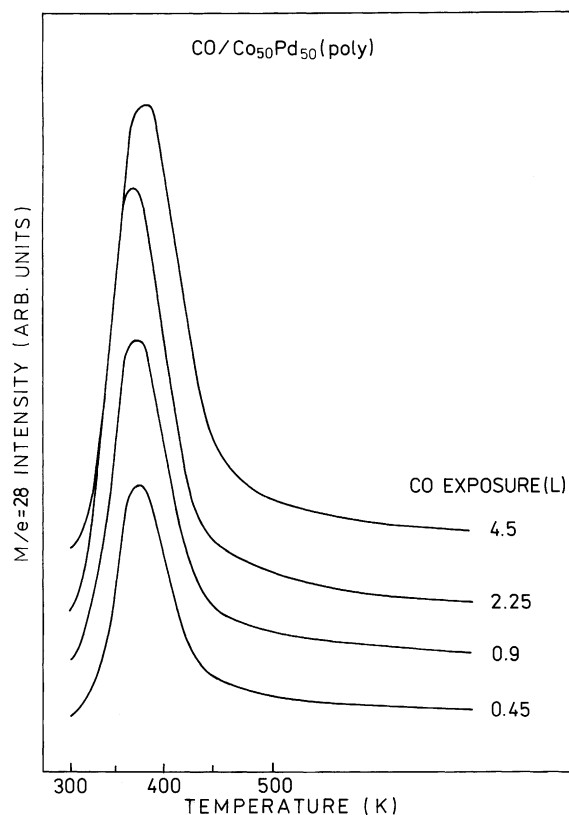


Fig. 1. Carbon monoxide ( $M/e = 28$ ) TD spectra from polycrystalline  $\text{Co}_{50}\text{Pd}_{50}$  alloy surface after different CO exposures ( $p = 1 \times 10^{-6}$  Pa) at 300 K. Heating rate 27.7 K/s.

the ionization gauge factor. Desorption products were analysed by a quadrupole mass spectrometer. The sample heating rate ( $\beta$ ) was about 26 K/s in all TDS experiments.

The XPS measurements were performed using a VG Scientific ESCALAB-210 spectrometer [8]. Quantitative XPS analysis [9] was based on the Co 2s, Co 2p, Pd 3s, Pd 3p and Pd 3d photoelectron spectra. Data were analysed using the ECLIPSE VG program, including satellite subtraction, Shirley background subtraction and fitting procedure.

### 3. Results and discussion

Exposures of both the  $\text{Co}_{50}\text{Pd}_{50}$  and  $\text{Co}_{37}\text{Pd}_{63}$  alloy surfaces to carbon monoxide and nitrous oxide at 300 K did not result any change of the respective surface composition analysed by AES and XPS [7,12]. This behaviour is quite different to that observed for the  $\text{Co}_{50}\text{Pd}_{50}$  exposure to oxygen at  $T > 300$  K where surface segregation of Co takes place [4].

Fig. 1 shows a set of CO-TD spectra from the  $\text{Co}_{50}\text{Pd}_{50}$  surface following exposures of 0.45–4.5 L (saturation) at 300 K. Under these conditions only one desorption peak is observed with its maximum around

365 K. This desorption state, lying significantly lower than the desorption peak from pure metals [10,11], is assigned to selective CO adsorption on Pd atoms in the alloy [12]. CO adsorbs preferentially on Pd sites, however the adsorption is destabilized with respect to pure Pd, which is reflected in the lower CO-desorption temperature [12]. Since a geometrical ensemble effect can be excluded because the CO molecules occupy the same adsorption sites on both Co–Pd and Pd surfaces, the weakened interaction is an unequivocal proof for an electronic effect [12–14]. Similar electronic and chemical perturbations have been reported for Co–Pd layer systems [6] and other Pd-based alloys [13–15].

The studied alloy surfaces proved to be active in dissociative chemisorption of  $\text{O}_2$  [4] and  $\text{N}_2\text{O}$  [7] (Fig. 2).  $\text{N}_2\text{O}$  decomposition process resulted only in molecular  $\text{N}_2$ , which promptly desorbed, and O atoms, which remained at the surface, poisoning further  $\text{N}_2\text{O}$  adsorption by a site blocking mechanism. Exposures of the Co–Pd alloy surfaces to  $\text{N}_2\text{O}$  at 300 K resulted in  $\text{O}_2$  desorption traces essentially similar to those seen after the  $\text{O}_2$  adsorption [4]. This result reveals that the same immobile oxygen adsorbate was bonded to cobalt surface atoms in both cases. Moreover, the increase of cobalt surface concentration promoted the oxygen chemisorption. Amount of

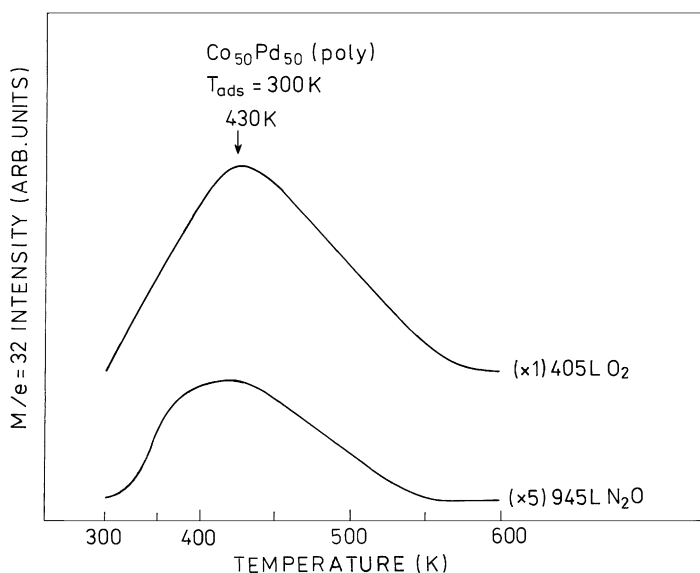


Fig. 2. Oxygen ( $M/e = 32$ ) TD spectra from polycrystalline  $\text{Co}_{50}\text{Pd}_{50}$  alloy surface after exposure to 405 L  $\text{O}_2$ , and 945 L  $\text{N}_2\text{O}$  at 300 K.

Table 1

The XPS core-level binding energies of Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> for bulk Co–Pd alloys and pure Pd (accuracy ± 0.2 eV)

Sample	BE (eV)	
	Pd 3d <sub>5/2</sub>	Pd 3d <sub>3/2</sub>
Pd	335.15	340.40
Co <sub>30</sub> Pd <sub>70</sub>	335.50	340.75
Co <sub>70</sub> Pd <sub>30</sub>	335.81	341.10

desorbing oxygen molecules significantly depended on the exposure of both O<sub>2</sub> and N<sub>2</sub>O adsorbates and the cobalt surface concentration (ensemble composition effect).

Finally, we used XPS to elucidate the variation of electronic properties of Pd and Co upon alloying. Table 1 shows the Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> core-level binding energies for two Co<sub>30</sub>Pd<sub>70</sub> and Co<sub>70</sub>Pd<sub>30</sub> (at.%) bulk alloys and pure Pd. The most interesting feature of the Co–Pd alloys is that the Pd 3d peaks shift to higher binding energy as the Co concentration increases. More details on the XPS results reported here are published elsewhere [12].

Generally, it is known that the core-level shifts are related to the changes in valence state through the hybridization that occurs between metal atoms upon alloying. The effect reported in the present paper has been already described in the case of Co–Pd layer systems [6].

#### 4. Conclusions

The studied Co–Pd alloy surfaces were characterised by gas adsorption (CO, O<sub>2</sub>, N<sub>2</sub>O) and electron

spectroscopies (AES, XPS). CO seems to chemisorb preferentially on Pd surface atoms with a distinct weakening of the Pd–CO chemisorption bond. The behaviour of oxygen originating from the dissociation of nitrous oxide is consistent with the general trend for the oxidation of the Co–Pd alloy surfaces using O<sub>2</sub>. The significant shifts of the Pd 3d core bands observed by XPS and, moreover, the change in the adsorption energy of CO are attributed to a strong electronic interaction between Pd and Co upon alloying.

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