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Oscillations of surface composition in Pt-Co alloys induced by CO chemisorption

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The influence of carbon monoxide adsorption on surface composition of cobalt alloys, containing 30 and 1 at.% platinum was studied by low energy ion scattering spectroscopy and X-ray photoelectron spectroscopy. Composition oscillations in Co/Pt ratio across the several outermost layers and caused by CO chemisorbed at 400 K were found. XPS indicated the presence of both molecular and dissociatively adsorbed CO. A possible explanation of the surface process which cause these oscillations is proposed.

Keywords: LEISS, AR XPS; binary alloys; surface segregation; compositional oscillations

1. Introduction

The study of the oscillation of the composition of surface layers is of direct interest for catalysis by metals and alloys, since they can reflect not only the thermodynamics of the surface but also reaction dynamics, including the well-known kinetic oscillations of catalytic reaction [1]. A discontinuous profile of the upper layer composition is expected from the sandwich model of segregation of exothermic solid solutions and ordered intermetallics [2]. However, experimental evidence of oscillations in surface composition are scarce. Video-LEED proved that they occur for $\mathrm{Pt}x\mathrm{Ni}_{1-x}$ alloys [3]. Recently the same conclusion was drawn for $\mathrm{Pt}_{80}\mathrm{Co}_{20}$ solid solution and CoPt_3 intermetallics [4], from a combination of ARXPS and LEISS measurements, but the conclusions reported are not unambiguous.

To our knowledge sandwich structures for bimetallic alloys with adsorbed adlayer have never been observed, although similar oscillations can be predicted in cases where the alloy components would have different reactivity and bond strength with molecule chemisorbed. Our ARXPS and LEISS study attempted to follow the upper layer composition in Pt-Co alloys, especially after CO chemisorption. Since Pt and Co greatly differ in catalytic activity in both CO oxidation and hydrogenation, and in their ability to dissociate CO, we may expect a mutual influence of these components on adsorptive behaviour and its dependence on surface and bulk composition. Unlike Pt-rich Co alloys studied previously [4,5], where the topmost layer was assumed to be pure Pt and only molecular CO adsorption was observed, we examined Co-rich alloys, where the competition for CO adsorption would be much stronger. In agreement with these expectations we have found both molecular and dissociative forms of CO adsorption, and also abnormal oscillations in the Co/Pt ratio in the first 6–8 layers, caused by CO chemisorbed at 400 K.

2. Experimental

The Pt-Co alloys (30% and 1% Pt) were obtained by direct melting of the metals in an inert atmosphere. X-ray diffraction revealed the formation of a solid solution of Pt in Co, with a face centre cubic lattice. XPS spectra were measured with Kratos XSAM-800 spectrometer using MgK_α source [6]. Initially the surface was annealed in vacuum at 623 K, and then cleaned additionally with Ar^+ for a short time, to avoid preferential sputtering and surface amorphization. The purity of the surface was checked by C 1s and O 1s lines, whose intensity did not exceed a few percent of the metal peak amplitude. The vacuum during measurement was better than $2*10^{-10}$ Torr. XPS spectra were detected at normal and grazing ($\Theta = 15°$, $\Theta = 5°$) take-off angles, to enhance the surface sensitivity. CO adsorption was performed in the preparation chamber of the spectrometer at 300 K and 400 K, and an exposure of 3600 L ($4*10^{-6}$ Torr × 900 s). After the sample was cooled to 300 K and CO excess was pumped out, the sample was transferred into the analysis chamber.

To obtain LEISS spectra, He^+ ions with 1 keV energy were excited, and the ion current was less that 100 nA. LEISS spectra were recorded immediately after exposing the sample to He^+ and scans were repeated at 3 min intervals.

3. Results

3.1. OSCILLATIONS OF SURFACE COMPOSITION

Fig. 1 demonstrates time-dependent LEISS spectra obtained for Co-30 Pt alloy pretreated with CO at 400 K. Two distinct changes with time are the increase of absolute amplitude, which is usually observed in ISS, and alternate changes of the relative intensity for both components. The latter changes are more distinct in fig. 2, which shows oscillations of the Co/Pt ratio, and a steady

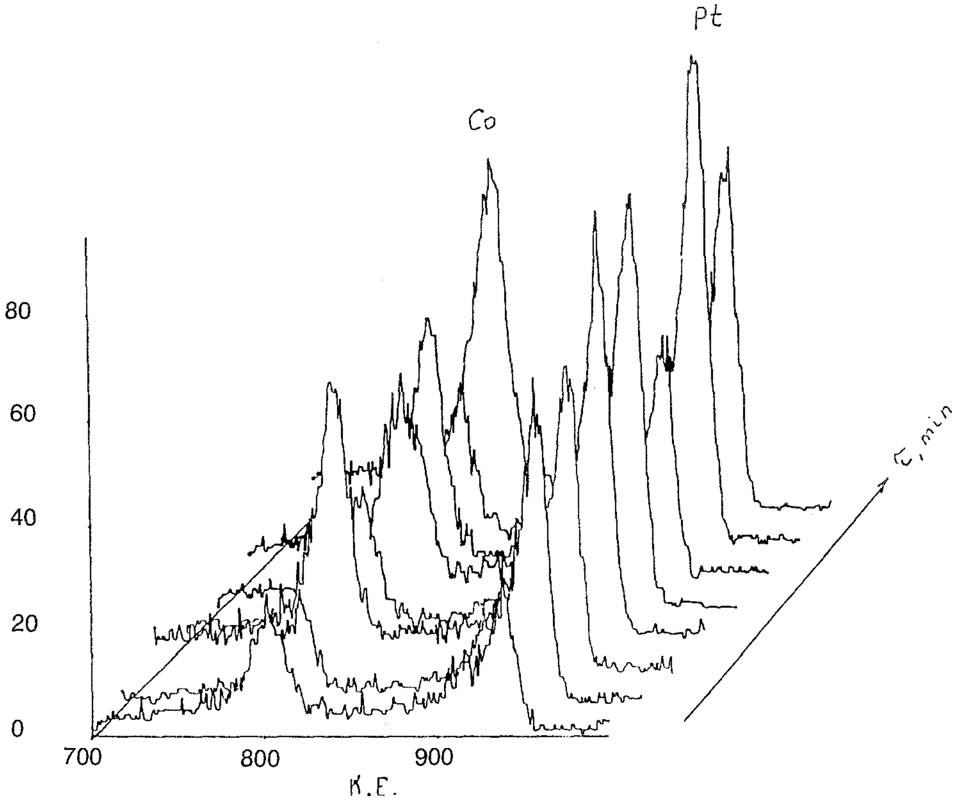

Fig. 1. Time-dependent LEISS spectra for the Co-30Pt alloy surface, pretreated with CO at 400 K. Spectra were recorded using He^+ ions at a primary energy of 1 keV.

decrease in the amplitude during four cycles. It must be underlined that oscillations were observed only after CO adsorption. No change of Pt/Co LEISS ratio was found when the initial specimen was measured for the same period (fig. 2, curve 3). This allows us to calibrate the ISS intensities via the XPS Co/Pt ratio for the initial alloy. Such a calculation indicates a slight surface enrichment with Pt for the initial Co-30Pt sample. Using this calibration factor from the alloy covered with CO, gives (Co/Pt) max ISS = 8.1 and (Co/Pt) min ISS = 1.2. That means we have Co-10Pt in Co-enriched region and 45Pt–55Co Co-depleted region. Except for the first point on curve 1, the analysed layer was in average enriched in Co with respect to the bulk. But the extent of this enrichment changes substantially and non-monotonously from layer to layer, the last two minimum corresponding to Pt-enriched layers with respect to initial alloy.

3.2. CO ADSORBED STATES

The alloy behaviour in CO chemisorption depends on Pt concentration (30 or 1%) and adsorption temperature. XPS spectra obtained after 300 K adsorption

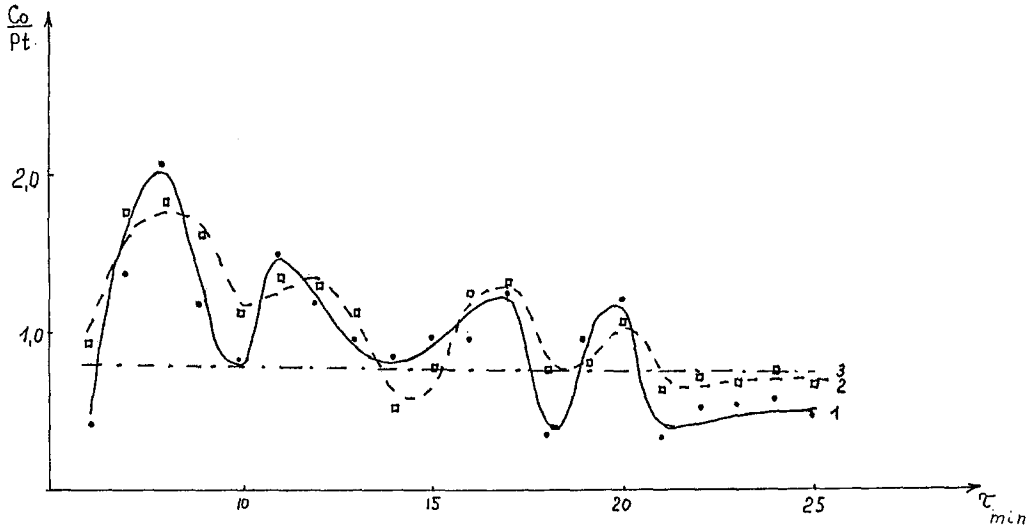

Fig. 2. Oscillations of Co/Pt LEISS intensity ratio after adsorption of CO (400 K, 3600 L) for the Co-30Pt alloy.

1-first set } CO, 400 K, 3600 L
2-second set }
3-pure surface.

revealed a C 1s peak with B.E. 285.9–286.0 eV and an O 1s peak with B.E. of 530.3–530.6 eV, which can both be attributed to moleculary adsorbed CO. The Co/Pt ratio remained practically the same, but the LEISS Co signal intensity decreased in upper layer. This can be explained by Co screening due to preferential CO adsorption on Co 'part' of the alloy. The Co 2p line position and shape remained the same as for the initial alloy.

When the adsorption temperature was raised to 400 K, an additional peak in the C 1s spectrum with B.E. 283.4 eV appeared, which can be assigned to surface carbon formed by CO dissociation [7]. This is additionally confirmed by the observation of an O 1s peak with B.E. of 529.4 eV, which belongs to 'oxidic' oxygen (fig. 3). The Co $2p_{3/2}$ line shape confirmed Co oxidation and the total Co/Pt ratio increased (table 1). the extent of Co oxidation for the Co-1Pt alloy after 3600 L exposure to CO corresponds to that which was obtained after 10 L exposure to oxygen at the same temperature [8]. The oxygen released from CO is likely to interact with Co atoms and draws them to the surface, since CoO formation is thermodynamically favourable. The depth of this altered layer can be estimated as 8–12 Å, taking into account that CoO and O 1s with B.E. of 529.4 eV became detectable only at $\Theta = 15°$.

All these trends are also valid for Co-30Pt alloy (table 1), the differences being the extent of CO dissociation and Co oxidation. The 'carbidic' carbon fraction decreased from 25 to 15% and the CoO fraction decreased from 28 to 12%. That means when the Pt concentration increased, more CO was adsorbed

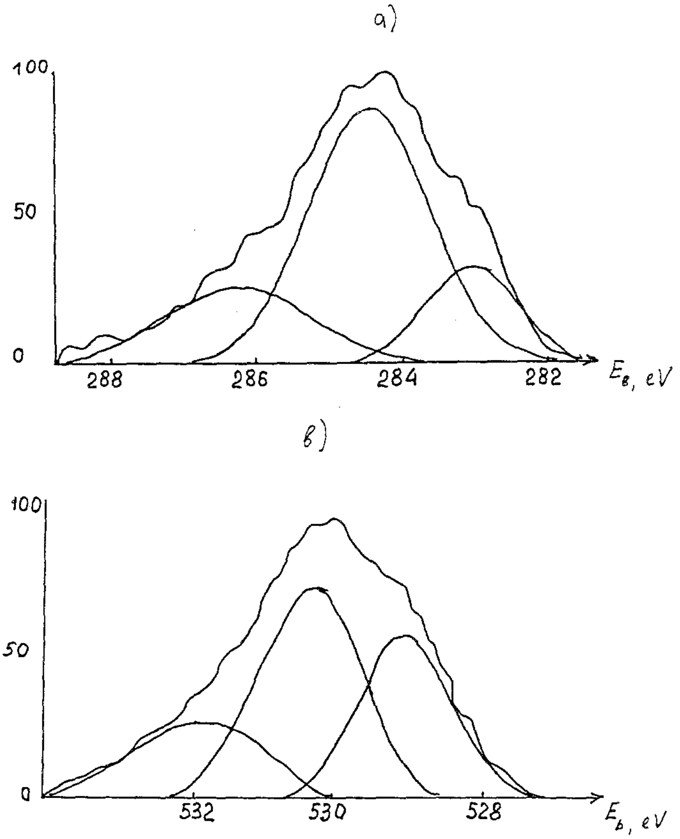

Fig. 3. C 1s and O 1s regions of XPS spectra ($\Theta = 15°$) for the Co-1Pt alloy, pretreated with CO at 400 K. a) C-1s; b) O-1s. The synthesis peak program was used to single out the components (the curves under the envelope). Peaks with B.E. 284.4 eV (C-1s) and 532.3–5 eV (O-1s) belong partially to contaminations.

in the molecular form, but there is also no doubt that a part of CO dissociates on Co-30Pt alloy. Again the XPS Co/Pt ratio ($\Theta = 15°$) increased, but at $\Theta = 90°$ no alteration of surface composition was observed by XPS.

4. Discussion

The most striking and intriguing feature found in this work are the non-monotonous changes of surface composition for Co-30Pt alloy. They are reproducible, and observable only after high temperature CO adsorption. Neither annealing the surface nor CO adsorption at room temperature results in similar oscillations. The oscillations are strongly correlated with the existence of two

Table 1
XPS data of adsorbate states and surface composition of Co-Pt alloys

Alloy	Co [b]	Co	% Co	E_B [a]	E_B [a]
	Pt, $\Theta = 90°$	Pt, $\Theta = 15°$		O-1s	C-1s
Co-1Pt 300 K, CO	36.80	39.20	100%	530.3-(74%) 532.4-(24%)	284.4-(58%) 285.9-(41%)
Co-1Pt 400 K, CO	41.20	48.20	72%	529.4-(28%) 530.6-(42%) 532.3-(30%)	283.4-(26%) 284.4-(54%) 285.8-(20%)
Co-30Pt 300 K, CO	1.29	1.27	100%	530.2-(50%) 532.5-(50%)	284.6-(66%) 286.0-(31%)
Co-30Pt 400 K, CO	1.26	1.66	88%	529.4-(17%) 530.2-(50%) 532.3-(32%)	283.6-(15%) 284.8-(60%) 285.9-(25%)

[a] XPS spectra have been measured at take-off angle of photoemission $\Theta = 15°$, the B.E. values and the relative concentrations (%) of certain states were determined from the peak synthesis procedure.

[b] Initially surface of alloys was slightly enriched in platinum and the Co/Pt ratios were 33.0 and 1.3 respectively.

different forms of CO adsorption–molecular and dissociative. This allows us to propose that the oscillations are related to 'mixed' adsorption and/or surface reactions which can accompany CO adsorption. We can rule out preferential sputtering or other ion-stimulated effects as the consequence of observed profile. XPS analysis performed after LEISS gives the same Co/Pt ratio at $\Theta = 15°$, and some Co oxide is still detected. That means that sputtering is not so extensive and its rate is much less than is usually the case with Ar^+. In our conditions this does not exceed 1 Å/min [6]. On the other hand, static ISS is not provided by our conditions, so we suggest that the observed pattern is actually a depth profile rather than just the first layer composition, which might appear to be changed during CO ion-stimulated desorption. Nevertheless, we cannot exclude the contribution of these effects completely. Bearing this in mind we believe that oscillations observed indeed reflect a periodic change of composition in several surface layers.

The two layer sandwich structure is characteristic of Pt-rich alloys [4,5,9,10] with electropositive elements (Ni, Co, Ti), but for Co-rich alloys such behaviour was not observed. We can, however, expect that after one component segregates to the surface the other one will enrich the second layer, due to intermetallic bonding. If so, Co segregation due to CO dissociation can lead to Pt, populating the second layer. It is likely that the observed multilayer sandwich structure can reflect more complicated processes that are involved in reconstruction and growth of the adlayer structure.

At the moment we have no definite explanation such a structure form does. One tentative suggestion is the following: CO dissociation results in Co surface segregation and displacement from the regular structure, due to formation of small oxide islands (at least included pair of Co atoms). The fact that the first point on the curve gives an enriched Pt composition can be explained by covering Co with adsorbate, or that Pt is on 'top' sites of the surface. We suppose that a few points up to the first maximum belong to the same first layer and that He^+ scattering by that time has desorbed weakly held CO. Because of possible Co atom displacement, the second layer is now exposed to He^+ ions, and we have found relative Pt enrichment in this layer (first minimum). After Co oxide formation in the first layer, CO dissociation will be stopped and molecular bonding CO with Pt will occur preferentially. But CO dissociation can be initiated again if CO, adsorbed on adjacent Pt sites, starts to react with surface oxygen:

$$CO + O - Co \dashrightarrow CO_2 + Pt\text{-}CO$$

to reduce Co on the surface. It is likely that only the surface monolayer rather than the subsurface layers will be involved in such CO oxidation. So, two more subsurface layers will keep the composition formed during initial CO adsorption: Pt rich layer beneath a Co rich layer [5]. After oxygen has been removed from the surface and/or diffused in the bulk, CO dissociation on Co atoms can start again leading to renewal of first and next surface layer. Due to oxygen migration into deeper layers, and further Co segregation, we will have again the same structure of the first two or three layers, but the alternating region will expand up to 4–6 layers. The occurrence of several such cycles of reaction will result in the picture observed.

An attempt to develop a more detailed mechanism of the surface and near-surface reconstruction by studying different alloy compositions and adsorbates is in progress.

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