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Surface core level spectroscopy of the Pt₂₅Co₇₅ (110) and (100) alloy surfaces

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Abstract: Core level photoemission spectroscopy of the Pt 4f_{7/2} level is used to investigate the surface and bulk Pt environments in the disordered alloy Pt₂₅Co₇₅. For the (110) face no Pt is observed at the surface, and only a single Pt bulk site is identified with a chemical shift of 250meV. For the denser (100) face the same bulk site is observed together with a surface peak, corresponding to a surface layer with Pt enrichment. The chemical shift at the surface is weaker than in the bulk.

1. INTRODUCTION

Pt-M alloys (where M is a 3d transition metal) have a great number of potential applications in the field of catalysis (e.g. M=Fe: [1,2]; M=Co: [3]) and as magnetic devices (e.g. M=Co: [4]). The studies of single crystal surfaces have shown interesting segregation phenomena [5,6]. To understand and predict these effects with theoretical models, different surface structures have to be carefully investigated. The relevant energy terms for the understanding of a semi-infinite crystal surface will also be important for diffusion at interfaces of lower dimensional systems such as deposited thin films or multilayers.

Various surface analysis techniques allow the determination of the concentration of the surface plane, but quantitative Low Energy Electron Diffraction (LEED) studies have proved their worth in determining layer concentrations of the adjacent planes as well [5,6].

It is well established that photoemission core level spectroscopy (PES) is sensitive to changes in the local environment of the emitter atom [7]. Limiting the elastic escape depth of the photoelectrons by the use of tunable synchrotron radiation makes it possible to distinguish between surface and bulk atoms, and to measure their respective core level shifts [8]. As well as the surface core level shift due to the structural difference between atoms at the surface and in the bulk, a shift caused by changes in the chemical environment can be measured. Thus, the core level shifts can be used as probe for changes in the chemical and structural environment of an emitter.

To test the facilities of PES for study surface segregation effects we have investigated two different surfaces (110) and (100) of a Pt₂₅Co₇₅ single crystal in the disordered alloy phase and compared them to

Figure 1: Oscillation of the Pt concentration (per layer) profile versus depth (layer 1=surface layer) of the $\text{Pt}_{25}\text{Co}_{75}$ (110) surface (from [6]).

The squares show the relative contribution of each layer to the photoemission intensity of a pure Pt sample for a small photoelectron elastic mean free path ($5\text{\AA}$), typical of that obtained by synchrotron radiation. Photoelectron diffraction effects are neglected in the calculation of the layer by layer intensities.

LEED results. For the (110) surface it was shown that the selvedge is a sequence of almost pure layers [6]: surface plane 100% Co, second plane 90% Pt and third plane 100% Co (fig. 1). The oscillation is weaker for the next two layers (50% Pt and 11% Pt) before reaching the bulk composition of 25% Pt.

This behavior is quite well described by a theoretical model developed by Tréglia, Legrand and coworkers for the similar Pt-Ni system using a tight binding Ising model [9,10]. Contrary to the segregation of M for the open (110) surface, this model predicts for the dense surfaces of the fcc crystal an enrichment of Pt. This was indeed shown by quantitative LEED experiments on the $\text{Pt}_{25}\text{Co}_{75}$ (111) surface (46% Pt at the surface) [11]. Thus, one might expect a segregation of Pt for the (100) surface studied in this paper, where no such definitive LEED investigation exists, but preliminary results using Auger spectroscopy at various angles of incidence give good indication of this trend, even in presence of a (5×1) reconstructed surface [12].

In this paper we present core level photoemission results of the single crystal alloy $\text{Pt}_{25}\text{Co}_{75}$ for the (100) and (110) orientations. These results will be an important reference for the study of diffusion at Pt-Co interfaces. By estimating that the core level shift depends linearly on the chemical environment around the emitter we can obtain information on the degree of interdiffusion. To check this estimation we compare our results with the theoretical shift calculated using the approach proposed by Johansson and Martensson (et.al.) [13,14].

2. EXPERIMENT

Both samples were spark cut from the same single crystal rod to produce 2mm thick slabs ($8\times 10\text{mm}^2$). The composition of the samples was checked by fluorescence measurements and Bragg X-ray reflection. After mechanical polishing and checking of the orientation by Laue diffraction, clean surfaces were obtained in a UHV-chamber (base pressure $2 \cdot 10^{-10}$ Torr) by repeated cycles of Argon ion bombardment (400eV , $15\text{mA}/\text{cm}^2$) and annealing at 750°C . The cleanliness of the surfaces was checked by Auger electron spectroscopy. The (110) surface showed the same LEED spot intensity energy dependence already reported [6]. The LEED pattern of the (100) surface showed " $(1\times N)$ " structure (with $4\leq N\leq 7$, where N may be incommensurate, corresponding to satellites at $\pm q = a^*/N$ and $\pm 2q$) depending on the annealing temperature and time [12]. In addition a weak $c(2\times 2)$ structure was always present, especially for high electron energies. Experiments were carried out with the (1×5) superstructure.

The experiments were performed at the Super ACO storage ring, Orsay, France (beamline SA73b). A TGM 7° monochromator was used, giving a overall resolution of 300-500 meV for photon

energies between 110 - 190 eV. The core level 4f_{7/2} of Pt (binding energy in the pure Pt bulk 71.15 eV [15]) was studied. To separate surface and bulk emission, we have changed the energy of the synchrotron radiation to privilege surface emission at smaller photon energies due to the smaller elastic mean free path of the photoelectrons [16]. Additionally, we have exposed the surfaces to 10L of carbon monoxide.

3. RESULTS AND DISCUSSION

Adsorption of CO shifts the 4f_{7/2} core level of surface Pt by about 1eV to higher binding energy [15]. It is possible to determine the position of the photoemission peak emitted by the atoms at the surface from the difference spectrum of the surface before and after CO adsorption. This is shown in fig.2a) for the (100) surface. The spectra have been normalised to the continuous background and a linear background function was subtracted. A part of the surface intensity (position ≈ 70.9 eV) is shifted due to the chemical influence of the CO (≈ 71.8 eV). The unchanged part of the spectrum (between 71.3 and 71.6eV) has to come from the bulk. This gives us a rough estimate of the positions of the core levels corresponding to the surface and bulk atoms and shows that the influence of the CO on the Pt core level at the alloy surface is comparable to that on pure Pt surfaces. The same procedure of the (110) surface (fig.2b) shows only a slight reduction of the total intensity of the spectrum (due to attenuation of the photoemission signal by the CO layer), but no displacement was observed. We conclude, that there is no Pt in the surface plane.

Figure 2: Background subtracted, normalised data showing the Pt 4f_{7/2} spectra of the clean alloy surfaces and the CO adsorbed surfaces and the respective difference spectra:
a) Pt₂₅Co₇₅ (100); b) Pt₂₅Co₇₅ (110).

Figure 3: Decomposition of the Pt 4f_{7/2} spectra for two different photon energies of the (100) and the (110) surface.

To fit the line shape of the Pt 4f7/2 core level, the "Rainbow" analysis program was used. A continuous "stepped" background (Shirley type [17]) was subtracted. A Doniach-Sunjić line shape [18] was fitted, broadened by a Gaussian instrument function (width determined at the Fermi level corresponding to each photon energy). For the (110) surface it was possible to fit a single peak independently of the photon energy with a Lorentzian width $2\Gamma=0.5\text{eV}$ and an asymmetry parameter $\alpha=0.11$, similar to those of pure Pt [15]. This supports the hypothesis of a single mean Pt bulk environment. Two examples of the decomposition for different photon energies ($h\nu = 130\text{eV}$ and 150eV) are given in fig. 3. Intensities are normalised with respect to the continuous background at a fixed point from the Fermi level, chosen so as to be on the low binding energy side of the 4f7/2 line and thus unaffected by the asymmetric energy loss tail of the core emission. The mean position found for the corresponding core level binding energy is $71.39 \pm 0.04\text{ eV}$. Despite the strong interplanar concentration oscillations as measured by LEED, this result shows that the mean local environment of Pt atoms near the surface is not radically different from that in the bulk. Hence we observe only a single photoemission peak despite the strong oscillatory depth profile.

For the (100) surface the fitting procedure with the same parameters as mentioned above leads to a binding energy of $71.41 \pm 0.04\text{ eV}$ for the bulk peak and of $70.86 \pm 0.05\text{ eV}$ for the surface peak. Fig.3 shows clearly the relative decrease of surface emission with the increasing elastic mean free path of the photoelectrons, as well as the increase of the total intensity due to the increasing cross section of Pt 4f7/2 level. The relative intensity difference between the two surfaces can be explained by the exponential attenuation of the intensity contribution of each layer with increasing distance from the surface, see fig.1. For the (110) seldedge the second layer shows a strongly enhanced Pt concentration and thus leads to the apparent increase of intensity.

The average binding energy for the Pt 4f7/2 core level in the bulk Pt₂₅Co₇₅ is thus $71.40 \pm 0.04\text{eV}$, corresponding to a chemical core level shift of +250 meV relative to the binding energy in pure Pt. On the other hand, the surface peak is shifted by only +60 meV in respect to the clean Pt (100) surface line [19]. Thus, the alloy shift at the surface is smaller than in the bulk.

As it was already shown [15], it is possible to estimate the concentration in the surface plane from the comparison of the intensity of the surface peak with that of the corresponding clean Pt surface. Keeping the same photon energy and identical experiment parameters we can deduce a concentration of $42 \pm 5\%$ Pt at this surface. This value neglects photoelectron diffraction effects, which may differ between the Pt (100) surface and the Pt₂₅Co₇₅ (100) surface, but is consistent with the preliminary surface composition of about 50%, obtained from the Auger spectroscopy measurements at variable angle of incidence [12].

The chemical core level shift for the bulk can be calculated by correlating the binding energy shift to the energy of solution in metals, based on a Born-Haber thermodynamical cycle, originally developed by Johansson and Martensson et al. [13,14]. For a very dilute alloy AB (concentration (A) < 10%) the shift $E_A(\mathcal{A}\mathcal{B})$ for A is expressed as follows:

$$E_A(\mathcal{A}\mathcal{B}) = E(A,B) + E(A+1,A) - E(A+1,B)$$

$E(A,B)$ represents the partial solution energy of A in B, A+1 denotes the element having a core charge Z+1 (in this case: $A \rightleftharpoons \text{Pt}$, $B \rightleftharpoons \text{Co}$ and $A+1 \rightleftharpoons \text{Au}$). Using the semi-empirical formula for the solution

energy proposed by Miedema et al. [20], we have calculated the following values:

$$E(\text{Pt},\text{Co}) = 0.26 \text{ eV/at}, E(\text{Au},\text{Pt}) = -0.19 \text{ eV/at} \text{ and } E(\text{Au},\text{Co}) = -0.35 \text{ eV/at}.$$

This leads to a shift of +420 meV for the case of Pt in a very Co rich environment. If we suppose a linear relation between the chemical shift and Pt concentration we find a theoretical chemical shift for Pt in Pt₂₅Co₇₅ of about 300 meV, in good agreement with the experimental value of 250 meV.

4. CONCLUSION

We have studied two different faces of the disordered alloy Pt₂₅Co₇₅ by core level spectroscopy. For the surface (110) we find a pure Co surface layer and confirm the results of quantitative LEED experiments. For the surface (100) we observe Pt segregation (42% Pt) at the surface. The measured mean position of the Pt 4f_{7/2} core level is 71.40 eV for the bulk, giving a chemical core level shift of 250meV relative to the pure Pt bulk, which is in good agreement with the calculated theoretical value. Comparison between the surface core level binding energy of the alloy (100) and a pure Pt(100) surface ($\Delta = 60$ meV) reveals variable chemical shift due to the Co on the Pt core level in the bulk and at the surface.

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