

X-Ray Photoelectron Spectroscopy Study of the Surface Composition of Pt-Cu Alloys

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The surface composition of the binary alloys $Pt_{0.95}Cu_{0.05}$, $Pt_{0.49}Cu_{0.51}$ and $Pt_{0.05}Cu_{0.95}$ has been determined by x-ray photoelectron spectroscopy. Measurements were performed on polished polycrystalline samples. After cleaning them, intensities of $Cu2p_{3/2}$ photoelectron lines were measured and then converted to atom fractions at the surface layer. The surfaces of annealed $Pt_{0.95}Cu_{0.05}$ and $Pt_{0.49}Cu_{0.51}$ samples have been found to be significantly enriched in Cu. The surface of $Pt_{0.05}Cu_{0.95}$ sample exhibited a small Pt segregation. These results are in qualitative agreement with current predictions based on *regular solution theory*.

A composição de superfície das ligas binárias $Pt_{0.95}Cu_{0.05}$, $Pt_{0.49}Cu_{0.51}$ e $Pt_{0.05}Cu_{0.95}$ foi determinada via espectroscopia de foto-eletrons, produzidos por raios x. As medidas foram executadas sobre amostras policristalinas polidas. Após sua limpeza, as intensidades das linhas de foto-eletrons $2p_{3/2}$ do Cu foram medidas e em seguida convertidas nas frações atômicas da camada superficial. As superfícies das amostras $Pt_{0.95}Cu_{0.05}$ e $Pt_{0.49}Cu_{0.51}$ recozidas mostraram-se significativamente enriquecidas de Cu. A superfície da amostra $Pt_{0.05}Cu_{0.95}$ exibiu uma pequena segregação de Pt. Estes resultados estão em conformidade qualitativa com as previsões correntes baseadas na teoria da solução regular (*regular solution theory*).

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1. INTRODUCTION

The study of alloy catalysts is receiving increasing attention in the literature¹ due to their scientific and technological importance. A few years ago Kummer showed² that the activity for CO oxidation is higher in platinum-copper (Pt-Cu) alloy catalysts than in pure Pt catalysts. A proper interpretation of the catalytic properties of alloys requires a knowledge of surface composition. Recent studies³ of a number of binary alloy surfaces using Auger Electron Spectroscopy (AES) have shown that the surface composition of alloys can be quite different from their bulk composition.

In AES, as it is difficult to measure the distribution curve $N(E)$ corresponding to a given Auger transition, the derivative, namely dN/dE , is measured and the peak to peak amplitude of this signal (i.e., of dN/dE) is assumed to be linearly proportional to the concentration. However, in X-ray Photoelectron Spectroscopy (XPS) one can measure $N(E)$ corresponding to the core level under consideration (for example, Cu2p) and knowing the area under the distribution curve and the dependence of electron mean free path of kinetic energy, one can evaluate the surface concentration in a more direct way (see section 3 below). Also unlike AES, in XPS one doesn't encounter the problem due to the contribution to the measured signal from the back scattered primary electrons⁴. Because of these reasons XPS is an attractive technique to study the surface composition in binary alloys. In this paper we report the results on the surface composition of Pt-Cu alloys as derived from our XPS measurements.

2. EXPERIMENTAL

X-ray photoemission measurements were carried out using a McPherson ESCA 36 photoelectron spectrometer and AlK_{α} radiation. In addition to the turbomolecular pumping station, this system was provided with a helium cryopanel in the sample chamber. Thus, with the cryopump operating, the pressure in the sample chamber during the measurements was 1.0×10^{-8} torr or less. *In situ* sample cleaning by sputtering was achieved using an argon ion gun. The sample could be annealed at high

temperatures by resistively heating the tantalum foil (0.001 inch thick) on to which the sample was spot welded.

The alloys used in this study ($\text{Pt}_{0.95}\text{Cu}_{0.05}$, $\text{Pt}_{0.49}\text{Cu}_{0.51}$ and $\text{Pt}_{0.05}\text{Cu}_{0.95}$) were prepared by melting the constituents in an arc furnace⁵ under argon atmosphere. The ingots obtained after melting were plastically deformed, homogenized by annealing at high temperatures (at $T \approx 0.8 T_{mp}$, where T_{mp} is the solidus temperature of the alloy) and then rolled into thin foils (except $\text{Pt}_{0.49}\text{Cu}_{0.51}$) of thickness 0.2 mm. The nominal bulk compositions of the samples as quoted here were determined from electron microprobe analysis of the homogenized alloy sample. These foils were then annealed in a flow of gaseous (90% N_2 /10% H_2) mixture at 900°C for 48 hours to remove any residual impurities such as sulfur and oxygen. Samples from these foils were polished to a mirror finish and then mounted in the ESCA spectrometer. As the $\text{Pt}_{0.49}\text{Cu}_{0.51}$ alloy was brittle, a thin disk of 1.05 mm thickness was cut from the homogenized ingot, polished to a mirror finish and then attached to the sample manipulator for ESCA analysis.

3. RESULTS

Figure number 1 shows in (a) the ESCA spectrum in the binding energy (B.E.) range of 0 to 1000 eV from the $\text{Pt}_{0.49}\text{Cu}_{0.51}$ alloy after annealing at 700°C for 30 minutes. The corresponding spectra from pure Cu and Pt standards are also shown in the same figure, (b) and (c). In figure 2 is shown the ESCA spectra in the B.E. range of 0 to 1000 eV of (a) $\text{Pt}_{0.95}\text{Cu}_{0.05}$ and (b) $\text{Pt}_{0.05}\text{Cu}_{0.95}$ alloys, obtained after annealing at 700°C for 30 minutes. In the alloy spectra one can identify all the photoelectron lines characteristic of Cu and Pt. Detailed analysis of Cu(2p) and Pt(4p, 4d and 4f) lines indicates that the Cu lines are shifted by about 0.6 eV in $\text{Pt}_{0.95}\text{Cu}_{0.05}$, 0.4 eV in $\text{Pt}_{0.49}\text{Cu}_{0.51}$ and 0.0 eV in $\text{Pt}_{0.05}\text{Cu}_{0.95}$ compared to pure Cu, while Pt lines show no noticeable energy shift. The origin of these shifts is discussed elsewhere⁶. For the present purpose we concentrate only on the intensity of $\text{Cu}2p_{3/2}$ photoelectron line from the alloys.

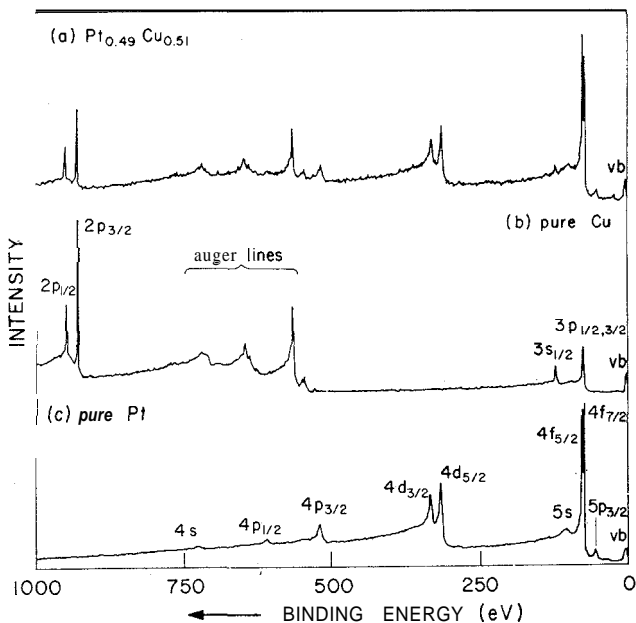


Fig. 1 - ESCA spectra from (a) $Pt_{0.49}Cu_{0.51}$ surface annealed at $700^{\circ}C$ for 30 minutes, (b) pure Cu and (c) pure Pt.

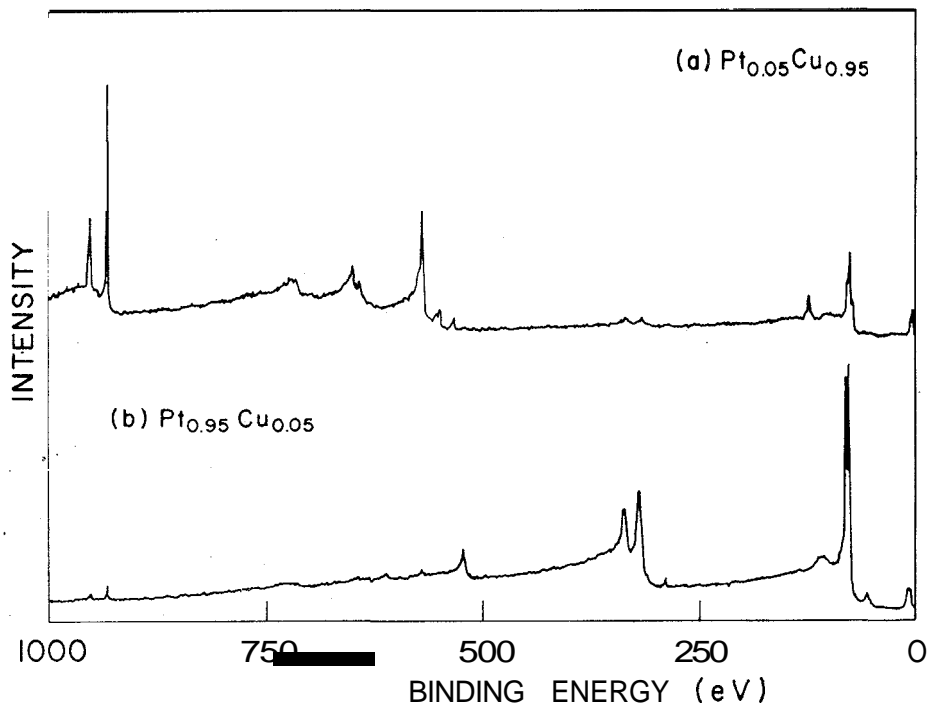


Fig. 2 - ESCA spectra from (a) $Pt_{0.95}Cu_{0.05}$ and (b) $Pt_{0.05}Cu_{0.95}$ surfaces annealed at $700^{\circ}C$ for 30 minutes.

The photoelectron (of kinetic energy E_1) signal strength of component A from a homogeneous binary alloy $A_x B_{1-x}$ can be written as⁷

$$I_A = J_0 P_A \lambda(E_1) D(E_1) x_A \quad (1)$$

where J_0 is the x-ray flux, P_A is the photoexcitation probability, x_A is concentration of component A, $\lambda(E_1)$ is the mean free path of electrons with kinetic energy E_1 and $D(E_1)$ is the fraction of these electrons detected at the analyser. If I_{St} is the corresponding photoelectron signal strength from component A in the pure state, then the concentration of A in the alloy is

$$x_A = I_A / I_{St} \quad , \quad (2)$$

assuming J_0 , $\lambda(E_1)$, $P(E_1)$ and $D(E_1)$ are the same for component A in the alloy and in the pure state. If the atomic volume densities ρ_a of the alloy and ρ_{St} of component A in the pure state are different, then Eq. (2) becomes

$$x_A = (I_A / I_{St}) \cdot (\rho_{St} / \rho_a) \quad (3)$$

Thus from the are under a given photoelectron line of component A in the alloy and that from component A in the pure state one can evaluate the atomic fraction of A in the alloy using Eq. (3).

However, if the concentration of component A in the alloy varies with distance from the surface, Eq.(3) would be modified⁸ to

$$I_A / I_{St} = \left(\sum_{n=1}^{\infty} \rho_a^n x_n \exp(-(n-1)d_a / \lambda \cos \theta) \right) / \left(\sum_{n=1}^{\infty} \rho_{St}^n \exp(-(n-1)d_{St} / \lambda \cos \theta) \right) \quad , \quad (4)$$

where d_a and d_{St} are the interlayer spacing of the alloy and of pure A respectively, θ is the angle between the sample surface and analyser axis (45° in our case), and ρ_a^n and ρ_{St}^n are the atomic densities of the n-th layer in the alloy and in pure A respectively. Assuming that only the surface layer composition is different from the uniform bulk value

below, we have $x_1, x_2 = x_3 = \dots = x_n = x_b$. We also assume that ρ^n is independent of n . Under these assumptions Eq. (4) reduces to

$$I_A/I_{St} = (\rho_a/\rho_{St}) \left\{ \frac{x_1(1-\exp(-d_a/\lambda\cos\theta)) + x_b\exp(-d_a/\lambda\cos\theta)}{1 - \exp(-d_a/\lambda\cos\theta)} \right\} \cdot \{1 - \exp(-d_{St}/\lambda\cos\theta)\} \quad (5)$$

To evaluate the surface composition from this expression one needs to know the interlayer spacing and the layer atomic densities in the alloy and in pure A. Since we have used a polycrystalline foil, we take $d_a = d_{St} = 2.0 \text{ \AA}$ and the ratio of the layer atomic densities equal to the square of the ratio of the lattice parameter of pure A to that of the alloy. Thus we have

$$\rho_a/\rho_{St} = (a_{St}/a_a)^2 ,$$

where a_{St} and a_a are the lattice parameter of component A in pure state and that of the alloy, respectively.

For the Pt-Cu system, the kinetic of $\text{Cu}2p_{3/2}$ photoelectron is about 550 eV (using AlK_{α} radiation). From Penn's table⁹ we evaluate λ corresponding to this energy to be 7.5 \AA and 8.2 \AA in pure Cu and Pt, respectively. As this variation in λ between pure Cu and Pt is rather small, we take λ to be 8.0 \AA in all our calculations. Thus Eq. (5) for Pt-Cu system under our experimental conditions becomes.

$$(I_{\text{Cu}})_{\text{alloy}}/(I_{\text{Cu}})_{\text{pure Cu}} = (a_{\text{Cu}}/a_a)^2 \cdot (0.298x_1 + 0.702x_b) \quad (6)$$

The left hand side in the above equation is an experimentally measured quantity and in the right hand side x_1 is the only unknown and hence can easily be evaluated,

4. IMPURITY PROBLEM

The above mentioned analysis is valid only when there are no adsorbed impurities such as carbon, oxygen, etc., on the surface. The

presence of such impurities would reduce the intensity of the photoelectron line exponentially¹⁰. As all our ESCA measurements were carried out under inoderate vacuum ($\sim 10^{-8}$ torr) conditions, some adsorbed impurities, mainly C and O, were always present. Hence the following experiment was carried out to correct for the impurity effects on the measured photoelectron line intensities. After cleaning pure Cu (argon ion sputtering followed by annealing to 700°C and quenching to room temperature), its ESCA spectrum in the BE range of 0 to 1000 eV was recorded repeatedly at different intervals of time, thereby letting the (adsorbed) impurities accumulate on the surface. The Cu2p_{3/2} line intensity (measured by the are under the 2p_{3/2} line) and the counts corresponding to the peak maximum of carbon (1s) and oxygen (1s) lines (these were the only impurities observed) were evaluated for each of the pure Cu spectra. Then the counts of C(1s) and O(1s) were added taking into consideration their photoelectron cross-sections¹¹ to give a single impurity count for each of the pure Cu spectra. Figure 3 shows a plot of the log Cu2p_{3/2} intensity versus impurity counts. The experimental data fall on a straight line as one would expect. Knowing the impurity counts from the alloy spectrum, this calibration curve was used to evaluate $(I_{Cu})_{\text{pure Cu}}$ in Eq.(6).

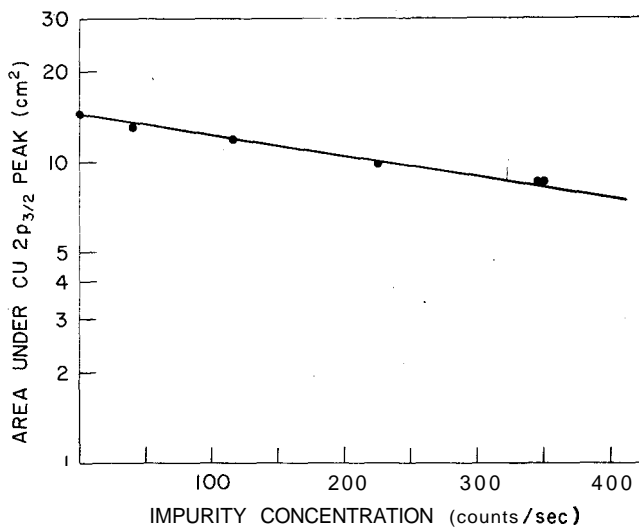


Fig.3 - Variation of the area under the spectral line 2p_{3/2} in pure Cu as a function of impurity content.

5. SURFACE CONCENTRATION

Figure 4 shows typical $\text{Cu}2p_{3/2}$ spectra from (a) pure Cu and (b) $\text{Pt}_{0.95}\text{Cu}_{0.05}$ to illustrate how the areas (I_{Cu}) mentioned above are measured. The results of our calculations using Eqs. (2), (3) and (6) for the three alloys studied are listed in table 1. As can be seen, while in the dilute Pt-Cu alloy there is a small Pt segregation, in the other two ($\text{Pt}_{0.95}\text{Cu}_{0.05}$ and $\text{Pt}_{0.49}\text{Cu}_{0.51}$) Cu segregates to the free surface (column 3, table 1). These results are discussed in the context of current theories on surface segregation in the next section.

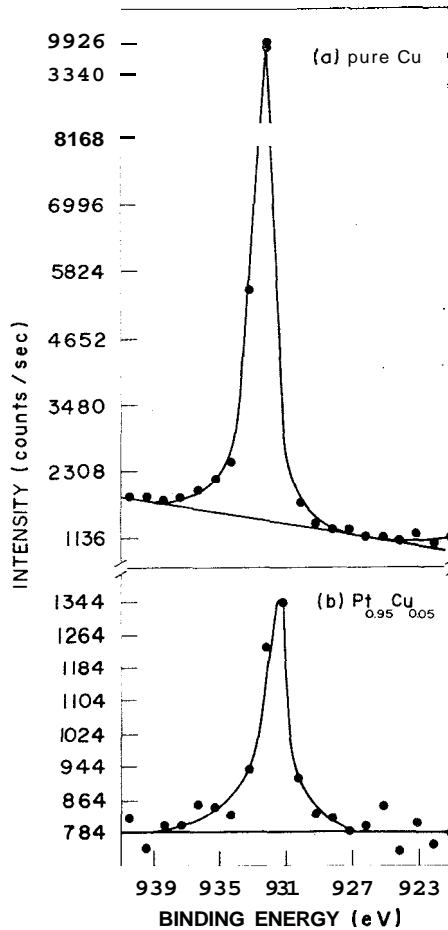


Fig.4 - Typical $\text{Cu}2p_{3/2}$ spectra (a) from pure Cu and (b) from $\text{Pt}_{0.95}\text{Cu}_{0.05}$, illustrating the measurement of the cited area.

Table 1

Nominal bulk composition of Cu (%)	Experiment			Theory
	1	2	3	4
5	9 ± 1	11.3 ± 1.5	23.5 ± 4.0	42 ± 3
51	57 ± 1	64 ± 1	88 ± 3	80 ± 2
95	93 ± 1	94 ± 1	91 ± 3	92 ± 2

Columns 1 and 2 correspond to composition determined from $\text{Cu}2p_{3/2}$ line using equations 2 and 3 respectively. Column 3 is the surface composition determined from equation 6 and column 4 lists theoretical surface composition for a (100) oriented alloy surface.

6. SURFACE SEGREGATION- THEORY AND EXPERIMENT

Theoretical calculations¹² using regular solution model have been proven to be quite successful in predicting the surface segregation behavior of a number of binary alloys. The basic parameters used in these calculations are: (i) the surface energies of pure metals σ_A and σ_B ; (ii) the heat of mixing, ΔH_m ; and (iii) the solute strain energy. In this theoretical approach (i.e., regular solution model) it can be shown that the surface energy term would indicate that *the component with lower surface energy to segregate to the free surface, while* the strain energy contribution would *always favor the solute* to segregate to the free surface.

However, in an equiatomic alloy AB, as the lattice can not identify a solute, the strain energy contribution to the total heat of segregation would be zero.

In the case of the Pt-Cu system, as Cu has lower surface energy ($\sigma_{\text{Cu}} = 1700 \text{ ergs/cm}^2$ and $\sigma_{\text{Pt}} = 2340 \text{ ergs/cm}^2$)¹³, the surface energy

term above would predict Cu to segregate in all Pt-Cu alloys. The strain energy term alone, on the other hand, would favor Cu and Pt to segregate to the surface in dilute Cu-Pt and in dilute Pt-Cu alloys respectively.

We have computed the composition profiles for the Pt-Cu alloys in the vicinity of a (100) surface by a previously developed Monte Carlo technique¹⁴, taking into consideration both surface and solute strain energy contributions. In these calculations the strain energy contribution to the total heat of segregation was evaluated using the expression¹⁵

$$\Delta H_{\text{elast}} = 24\pi K_A G_B r_A r_B (r_A - r_B)^2 / (3K_A r_A + 4G_B r_B) \quad (7)$$

where K_A and G_B are the bulk modulus of elasticity and the shear modulus of elasticity of the solute and the solvent, respectively; r_A and r_B are the atomic radii of the solute and the solvent, respectively. It is to be noted that the above expression is strictly valid only for very dilute solutions and application of this to concentrated alloys such as 5% Cu in Pt or 5% Pt in Cu would give the upper bound on the magnitude of strain energy contribution. The parameters used in our Monte Carlo calculation are taken from the literature¹⁶ and are listed in tables 2 and 3. In figure 5 we show a typical composition profile for the $\text{Pt}_{0.95}\text{Cu}_{0.05}$ alloy at 1000°K. The surface composition evaluated from such profiles for the different alloys are tabulated in column 4 of table 1.

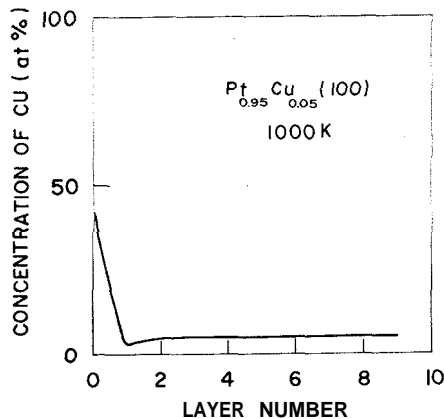


Fig. 5 - The dependence of Cu concentration on layer number in a $\text{Pt}_{0.95}\text{Cu}_{0.05}$ alloy at 1000°K, as derived from a Monte Carlo calculation.

Table 2. Parameters used in Monte Carlo calculation

Element	K ($\times 10^{-6}$ kg/cm ²)	G ($\times 10^{-6}$ kg/cm ²)	σ (ergs/cm ²)	λ (Å)
Cu	1.354	0.46	1700	1.276
Pt	2.416	0.622	2320	1.385

Table 3

Alloy	ΔH_m (cals/mole)	Heat of segregation due to		Resultant (cals/mole)
		surface energy	strain energy	
Pt _{0.95} Cu _{0.05}	-344.5	3643	2091	5734
Pt _{0.49} Cu _{0.51}	-2650	3397	0	3397
Pt _{0.05} Cu _{0.95}	-614	3156	1934	1222

As can be seen from table 1 there is fairly good agreement between experiment (column 4) and theory. The errors shown in table 1 (columns 1-3) correspond to uncertainties in the measured areas as in figure 4. While the theory correctly predicts the segregation component, quantitative comparisons are difficult because (1) the experiments were done on polycrystalline samples while the theory corresponds to (100) oriented alloy surface and (2) the approximations involved in evaluating the surface composition theoretically as well as from the experimental data (see section 3).

7. CONCLUSIONS

The feasibility of using ESCA for quantitative surface composition analysis has been demonstrated for Pt-Cu system and this can be easily extended to other multicomponent alloys. Our results on the sur-

face segregation behavior in Pt-Cu alloys are in qualitative agreement with current theoretical predictions.

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