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$Pt_{10}Ni_{90}(111)$ SINGLE CRYSTAL ALLOY: DETERMINATION OF THE SURFACE COMPOSITION BY AES, XPS AND ISS

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The surface composition of the $Pt_{10}Ni_{90}(111)$ single crystal alloy has been determined from AES, XPS and ISS experiments. The clean surface is largely enriched with platinum: 30–40% in the top layer instead of 10% in the bulk. This enrichment concerns mainly the ultimate surface layer and appears to be only slightly dependent on the sample temperature.

1. Introduction

In order to investigate the modifications of the properties of surface Ni and Pt atoms by alloying, experiments have been undertaken on well-defined low index planes of Pt–Ni single crystal alloys with various compositions. The most fundamental problem in such studies is to obtain a good knowledge of both surface composition and crystallography. Up to now only few data are available on the eventual surface segregation of one of the components and the kinetics and thermodynamics of this process [1,2]. Superficial composition can be determined either by selective chemisorption of gases [3] or by physical

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techniques that are sensitive to the ultimate layer of the sample. Results based on selective chemisorption must be considered cautiously since additional segregation may be induced by the adsorption process itself, mainly when the bond strengths of the adsorbed species are different for the two components of the alloy. Two kinds of physical method are appropriate to such a determination: either by low energy electron spectroscopy, electron excited Auger spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS), or by backscattered low energy ion analysis (ISS).

In the following, results relative to the $Pt_{10}Ni_{90}(111)$ alloy, obtained by LEED, AES, XPS and ISS, are reported and compared.

2. Materials and experimental techniques

The Pt–Ni single crystal alloy, in the form of a cylindrical rod of 8 mm diameter, has been purchased from “Cristal-Tec”. The nominal bulk concentration is 10 at% Pt. After X-ray orientation, the samples are cut by spark erosion in the shape of 1 mm thick discs exposing the (111) plane. After mechanical polishing, down to 1 μm, the surface is restructurated by prolonged annealing at 1300 K in vacuum. The surface restructuration is controlled by LEED. The cleaning is then achieved by repeated cycles of argon ion bombardment and annealing up to 1100 K. The clean surface, as controlled by AES (or XPS, or ISS), exhibits a well contrasted (1 × 1) LEED pattern with sharp and intense diffraction spots.

The AES, XPS and ISS experiments have been performed in three distinct ultra-high vacuum systems.

The AES experiments were done with a Riber model OPC 105 cylindrical mirror analyser (CMA) with a modulation amplitude of 3.4 V peak-to-peak, leading to the measurement of the derivative form of the energy spectrum. A coaxial electron gun is delivering a primary beam of 1–2 μA with an energy adjustable up to 3 keV.

The photoelectron spectrometer is a Vacuum Generators ESCA III model using an hemispherical electron energy analyser and an Al K_α X-ray excitation source ($h\nu = 1486, 6$ eV). The direction of detected photoelectrons with respect to the surface can be varied by rotating the sample.

The ISS spectrometer was built at the Physico-Chemical Laboratory of the Catholic University in Leuven. The apparatus mainly consists of four parts: a differentially pumped ion gun, a Wien filter for mass selection, a decelerator that permits the accurate energy setting of the primary ions impinging on the surface, and finally the rotatable 180° electrostatic analyser for the energy analysis of the scattered ions.

2. Methodology and experimental results

3.1. Electron spectroscopies

Pt and Ni atoms exhibit well-defined XPS peaks and Auger transitions. The intensity of one peak A relative to the element a (Pt or Ni) in a monocrystalline matrix X (pure components or alloy), due to the electrons emitted with the kinetic energy E_A, may be expressed as a summation over the successive layer contributions with an attenuation factor depending on their respective depth according to the general formulation:

$$\left(I_A^X\right)_a \propto I_p r_A^X \sum_{n=0}^{\infty} \sigma_A (N_a)_n \exp\left(\frac{nd^X}{\lambda_A^X \cos\theta}\right) T_A, \tag{1}$$

where I_p is the intensity, or the flux, of the excitation beam; r_A^X is the backscattering factor (which reflects the increase of the primary excitation beam intensity by backscattering on the underlayers – in the Auger process, r is larger than one and depends on the nature of the substrate and the energy of the considered transition); σ_A represents the cross section for the electron emission and is characteristic for the element a and for the considered transition; d^X is the interatomic distance between the successive layers in the matrix X; $(N_a)_n$ is the number of atoms a per cm^2 in the layer of index n; λ_A^X is the mean free path of the electrons of energy E_A in the matrix X; θ is the emergence angle of electrons with respect to the surface normal; and T_A is the electron analyser transmission at the energy E_A, the accepted solid angle included.

For an alloy, if enrichment is assumed to occur only in the outer plane – which theoretically is the main affected plane for a regular solution – the expression (1) can be modified as follows:

$$I_A^{\text{alloy}} \propto I_p r_A^{\text{al}} \sigma_A T_A N^{\text{al}} \left[C_a^{\text{o}} + \sum_{n=1}^{\infty} C_a^{\text{b}} \exp\left(-\frac{nd^{\text{al}}}{\lambda_A^{\text{al}} \cos\theta} \right) \right],$$

where N^{al} is the atomic density of one layer in the alloy, and C_a^{b} and C_a^{o} are respectively the nominal bulk and outer plane concentrations of atoms a.

Moreover, use of intensity ratios avoids introduction of I_p and other possible factors, which are difficult to determine. Then, the superficial composition in the elements a, or b ($C_b^{\text{o}} = 1 - C_a^{\text{o}}$), can be deduced from the intensity ratio of two peaks A and B, characteristic of these two elements:

$$\frac{\left(I_A^{\text{al}}\right)_a}{\left(I_B^{\text{al}}\right)_b} = \frac{\sigma_A T_A r_A^{\text{al}}}{\sigma_B T_B r_B^{\text{al}}} \; \frac{C_a^{\text{o}} + \sum_{n=1}^{\infty} C_a^{\text{b}} \exp\left[-nd^{\text{al}}/\left(\lambda_A^{\text{al}} \cos\theta\right)\right]}{\left(1 - C_a^{\text{o}}\right) + \sum_{n=1}^{\infty} \left(1 - C_a^{\text{b}}\right) \exp\left[-nd^{\text{al}}/\left(\lambda_B^{\text{al}}\, cos\, \theta\right)\right]}. \tag{2}$$

3.1.1. AES

For Auger electron spectroscopy, no values are available for σ. In order to solve this problem one has to use results obtained in the same standard conditions for the same transitions in reference samples of the pure elements having a known crystallographic structure. The I_A^{pur} in the relation (1) can be alternatively expressed as:

$$(I_A^{pur})_a = N_a^{pur}(i_A^o)_a \left[\sum_{n=0}^{\infty} \exp\left(- \frac{nd^{pur}}{\lambda_A^{pur}\cos\theta} \right) \right] I_p r_A^{pur}, \tag{3}$$

where N_a^{pur} is the surface density in one layer and $(i_A^o)_a$ the non-attenuated signal given by a single atom isolated in the space. For the alloy one then obtains:

$$(I_A^{al})_a = N^{al}(i_A^o)_a \left[C_a^o + \sum_{n=1}^{\infty} C_a^b \exp\left(- \frac{nd^{al}}{\lambda_A^{al}\cos\theta} \right) \right] I_p r_A^{al}.$$

Taking i_A^o (and i_B^o) from the expression (3) one gets, for Pt and Ni:

$$\frac{(I_A^{al})_{Pt}}{(I_B^{al})_{Ni}} = \frac{(I_A^{pur})_{Pt}}{(I_B^{pur})_{Ni}} \frac{r_A^{al} r_B^{Ni}}{r_B^{al} r_A^{Pt}} \frac{N^{Ni}}{N^{Pt}} \frac{\sum_{n=0}^{\infty} \exp\left[-nd^{Ni}/\left(\lambda_A^{Ni}\cos\theta\right)\right]}{\sum_{n=0}^{\infty} \exp\left[-nd^{Pt}/\left(\lambda_B^{Pt}\cos\theta\right)\right]}$$

$$\times \frac{C_{Pt}^o + \sum_{n=1}^{\infty} C_{Pt}^b \exp\left[-nd^{al}/\left(\lambda_A^{Pt}\cos\theta\right)\right]}{\left(1 - C_{Pt}^o\right) + \sum_{n=1}^{\infty} \left(1 - C_{Pt}^b\right) \exp\left[-nd^{al}/\left(\lambda_B^{Ni}\cos\theta\right)\right]}. \tag{4}$$

In this way, one can determine the superficial composition by measuring the intensity ratio of two Auger peaks characteristic of the two components of the alloy and of the pure elements in standard conditions. All the parameters are available, but some uncertainties remain for the data on backscattering factors r and mean free path λ.

AES spectra are reported for pure Ni(111) and Pt(111) in fig. 1. To determine the alloy surface composition, two well-separated characteristic peaks, at low kinetic energy in order to be the most sensitive to the top layers and with highest intensity, have to be selected. Peaks at 102 and 237 eV are most suitable for respectively Ni and Pt. The $I_{237}^{Pt}/I_{102}^{Ni}$ ratio, as measured by peak-to-peak heights, is equal to 1.09: in the alloy (fig. 1c) this $I_{237}^{al}/I_{102}^{al}$ ratio is 0.24. To be accurate it would be necessary to use the surface of the integral signals, but the approximation of the intensity by the peak-to-peak height may be considered as correct since no significant modifications of both the width and energetic position of these peaks have been observed in the alloy with respect to the pure metals.

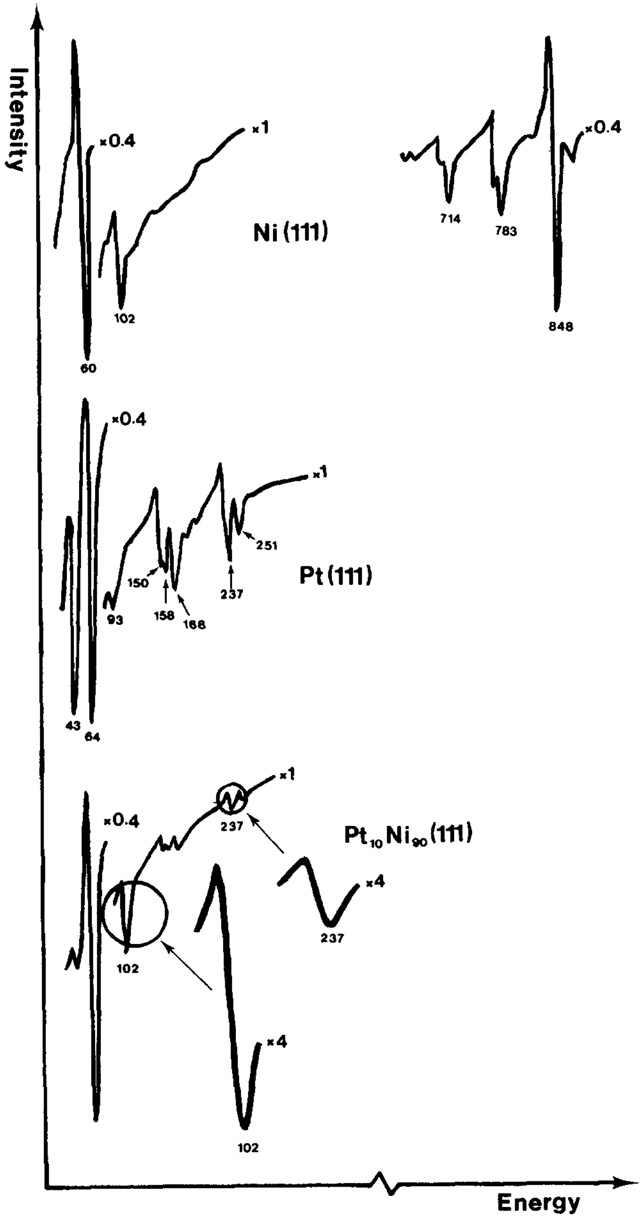

Fig. 1. AES spectra of: (a) pure Ni(111); (b) pure Pt(111); (c) $Pt_{10}Ni_{90}(111)$ alloy ($E_p = 1500$ eV; $V_{mod} = 3.4\ V_{p-p}$).

The angular parameter $\cos\theta$ is fixed by the geometrical arrangement of the CMA: $\cos\theta = 0.74$. The interatomic distances between (111) planes of pure Ni, pure Pt and $Pt_{10}Ni_{90}$ [4] are respectively 2.03, 2.261 and 2.062 Å. The ratio of surface densities N^{Ni}/N^{Pt} equals 1.23.

Taking into account relations given by Reuter concerning the dependence of the backscattering factor r on both the atomic number Z of the material and the binding energy E_b of the deep level involved in the Auger process with respect to the primary energy E_p [5]:

$$r = 1 + 2.8\eta(1 - 0.9E_b/E_p),$$

with $\eta = -0.0254 + 0.016\ Z - 1.86 \times 10^{-4}\ Z^2 + 8.3 \times 10^{-7}\ Z^3$, the r values have been determined. The term implying the backscattering factors in eq. (4), $r_A^{al} r_B^{Ni}/r_B^{al} r_A^{Pt}$, equals 0.8. The values so gained agree, within only a few percent of accuracy with those reported by Kuijers [6] or calculated by Ichimura and Shimizu [7].

A quite large uncertainty remains on the mean escape depth values reported in the literature [6]. Theoretical calculations, based on electron–electron interaction for free-electron-like materials, have recently been carried out [8]. Nevertheless, the model seems valid for electron energies larger than 200 eV and essentially for all elements that are not transition metals, noble metals or rare earths. So, it would be better to use values carefully determined experimentally and which take into account the crystallographic surface structure of materials: for (111) planes of metals $\lambda_{102} = 4$ Å and $\lambda_{237} = 7.3$ Å [6].

From the intensity ratio $I_{237}^{al}/I_{102}^{al}$ measured on fig. 1c, the surface atomic concentration in platinum calculated from the relation (4) is 0.3. This represents the mean value of several experiments from which the extreme values of the intensity ratio differ by ± 0.02, leading to an error of ± 0.03 on determination of the superficial concentration.

An important Pt segregation to the surface is evidenced. A question arises about the thermodynamics and kinetics of the segregation process. In order to get more information, the superficial composition has been determined at several temperatures (750–1150 K). But, since the heating mode disturbs the functioning of the electron spectrometer, we have performed the measurements in a few seconds just after switching off the heating, which diminishes the precision of the 237 and 102 eV Auger peak intensity determinations by decreasing the signal/noise ratio in the AES spectra and introduces an inaccuracy of about 10% for the target temperature. Moreover, one has to notice that the equilibrium kinetics is sufficiently fast to make the measurements accurate, as verified by measuring these intensity values versus time for a given temperature in the investigated range. In the experimental uncertainty for these peculiar determinations of the segregation at different temperatures no noticeable variations are evidenced ($I_{237}^{al}/I_{102}^{al} = 0.24 \pm 0.04$ leading to $C_{Pt}^{o} = 0.3 \pm 0.06$). By using the classical thermodynamical formulation:

$$\frac{C_{Pt}^{o}}{C_{Ni}^{o}} = \frac{C_{Pt}^{b}}{C_{Ni}^{b}} \exp\left(-\frac{\Delta G}{RT}\right), \quad \text{with} \quad \Delta G = \Delta H - T\Delta S$$

(where ΔG, ΔH and ΔS are the free enthalpy, the enthalpy and the entropy of segregation), and from the experimental data, one may estimate ΔH to be 0 ± 2 kcal/mole and ΔS to be 2 ± 2 cal/mole · K.

3.1.2. XPS

For X-ray photoelectron spectroscopy ($h\nu = 1486.6$ eV) the general equation (2) can be used directly since photoionization cross sections are available for atomic levels from theoretical calculations [9]. In order to minimize the inaccuracy introduced by uncertainties on transmission efficiency and mean free path values, it would be adequate to choose the characteristic peaks of both elements as close as possible in kinetic energy. The Pt 4f and Ni 3p levels, split only by 10 eV in energy, are selected. In this case the transmission factors T_A and T_B cancel each other. In the kinetic energy range of 1410–1420 eV, experimental data lead to $\lambda = 22$ Å, a value retained for both Pt 4f and Ni 3p lines. The cross sections σ are 15.46 and 2.22 for, respectively, Pt $4f_{5/2,7/2}$ and Ni $3p_{1/2,3/2}$ ionization. Since these values are obtained from theory, their use

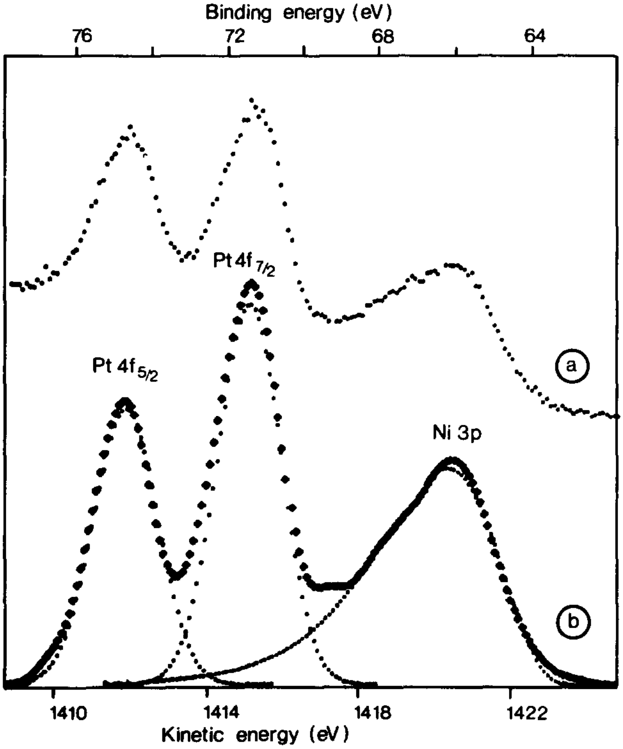

Fig. 2. Pt 4f and Ni 3p XPS spectra of $Pt_{10}Ni_{90}(111)$ alloy: (a) raw spectrum; (b) after smoothing, background subtraction and resolution into the three components Pt $4f_{5/2}$, Pt $4f_{7/2}$ and Ni 3p.

may induce systematic errors in stoichiometry measurements. However, in the present case, use of these values is justified "a posteriori". Large emergence angle measurement – which favours the bulk with respect to the surface – leads indeed to a determination of the atomic ratio [Pt]/[Ni] close to the nominal bulk value of 10 at.%.

In order to enhance the surface contribution with regard to the bulk, the emergence angle relative to the surface, $\beta = \frac{1}{2}\pi - \theta$, should be rather small. But for very small angles β, first an important loss is observed in total signal intensity and it follows that longer counting time is required for achieving good statistics. Second additional ill-known perturbation effects such as large modifications in electron backscattering and photon refraction effects may deviate the electron attenuation coefficient from the $\exp(-d/\lambda \cos\theta)$ law. Therefore, to avoid these difficulties, the β angle is kept equal to 16°.

The recorded spectrum (fig. 2a) is first smoothed (Fourier transform) and background subtracted (the background is assumed to be proportional to the area under the peak) (fig. 2b). The net areas under the Pt 4f and Ni 3p peaks are calculated after decomposition of the spectrum into three components (Pt $4f_{5/2}$, Pt $4f_{7/2}$ and Ni 3p). In addition, a contribution of 4% of the Pt 4f peak, due to the excitation of the Pt 4f levels by the Al $K\alpha_{3,4}$ satellite lines of the photon source, has to be subtracted from the initial area determined for the Ni 3p line intensity. The intensity ratio so determined is, for four experiments, $I^{\text{al}}_{\text{Pt 4f}}/I^{\text{al}}_{\text{Ni 3p}} = 1.43 \pm 0.04$. From eq. (2), the calculation leads to a superficial composition in platinum of 0.34 ± 0.02.

3.2. Low energy ion spectroscopy

In the scattering event ions lose energy by simple binary collisions. This energy loss depends on the scattering angle θ and the atomic ratio γ of the surface atoms to that of the primary ions, according to the formula:

$$\frac{E_1}{E_0} = \left(\frac{\cos\theta + \sqrt{\gamma^2 - \sin^2\theta}}{1+\gamma} \right)^2, \quad \gamma = \frac{m_{\text{atom}}}{m_{\text{ion}}},$$

where E_0 is the primary energy of the ions and E_1 their final energy after scattering.

An energy spectrum for a constant scattering angle θ is therefore equivalent to a mass spectrum of the atoms at the very surface. Indeed, one major advantage of this technique is its absolute surface sensitivity, since ions that have penetrated beneath the first atomic layer are effectively neutralized and cannot be detected anymore.

For alloys, the quantitative determination of the surface concentration of their components can be obtained by normalizing the heights of the characteristic peaks with those recorded under the same conditions on reference samples of the pure elements. In order to avoid eventual crystallographic effects in

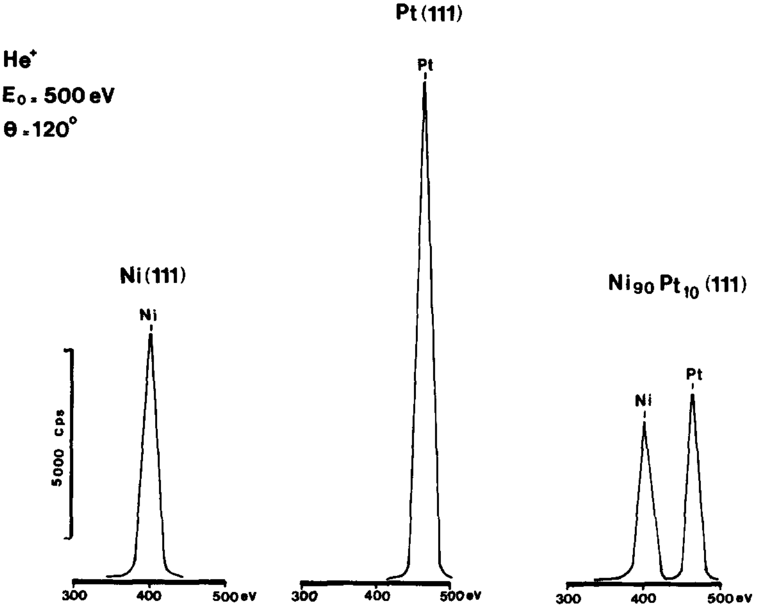

Fig. 3. ISS spectra of Ni(111), Pt(111) and $Pt_{10}Ni_{90}(111)$ with He^+ (500 eV, 200 nA) (the scattering angle θ was 120° in the specular configuration; angle of incidence with respect to the surface $\psi = \theta/2$).

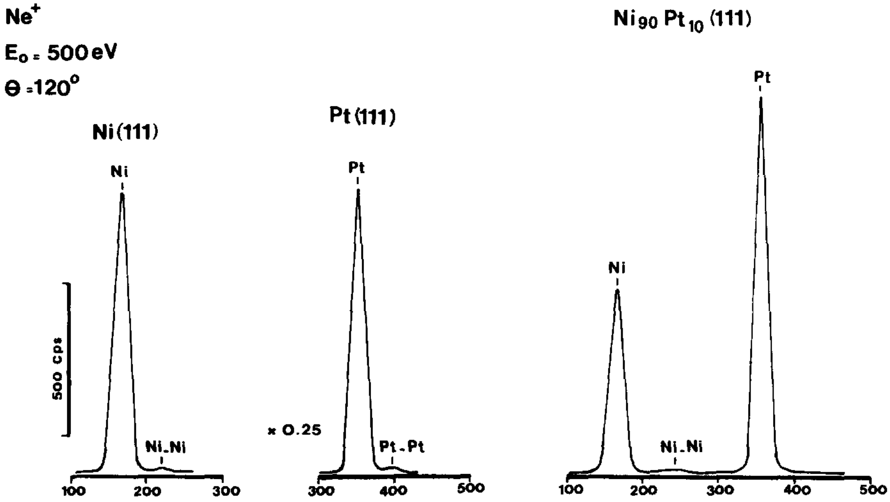

Fig. 4. ISS spectra of Ni(111), Pt(111) and $Pt_{10}Ni_{90}(111)$ with Ne^+ (500 eV, 140 nA) (same scattering geometry as for He^+).

Table 1
Superficial composition of clean $Pt_{10}Ni_{90}(111)$ as determined by various techniques

	Superficial composition	
Technique used	% Pt	% Ni
AES	30 ± 3 [a]	70 ± 3 [a]
XPS	34 ± 2 [a]	66 ± 2 [a]
ISS Ne^+		
Measured on the Pt peak	33.2 (27.6) [b]	
Measured on the Ni peak		64.4 (66.4) [b]
ISS He^+		
Measured on the Pt peak	37 (30.8) [b]	
Measured on the Ni peak		65 (67.1) [b]
Selective CO chemisorption [3]	40	60

[a] The reported uncertainties are only relative to the experimental errors on the peak area, or height determination.

[b] Note added in proof.

single crystals, the samples must be analysed under the same azimuthal angle of incidence. Because of a slight erosion of the surface under ion bombardment due to sputtering, which modifies the surface composition with time, one has to make the measurements during an initial period before erosion becomes significant. This sputtering effect is more pronounced for heavy ions, and moreover a preferential character with respect to the elements that make up the alloy cannot be excluded. At a time $t=0$ after the sample equilibration, however, one thus measures the very segregation equilibrium.

All the samples were oriented by X-ray diffraction and mounted with the (112) azimuth in the scattering plane. Measurements have been carried out with 500 eV Ne^+ and He^+ ion beams of 0.3 mm diameter and 140–200 nA intensity using a scattering angle $\theta = 120°$. At time $t=0$, after a sufficient equilibration period at 720 K for the alloy, the peak heights were recorded within a few seconds after the ion beam had been put on. The results, reported in table 1, show a quite pronounced enrichment of the surface in Pt: about 30–35% instead of 10% in the bulk.

4. Discussion and conclusions

The observation of a well-contrasted (1 × 1) LEED pattern on the $Pt_{10}Ni_{90}(111)$ alloy indicates that no long range ordering of Pt or Ni atoms appears in the surface. Moreover, it is reasonable to assume that the surface parameter is the same as in the bulk.

A noticeable surface enrichment in Pt is evidenced, whatever surface analysis technique is used. For the measurement of the ultimate layer composition, ISS spectroscopy is the most direct and convenient technique if one uses low energy ion beams of small intensity and very short analysing times in order to avoid sputtering effects after reaching the surface equilibrium. From electron spectroscopy experiments the surface composition determination implies the knowledge of the attenuation factor of electron beams through the matter and the use of a model. The model with segregation in the uppermost layer only leads to the same determination of surface concentrations of Pt and Ni in the $Pt_{10}Ni_{90}(111)$ alloys from AES and XPS results, as that obtained more directly by ISS. This agreement, within the experimental precision range, validates this model in first approximation.

The same conclusions on monolayer segregation, with about the same Pt enrichment, are drawn from selective CO chemisorption [3] (table 1). The superficial composition determined from CO adsorption, which is based upon an aleatory distribution of both Pt and Ni at the surface as it is in the bulk [4,10], is very near that obtained from physical techniques. The statistical distribution of superficial Pt and Ni is probable and agrees with the observation of a (1 × 1) LEED pattern.

The low dependence of the superficial composition on temperature increase ($\Delta H = 0 \pm 2$ kcal/mole) indicates that, whatever the treatment, a quite reproducible surface composition is obtained for a clean $Pt_{10}Ni_{90}(111)$ alloy.

In conclusion, the clean surface of a $Pt_{10}Ni_{90}(111)$ alloy is, in surface, enriched in Pt: 30–40% at the surface instead of 10% in the bulk. This enrichment concerns mainly the ultimate surface layer and a statistic distribution of both Pt and Ni seems the most suitable. The Pt enrichment is "a priori" unexpected if one refers to classical segregation theories in the broken bond approximation for dilute regular solutions [11], which take into account the difference of surface energy of the pure components and their enthalpy of mixing and predict a superficial Ni enrichment. So other effects, such as elastic strain energy which favours segregation of the solute atoms mainly when they are oversized [11], have to be considered.

Note added in proof

The correction of the raw ISS results for the differences in atomic densities between the alloy samples and the Pt and Ni standards have been performed using the assumption of an epitaxial ordering of the outermost segregation enriched atomic layer.

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