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Surface-sandwich segregation on nondilute bimetallic alloys: $Pt_{50}Ni_{50}$ and $Pt_{78}Ni_{22}$ probed by low-energy electron diffraction

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A short-wave large-amplitude compositional oscillation versus depth at the (111) surface of $Pt_{50}Ni_{50}$ and $Pt_{78}Ni_{22}$ alloys is observed by means of low-energy electron diffraction (LEED). In the LEED calculation, the substitutional disorder of the alloys is successfully mimicked by the averaged t-matrix approximation. The occurrence of a well-developed Pt-Ni surface sandwich on top of the Pt-Ni alloys is interesting in view of the chemisorptive and catalytic properties of these alloys.

Auger electron spectroscopy and x-ray photoelectron spectroscopy are used to measure the segregation at the surface of monocrystalline and polycrystalline alloys,[1] but the composition-versus-depth resolution of these spectroscopies is not well established.[2] Low-energy ion scattering and secondary-ion mass spectroscopy are sensitive to the surface composition,[3] but assessment is difficult because of alloy effects on the sputtering yield. Field-ion microscopy combined with time-of-flight measurement of the field-evaporated ions is a method which exhibits a large composition-versus-depth resolution[4] and is applied to dilute alloys. For instance, near the (111) surface of Cu_5Ni_{95} alloy one finds multilayer segregation with a 54% copper concentration in the top layer, followed by a nonmonotonic 2—9 % copper content.[4] In Au_4Pt_{96} alloy there is a 99% gold enrichment in the (100) top layer, decreasing monotonically to the gold ratio of the bulk over three layers.[5]

In this paper we establish that low-energy electron diffraction (LEED) is capable of measuring, with great accuracy, the composition of the three outermost layers of substitutionally disordered bimetallic alloys. This conclusion is drawn from LEED experiments and calculations on the (111) surface of the two fcc platinum-nickel alloys, $Pt_{50}Ni_{50}$ and $Pt_{78}Ni_{22}$, which are substitutionally disordered in the bulk. As illustrated in Fig. 1, we observe that the Pt-Ni composition oscillates across three layers with important enrichments and depletions of the constituent elements in relation to the bulk composition. At its surface each one of the studied alloys segregates into a well-developed Pt-Ni sandwich with platinum on top.

The platinum-nickel samples were spark cut from monocrystalline rods and mechanically polished. The (111) planes were essentially parallel to the macroscopic surface (tilt $<20'$) as evidenced by specular reflections produced by an x-ray source and a laser. The crystalline phase of the samples was checked to be fcc, and the quadratic phase[6] was in no case observed. Surface cleanliness, monitored by Auger measurements, was achieved by repeated argon bombardment and successive annealing up to 900 °C (Ref. 7). The LEED patterns were perfectly sharp, with a low background and with intense beam threshold effects, which altogether indicate well-prepared surfaces. The data were taken at room temperature, and the Auger and LEED spectra proved to be independent of the annealing procedure.

In our LEED experiments on $Pt_{50}Ni_{50}$ and $Pt_{78}Ni_{22}$ we recorded $I(V)$ spectra of 21 and 25, respectively, nonequivalent beams corresponding to three polar angles of incidence: $\theta=0°$, 10°, and 20°. The measurements were made in the range 30—330 eV, and spectra over symmetrically equivalent beams were averaged. The $I(V)$ spectra of the two alloys proved more similar to one another than to the spectra of either of the pure metals. This is an indication that the surface regions of the two alloys have similar composition and geometry.

We limited the LEED calculations to the range 30 to 200 eV and 30 to 230 eV, respectively, because of lower sensitivity to surface composition at higher energies, where the penetration of the LEED electrons is large. A layer-KKR (Korringa-Kohn-Rostoker) program equipped with a layer-doubling routine was employed.[8,9] We calcu-

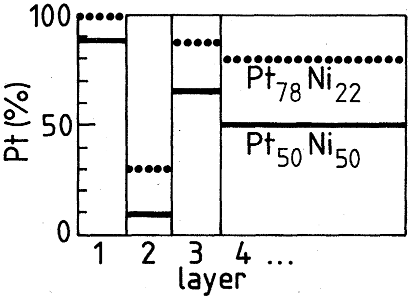

FIG. 1. Compositional oscillation at the (111) surface of $Pt_{50}Ni_{50}$ and $Pt_{78}Ni_{22}$.

TABLE I. Compositional profile near the (111) surface of two Pt-Ni alloys. x is Pt concentration; d is (111) interlayer separation.

	$Pt_{50}Ni_{50}$		$Pt_{78}Ni_{22}$	
	x (at. %)	d (Å)	x (at. %)	d (Å)
Layer 1	88±2	2.12±0.02	99±1	2.18±0.02
Layer 2	9±5	2.12±0.02	30±5	2.18±0.02
Layer 3	65±10	2.16	87±10	2.22
Bulk	50	2.164	78	2.220

lated excited-state ion-core potentials for platinum and nickel, starting from self-consistent ground-state band-structure calculations and applying the local-density approximation of Hedin and Lundqvist.[10] This scheme gives ion-core scattering phase shifts referred to an energy-dependent inner potential.[11] For platinum the calculations were carried through relativistically.

We represent the random occupation of the lattice sites by the averaged t-matrix approximation (ATA),[12,13] which fits in with the layer-KKR framework on which current LEED theory is based. ATA is the zeroth approximation of the coherent potential approximation which accurately mimics the electronic structure of bimetallic alloys near the Fermi energy.[12] The present multilayer application shows that ATA excellently describes the ion-core scattering taking place at the relatively high energy of LEED. For the average atom of layer n, the scattering amplitude of partial wave l is

$$t_l^{(n)}=x^{(n)}t_{l,\mathrm{Pt}}+(1-x^{(n)})t_{l,\mathrm{Ni}}\ , \tag{1}$$

where $t_{l,\mathrm{Pt}}$ and $t_{l,\mathrm{Ni}}$ refer to the pure-metal amplitudes and $x^{(n)}$ is the platinum concentration in layer n. Nonstructural parameters such as inner potential, atomic mass, and Debye temperature are averaged, to a reasonable approximation, with the same compositional weights as in expression (1).

The LEED theory is conveniently compared with experiment by means of metric distances between spectra.[14,15] A total range for all beams of 2400 and 3000 eV, respectively, is utilized in the analysis. We set up variational grids for the platinum concentrations and the interlayer separations of the three top layers and include, in addition, a grid for possible shifts of the inner potential. Optimizing these parameters simultaneously, we find for $Pt_{50}Ni_{50}$ and $Pt_{78}Ni_{22}$ the surface structures given in Table I. The agreement between calculated and measured spectra has similar quality as for LEED spectra from pure metals. A few LEED spectra for $Pt_{50}Ni_{50}$ are shown in Fig. 2, and the sensitivity of the metric comparison is illustrated in Fig. 3. Layer arrangements with stacking faults are found to disagree with the experiments. Table I extends previous ion-scattering and AES results[7,16] concerning the composition of the first layer.

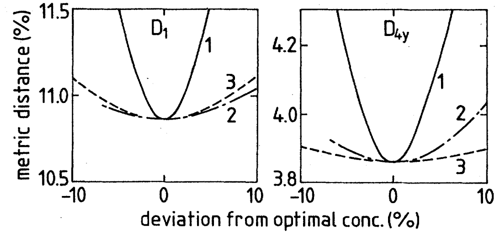

FIG. 3. Metric distance between LEED spectra versus deviation from optimal Pt concentration for layers 1,2,3 of $Pt_{50}Ni_{50}$. D_1 and D_{4y} as in Ref. 14.

The existing literature on segregation does not seem to formulate, explicitly, the driving force that sustains the short-wave large-amplitude compositional oscillation near the surface of Pt-Ni alloys. A phenomenological approach commonly used for explaining segregation at surfaces of alloys is based on thermodynamics and the pair bonding model (Defay *et al.*[17]). On the assumption that the surface bond enthalpies are relaxed in relation to the corresponding bulk band enthalpies,[18,19] this model can be adjusted to measured top-layer concentrations as, for instance, those of Refs. 4 and 7. The band enthalpy relaxations are, however, determined *a posteriori* from the measured surface compositions. Recent first-principles studies relate the segregation energy to the electronic structure of the surface region. Riedinger and Dreysse[20] treat dilute transition-metal alloys in terms of substitutional impurities and the tight-bonding model, and Barnett *et al.*[21] consider simple-metal alloys in a pseudopotential picture. However, a first-principles approach, explaining the compositional oscillations found in the Pt-Ni alloys under consideration, should be able to distinguish effects due to heavy and transition metals, nondilute alloys, ion-ion repulsion, and lattice relaxation.

In summary, we observe on top of the $Pt_{50}Ni_{50}$ and $Pt_{78}Ni_{22}$ alloys a well-developed Pt-Ni sandwich, which

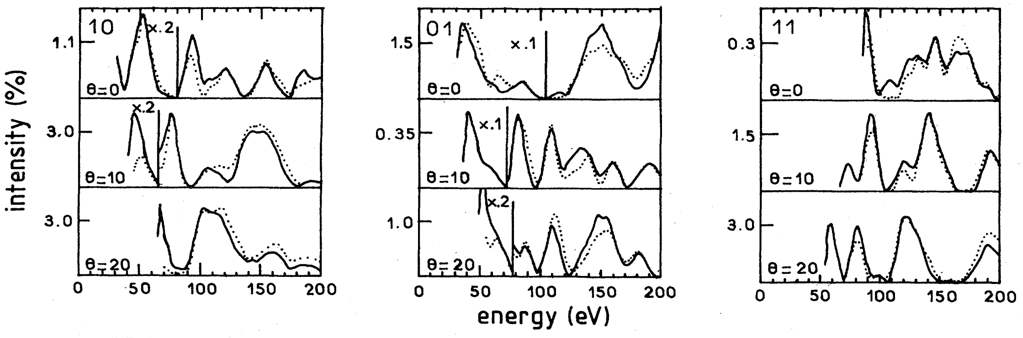

FIG. 2. LEED spectra from $Pt_{50}Ni_{50}$. Experiment, dotted line; theory, solid line.

appears as a new and important element in the discussion of the chemisorptive[7] and catalytic[22] properties of these alloys. Further, we establish that LEED combined with ATA has a great promise of determining the compositional profile of three surface layers of substitutionally disordered bimetallic alloys. It has come to our knowledge that other groups[23] have started work along similar lines as in this paper.

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[1] M. P. Seah, J. Catal. **57**, 450 (1979).

[2] P. A. Dowben, M. Grunze, and D. Wright, Surf. Sci. **134**, L524 (1983).

[3] H. H. Brongersma, J. M. Sparnaay, and T. M. Buck, Surf. Sci. **71**, 657 (1978).

[4] Y. S. Ng, T. T. Tsong, and S. B. McLane, Phys. Rev. Lett. **42**, 588 (1979).

[5] T. T. Tsong, Y. S. Ng, and S. B. McLane, J. Chem. Phys. **73**, 1464 (1980).

[6] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelle, *Selected Values of the Thermodynamic Properties of Binary Alloys* (American Society of Metals, Metal Park, OH, 1973).

[7] J. C. Bertolini, B. Tardy, M. Abon, J. Billy, P. Delichere, and J. Massardier, Surf. Sci. **135**, 117 (1983).

[8] J. B. Pendry, *Low Energy Electron Diffraction* (Academic, London, 1974).

[9] J. Rundgren and A. Salwén, J. Phys. C **9**, 3701 (1976).

[10] L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[11] J. Neve, P. Westrin, and J. Rundgren, J. Phys. C **16**, 1291 (1983).

[12] B. L. Györffy and G. M. Stocks, in *Electrons in Disordered Metals and at Metallic Surfaces,* edited by P. Phariseau, B. L. Györffy, and L. Scheire (Plenum, New York, 1979).

[13] F. Jona, K. O. Legg, H. D. Shih, D. W. Jepsen, and P. M. Marcus, Phys. Rev. Lett. **40**, 1466 (1978).

[14] S. A. Lindgren, L. Walldén, J. Rundgren, and P. Westrin, Phys. Rev. B **29**, 576 (1984).

[15] Y. Gauthier, R. Baudoing, Y. Joly, C. Gaubert, and J. Rundgren, J. Phys. C **17**, 4547 (1984).

[16] L. De Temmerman, C. Creemers, H. Van Hove, A. Neyens, P. Delichere, J. Massardier, B. Tardy, M. Abon, and J. C. Bertolini, Vide Couches Minces **38**, 217 (1983).

[17] R. Defay, I. Prigogine, A. Bellemans, and D. H. Everett, *Surface Tension and Adsorption* (Longmans, London, 1966).

[18] F. L. Williams and D. Nason, Surf. Sci. **45**, 377 (1974).

[19] M. S. Spencer, Surf. Sci. **145**, 153 (1984).

[20] R. Riedinger and H. Dreysse, Phys. Rev. B **27**, 2073 (1983).

[21] R. N. Barnett, U. Landman, and C. L. Cleveland, Phys. Rev. B **28**, 6647 (1983).

[22] J. Massardier and J. C. Bertolini, J. Catal. **90**, 358 (1984).

[23] D. F. Ogletree, M. A. van Hove, and G. A. Somorjai, Bull. Am. Phys. Soc. **29**, 222 (1984); D. Sondericker, F. Jona, and P. M. Marcus, *ibid.* **29**, 222 (1984).