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Surface Composition of Nickel–Gold Alloys

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Nickel–gold alloy foil surfaces were analyzed with Auger electron spectroscopy. The gold atom fraction, x^s, at a clean surface is higher than that in the bulk, x^b. Thus, for an alloy with $x^b = 0.005$, the clean surface showed $x^s = 0.5$. This alloy chemisorbed oxygen at room temperature, after which gold was not detected at the surface. However, oxygen was not chemisorbed at room temperature on alloys with $x^s = 0.7$ or 0.86 and these values of x^s corresponding to the clean surface did not change after 3×10^{-4} Torr/sec oxygen exposures. The gold enrichment at the clean surface can be explained quantitatively by a simple thermodynamic argument. The change in x^s due to oxygen is understood qualitatively. The lack of chemisorption of oxygen on surfaces containing as much as 30% nickel suggests electronic effects due to alloying.

INTRODUCTION

Auger electron spectroscopy (AES) has been extensively applied to surface studies of materials in order to ascertain their cleanliness or the extent of chemisorption (*1–3*). The determination of the surface composition of alloys has been understood as an important application of AES as indicated by Harris (*4*) in one of the first papers heralding the recent surge in AES. In particular, AES has been used to analyze the surface composition of nickel–copper alloys. Ertl and Küppers (*5*) analyzed the (110) face of a 50% nickel–50% copper single crystals with AES and determined that the surface and bulk composition were equal. Quinto, Sundaram, and Robertson (*6*) reported that over the entire range of bulk alloy composition the surface and bulk compositions are the same for a clean surface of nickel–copper foils after argon bombardment and subsequent annealing. Natayama, Ono and Shimizu (*7*) have investigated the surface composition of copper–nickel alloy foils after ion bombardment or oxygen and hydrogen treatments. Taring and Wehner (*8*) demonstrated selective sputtering from nickel–copper (45% nickel) foil. Unfortunately all of these authors have used high energy (>680 eV) Auger transitions for the surface analysis. The large mean escape depth of electrons with those high energies necessarily requires the Auger surface composition to be an average over at least 10 atomic layers (*9*). Therefore information about changes in composition in the first one or two atomic layers at the surface would be lost.

Ferrante (*10*) has reported the enrichment of copper–aluminum alloy surfaces with aluminum. He used Auger transitions of low energy (<100 eV) and therefore may have the first determination of the composition of the first layer of an alloy surface with Auger spectroscopy. Unfortunately he calibrated the spectra by assuming that an extensively sputtered surface would have the same composition as the bulk alloy. This assumption does not appear sound when considered with Tarng and Wehner's recent results (*8*).

The determination of the composition of the first two atomic layers of an alloy surface has obvious application to heterogeneous catalysis. An Auger electron spectroscopic analysis of an alloy surface allows us to determine the surface composition averaged over layers at the surface from which Auger electrons can escape. Unfortunately escape depths are not known for all materials and electron energies. Therefore the surface composition determined by AES cannot generally be assumed to be the composition of the first two atomic layers of the alloy. The best that can be done experimentally is to use Auger transitions with energies corresponding to the minimum escape depth when determining surface compositions.

In a study of alloy surfaces, we were guided by two considerations. First, we restricted our choice to binary alloys of catalytic interest, namely nickel, palladium or platinum on the one hand, with copper, silver or gold, on the other hand. Alloy composition variation for any of the nine alloy pairs represents a transition from unfilled to filled *d* bands and from good to poor activity for making or breaking of H–H and C–H bonds. The second consideration involved the ability to resolve the Auger spectra of the elements present at the alloy surface. Nickel and gold contributions to the spectra can be easily resolved at high energies (>100 eV).

EXPERIMENTAL METHODS

Most samples were prepared by electrodeposition of one element onto a foil of the other. The electroplating solution for nickel was made from the nickel chloride salt with boric acid added to adjust pH to 1.5–2.0. Chlorauric acid solutions adjusted to pH 6 with sodium hydroxide were used to deposit gold. Foils of Grade "A" nickel (99.4%), 99.999% nickel and 99.999% gold were used for various samples. After electrodeposition the samples were washed in distilled water and dried in air. We prepared another alloy by annealing 99.999% nickel and 99.999% gold foils together in hydrogen at 1 atm and ca. 1200 K for 72 hr. All samples were suspended in the vacuum chamber on Grade "A" nickel wires for annealing and cleaning by exposures of the alloys to oxygen and then hydrogen at 10^{-5} Torr and high alloy temperatures ($\sim$1300 K). Ion bombardment was avoided to avoid changes in surface composition it may induce. Since the Auger spectra recorded during the course of cleaning and annealing are interesting in themselves, the treatment of each sample after initial (out of vacuum chamber) preparation will be described along with the results for each alloy.

Auger spectrometry was performed in a Varian-240 LEED system that was modified for AES (*11*). An electron beam of 2.5 keV energy was used to excite Auger transitions and struck the surface at an angle of approximately 15° with respect to the surface for maximum surface sensitivity (*12*). Energy analysis of the emitted gridded, retarding field analyzer. Temperature was measured with tungsten–rhenium thermocouples that were spot welded to the back of the alloy foil samples. The foils were resistively heated inside the vacuum chamber.

The calculation of the surface composition is based on the peak to peak heights of the derivative spectrum and the relative sensitivity of the Auger transitions for the pure metals. We need to know the number of atoms, for each species within the sampled region to determine the atom fraction. If the number of atoms is proportional to the derivative Auger peak to peak height, $H(E)$, for the element's Auger transition of energy E, then the Auger surface atom fraction of gold, x^s is determined from the relationship

$$x^s = \frac{1}{1 + S(H_{\mathrm{Ni}}(E)/H_{\mathrm{Au}}(E))},$$

where S is the ratio of the peak to peak heights $H^0(E)$ for the Auger transition of energy E of the pure metals,

$$S \equiv H_{\mathrm{Au}}{}^0(E)/H_{\mathrm{Ni}}{}^0(E).$$

If we assume that the escape depth for Auger electrons in the pure materials and the alloys is the same and that the rates of ionization are unchanged by alloying, then the Auger composition is an average composition of the sampled atomic layers. For the nickel–gold system we used the Auger transition of gold at 145 eV and nickel at 840 eV with $S = 0.27$ to calculate surface compositions. The difference in escape depth of the electrons from gold and nickel should be compensated by the fact that the more dense material has a lower Auger transition energy and is less sensitive than nickel. That is, the effective escape depth of the analysis should be between the escape depths of the two pure metals. Since there are no independent determinations of the surface compositions we must assume that the relative sensitivity of the Auger transitions is not changed upon alloying. The value of S was determined at Varian by comparison of their data for pure elements under the same experimental conditions and given to us through private communication (*13*). These two transitions were used rather than the nickel 60 eV and gold 72 eV Auger transitions because of the high background slope in the derivative Auger spectra in the energy range of the latter transitions (*14*). Composition profiles could not be determined since we do not have atom ionization or electron escape probabilities as a function of depth, Auger transition and alloy composition.

RESULTS

Sample A

Sample A was prepared by electrodeposition of gold on a 99.999% nickel foil. The nominal, equilibrated composition was 99.5% nickel. After the AES work, electron microprobe analysis showed the sample to be 99.6% nickel averaged over the 1 μm penetration depth below the surface. A cross section of the sample was also analyzed with the electron microprobe and found to be 0.12% gold at the center. X-Ray diffraction showed no signs of separate phases or gold crystallites.

AES analysis during the cleaning of this sample showed sulfur, carbon, and oxygen as impurities. The ratio of nickel to gold increased when the level of sulfur or oxygen at the surface increased. Chlorine, presumably from the plating solution, was removed during the first heating of the sample in vacuum. Annealing for over 1 hr at ~1300 K was carried out during the cleaning and equilibration stage. We found the equilibrated, clean surface to be 50% nickel.

The clean surface chemisorbed oxygen with an initial sticking coefficient of 0.02 at room temperature and 3×10^{-7} Torr oxygen. Oxygen chemisorption continued until a constant AES oxygen signal was obtained. Exposures over 3×10^{-3} Torr/sec at 10^{-5} Torr oxygen did not increase the AES oxygen signal. We used the constant AES oxygen signal to define monolayer oxygen chemisorption.

The chemisorption of oxygen induced a dramatic change in the rest of the Auger spectrum. Comparing Figs. 1 and 2, we see that the large gold peaks have disappeared

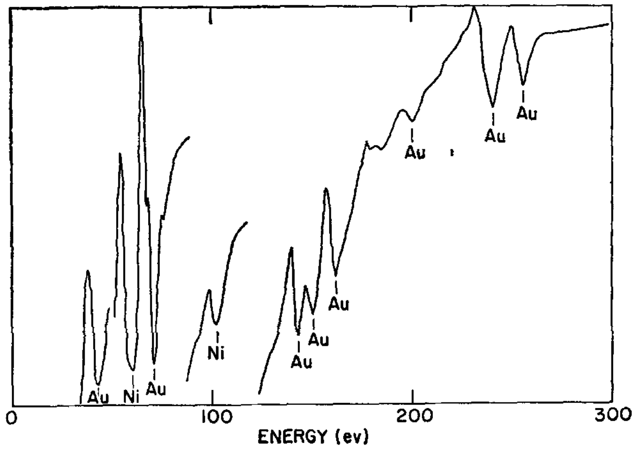

FIG. 1. Auger electron spectrum from clean nickel–gold alloy sample A: Second derivative of current with respect to voltage (arbitrary units) as a function of electron energy.

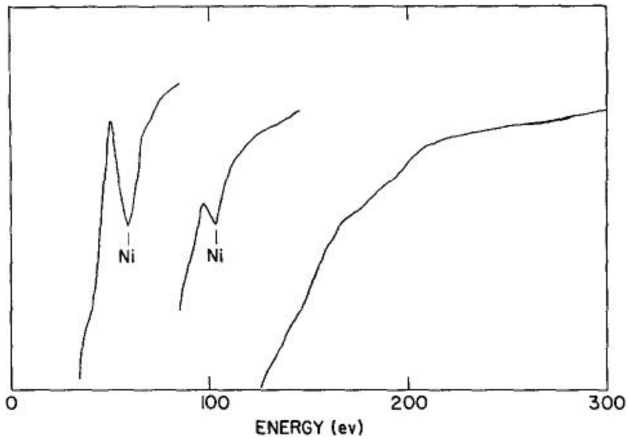

FIG. 2. Auger electron spectrum from nickel–gold alloy sample A after oxygen chemisorption: ordinates as in Fig. 1.

after monolayer oxygen chemisorption. Heating the foil to ~1300 K in vacuum removed the oxygen from the AES spectra and restored the equilibrium clean surface composition.

When the clean surface was exposed at room temperature for 300 sec at 10^{-5} Torr hydrogen, which cannot be analyzed by AES, the nickel composition of the surface increased to 65%. Exposure of the surface at room temperature to a stoichiometric mixture of hydrogen and oxygen at 10^{-5} Torr for 300 sec resulted in a surface composition identical to that found after exposure to pure oxygen. Whether the catalytic reaction to form water was occurring on the alloy could not be ascertained.

Sample B

Sample B was prepared by electrodeposition of gold on a Grade "A" nickel foil. The nominal, equilibrated composition was 96.5% nickel. The deposition was known to be uneven and the gold rich end of the sample was used for AES. After AES analysis, the composition of the studied region was 96.5% nickel by electron microprobe analysis. X-Ray diffraction did not reveal separate phases or gold crystallites.

After repeatedly heating the sample to 1000 K in 10^{-6} Torr hydrogen, the AES spectrum did not change. However, heating the sample to 1300 K for ~15 sec in vacuum greatly reduced the nickel/gold ratio and the impurity level as well. Another 1300 K treatment in vacuum for 120 sec showed a large increase in nickel and sulfur peaks in the AES spectra. A 10 min treatment in vacuum at 1300 K showed a gold rich surface with perhaps a very low level of sulfur impurity. Annealing in vacuum for over 70 min at 1300 K gave a surface that did not change with further annealing. The surface composition was approximately 30% nickel. The surface did not adsorb oxygen when exposed to 10^{-6} Torr oxygen at room temperature for 300 sec. Thus the oxygen sticking coefficient based on 10% of a monolayer detectability by AES is necessarily less than 3×10^{-5}.

Sample C

This sample was prepared from two, 99.999% pure, foils by high temperature annealing in hydrogen. The nominal equilibrated composition was 77% nickel. Electron microprobe analysis of the sample after the AES experiments showed the surface composition to be 74% nickel. Sample C was the most easily cleaned sample we used. The sample was cleaned by heating in vacuum to 1300 K. The equilibrium surface composition was determined to be 14% nickel. Surface oxygen could not be detected after exposure to oxygen of 300×10^{-5} Torr/sec and room temperature. The surface became enriched in nickel up to 20% as the sample was heated in vacuum.

At 1300 K we estimate the composition to be 20% nickel.

Sample D

Pure gold foils (99.999% gold) were mounted on gold wrapped clamps in the vacuum chamber. Auger peaks characteristic of reported gold spectra were observed as well as sulfur, carbon, nitrogen, and oxygen at the surface. A clean AES spectrum was never achieved even when the samples had been heated to the melting point in vacuum or 10^{-5} Torr oxygen.

Discussion

The nickel–gold alloy system clearly shows the deviation of surface composition from bulk composition even for a 99.6% nickel sample (Sample A) that was shown to be nearly homogeneous by electron microprobe analysis of a cross section of the sample. The measured AES surface compositions (Fig. 3) all reflect the adsorption of gold at the clean nickel–gold interface. As can be seen, all of the experimental results are consistent with the theory developed for the determination of the surface composition of alloys (*11*). The theory is based on pair bond energies determined from bulk alloy activity coefficient and the pure metal heats of vaporization. The alloy component with the lower heat of vaporization is predicted to absorb at the surface.

Oxygen chemisorption on Sample A gives dramatic evidence for the changes in the surface composition of binary alloys that can occur upon chemisorption. The nickel–oxygen bond is stronger than the gold–oxygen bond (*15*) and therefore the surface may be expected to become nickel rich. The oxygen chemisorption at room temperature also demonstrates the surface sensitivity of AES for the nickel–gold system. The change in the surface composition can only occur over a few atomic layers and that change is readily observable with AES as can be seen in Figs. 2 and 3.

Hydrogen chemisorption on Sample A causes the nickel concentration to increase also, but to a lesser extent than for oxygen chemisorption. This result can be understood if the nickel–hydrogen bond is stronger than the gold–hydrogen bond but the difference in bond strengths is less than for the case of oxygen chemisorption.

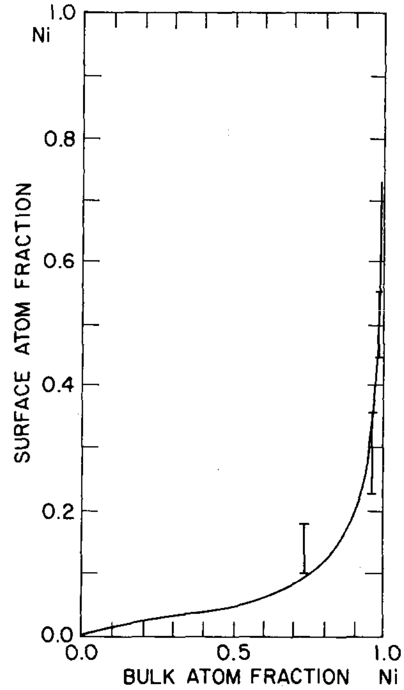

Fig. 3. Nickel–gold alloy AES surface compositions. Details are in the text for each sample A, B, and C. The calculated curve is drawn according to a theory developed to predict alloy surface compositions from bulk alloy thermodynamic data (*11*). The error bars reflect uncertainty in surface compositions for well-known bulk compositions.

We did not observe oxygen chemisorption on Sample B or C. The oxygen sticking coefficient on these alloys is less than 3×10^{-5} compared to the measured sticking coefficient, $\gamma = 0.02$, on alloy A. We eliminate the possibility that the whole first atomic layer of alloys B and C is gold, and therefore chemisorbs as gold would, because the thermodynamic theory as well as the AES results indicate the presence of nickel at the surface. If oxygen chemisorption required two adjacent nickel atoms the fall in sticking coefficient should be less dramatic. A plausible explanation is that as the nickel concentration at the surface is decreased from 50 to 30%, the electronic configuration of the nickel is altered to the extent that the chemisorption is at best slow at room temperature.

The Auger surface composition of Sample C increased in nickel content when the sample was heated. The differences in bonding energies become less important and entropy effects relatively more important at higher temperatures. Therefore as the temperature increases the surface composition should approach the bulk composition.

The surface composition of all the alloy samples is richer in nickel than what we would expect for the clean surface, when sulfur is detected as an impurity. The sulfur impurity effect is analogous to the oxygen chemisorption, since sulfur and oxygen are chemically similar.

The inability to clean a pure gold surface, whereas alloys of gold with nickel were relatively easier to clean, is an interesting result in itself. We consider the nickel atoms at the surface of the alloy to be a source of oxygen (or hydrogen) atoms that can migrate to the impurity atoms associated with gold. The spillover of atoms from nickel to gold thereby facilitates cleaning the alloy. Pure gold has no such sources of atoms and therefore is not cleaned under the same conditions as those producing clean alloy surfaces.

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