JOURNAL OF CATALYSIS 36, 114–117 (1975)

Observation of the Segregation of Cu to the Surface of a Clean, Annealed, 50% Cu–50% Ni Alloy by Auger Electron Spectroscopy[1]

There has been considerable interest in the catalytic properties of the Cu–Ni alloys, with the primary goal of determining the relationship between catalytic activity and electronic structure (*1*). In attempting to interpret data from the numerous catalytic studies of these alloys, two factors appear to be of prime importance. First, what is the effect of the electronic interaction between the Cu and Ni atoms at the surface and, second, what is the effect of a deviation from the bulk composition in the surface layer (*1*)?

To answer the second question there have been numerous studies of the Cu–Ni alloys by Auger electron spectroscopy (AES) (*2–5*) with the hope of determining the surface composition with this technique. For the most part, these workers found that the transitions in Cu and Ni that should be most surface sensitive, those at approximately 60 and 100 eV, could not be easily resolved in energy (*6*). Most of the quantitative measurements were therefore made on Auger transitions ranging from 700 to 950 eV, which can be sensitive to considerably more than the first layer. In these studies the composition as measured by the high energy transitions was found to follow quite closely that of the bulk.

The sensitivity of AES to the surface layer is determined by the escape depth of the emitted electrons. This is plotted in Fig. 1 for Cu and Ni (*7–10*) versus the electron's energy above the Fermi level. The uncertainty indicated is considered the worst case limit on the escape depth. As can be seen from Fig. 1, the high energy Auger transitions for Cu and Ni average over at least five and possibly up to eight atomic layers. Thus, the effect of deviations from stoichiometry in the first layer on the Auger spectra would be minimal.

In this letter we report on preliminary measurements of the surface composition of a 50% Cu–50% Ni crystal of approximately (100) orientation by AES at approximately 100 eV, the energy range at which the best surface sensitivity should be attained. We observe a substantial deviation from the bulk composition tending toward the Cu-rich side in agreement with other indirect measurements (*1, 11*) and a recent calculation of surface composition of homogeneous binary alloys (*12, 13*).

The experiments were performed in a standard Varian system with a four-grid LEED optics and grazing incidence electron gun. Sputtering of the samples for cleaning purposes was done using a Varian sputter ion gun as described below. System base pressure was better than 10^{-10} Torr.

The sample was a 50% Cu–50% Ni (atomic percentage) wafer cut from a mechanically polished ingot grown by the Bridgman technique. X-ray diffraction indicated that the wafer was polycrystalline with crystallites a few millimeters in diameter all with approximately a (100) orientation. Electron microprobe analysis indicated that the "bulk" composition was 50 ± 5% across the surface of the wafer. Cleaning of the samples required a number of sputter–anneal cycles to remove sulfur present as a bulk impurity. Sputtering was done using an argon ion beam of approximately 300 eV; the argon pressure was approximately 5×10^{-4} Torr and the cur-

---

[1] Supported by NSF Grants GH 34567 and GK 17451X.

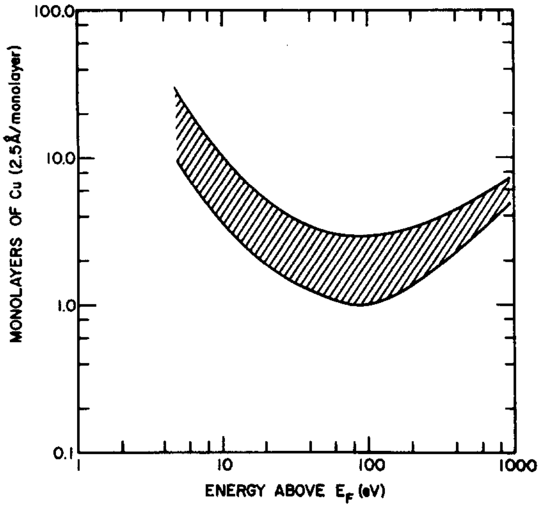

FIG. 1. Electron escape depth for Cu and Ni plotted as monolayers of Cu versus electron energy above the Fermi level.

rent density was approximately 2 μA/cm^2. Approximately 100 Å was removed during the ten sputter–anneal cycles. Annealing was done at approximately 600°C for 15 min after each sputter. The "clean" sample was characterized by impurity levels as indicated in Table 1 where the ratio of the second derivative impurity peaks to the Ni/Cu peak at ~60 eV are presented at a beam energy of 2500 eV. It is estimated that the total impurity concentration as indicated in Table 1 corresponds to less than 5% of a monolayer.

In Table 2 the major Auger transitions from Cu and Ni and their observed energies are indicated. The observed energy is defined as the position of the negative going peak in the second derivative Auger spectrum *uncorrected* for the electron optics work function. The calculated values were taken from Coghlan and Clausing (*14*), obtained using the method of Chung and Jenkins (*15*).

TABLE 1
IMPURITY LEVEL ON CLEAN SAMPLE

Impurity	Peak ratio
Sulfur (150 eV)	0.001
Carbon (270 eV)	0.0005
Nitrogen (380 eV)	0.0001
Oxygen (510 eV)	0.0001

TABLE 2
OBSERVED AUGER TRANSITION ENERGIES FOR Cu AND Ni (ENERGIES IN eV)

Transition	Observed energy	Calculated energy
Cu $M_{2,3}M_{4,5}M_{4,5}$	58.2 ± 0.2 60.9 ± 0.2	63
Cu $M_1M_{4,5}M_{4,5}$	106.0 ± 0.5	109
Cu $L_3M_{2,3}M_{2,3}$	778 ± 3	770
Cu $L_3M_{2,3}M_{4,5}$	848 ± 3	845
Cu $L_3M_{4,5}M_{4,5}$	920 ± 2	920
Ni $M_{2,3}M_{4,5}M_{4,5}$	61.0 ± 0.5	62
Ni $M_1M_{4,5}M_{4,5}$	100.0 ± 0.5	106
Ni $L_3M_{2,3}M_{2,3}$	714 ± 2	713
Ni $L_3M_{2,3}M_{4,5}$	778 ± 3	781
Ni $L_3M_{4,5}M_{4,5}$	848 ± 3	849

An Auger second derivative spectrum from the sample is shown for energies greater than 700 eV in Fig. 2a for the clean, annealed sample and in Fig. 2b for the sample after sputtering for 5 min. As discussed above, the transitions between 700 and 950 eV are sensitive to approximately 5–8 monolayers. *Both* Cu

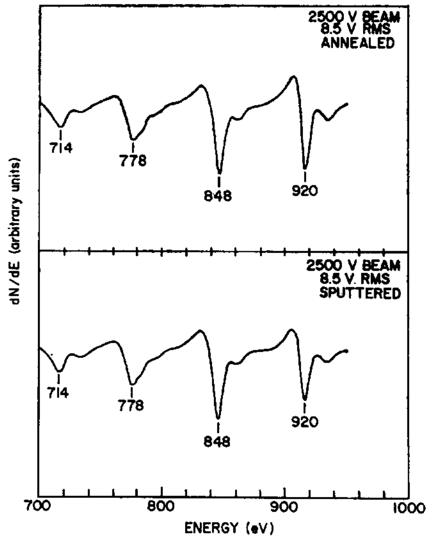

FIG. 2. Second Derivative Auger spectrum of a 50% Cu–50% Ni sample plotted versus the electrons energy for energies greater than 700 eV.

($L_3M_{4,5}M_{4,5}$ transition at 920 eV) and Ni ($L_3M_{2,3}M_{2,3}$ transition at 714 eV) are clearly present in this spectra. A crude measure (*16*) of the Ni/Cu ratio, R(Ni/Cu), within this depth can be obtained by taking the ratio of the $L_3M_{4,5}M_{4,5}$ transition strengths (*16, 17*). For the sputtered sample, R_{L_3} (Ni/Cu) = 1.0 ± 0.1; for the annealed sample, R_{L_3} (Ni/Cu) = 0.55 ± 0.025. The composition of the first five monolayers is therefore severely affected by the surface treatment, as found by other workers.

To obtain better sensitivity to the surface layer, one would like to use the $M_{2,3}M_{4,5}M_{4,5}$ transitions due to their strength. For Cu and Ni, however, these transitions are too closely spaced in energy to be resolved (see Table 2). The $M_1M_{4,5}M_{4,5}$ transitions, however, although much weaker, could be resolved in this experiment and therefore provided a means of looking much closer to the surface.

In Fig. 3 the Auger spectrum at around 100 eV is plotted for the same conditions as those of Fig. 2. For the clean annealed surface, *no* Ni whatsoever is detected (*18*).

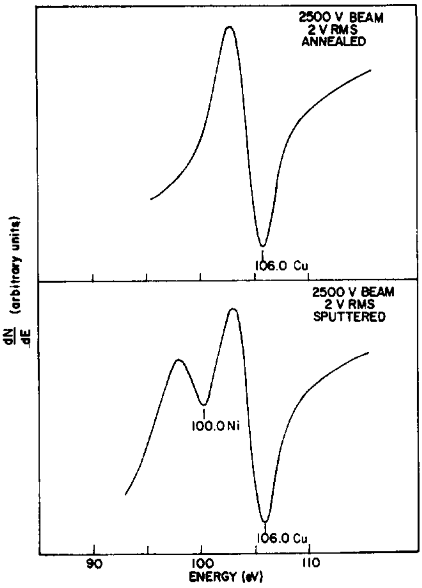

FIG. 3. Second Derivative Auger spectrum of a 50% Cu-50% Ni sample in the energy around 100 eV.

After sputtering, however, some Ni is detected, consistent with the changes observed in the high energy transitions. As with the high energy transitions, a crude estimate of the Ni/Cu ratio can be obtained by taking the ratio of the $M_1M_{4,5}M_{4,5}$ transition strengths. R_{M_1} (Ni/Cu) for the sputtered and annealed sample determined in this way are 0.2 ± 0.025 and $0.0\begin{Bmatrix}+0.5\\-0.0\end{Bmatrix}$, respectively (*18*). Further annealing after sputtering reproduces the curve of Fig. 3b.

The variation in the Cu–Ni ratio between the $L_3M_{4,5}M_{4,5}$ transition where substantial quantities of Ni were observed and the $M_1M_{4,5}M_{4,5}$ transition where no Ni is observed is consistent with the variation in electron escape depth with electron energy. From Fig. 1 at 100 eV, the $M_1M_{4,5}M_{4,5}$ transition measures approximately 1–3 monolayers which, for the annealed sample, is virtually 100% Cu. At approximately 900 eV, however, the $L_3M_{4,5}M_{4,5}$ transition averages over approximately 5–8 monolayers where appreciable amounts of Ni are detected.

The data we have obtained on only one alloy composition of one crystallographic direction are not sufficient to distinguish between the various models that predict surface segregation for the Cu–Ni alloys (*11–13, 19*). One model due to Sachther and co-workers and Takasu and Shimizu suggest that the Cu–Ni alloys are not miscible for all compositions at low temperature (below ~ 300°C). One thus might expect phase separation at the surface as observed in this work. In a more recent work, Williams and co-workers have calculated the surface composition of *miscible* binary alloys using a broken bond model and regular solution theory (*12, 13*). For Cu–Ni the atom fraction of Ni in the first atomic layer is plotted versus the bulk atom fraction in Fig. 4 (*12, 13*). The bar at a 50/50 bulk composition is the data from the present work. It should be noted that this theory has been applied with success to the Au–Ni system where substantial enrichment of the surface in Au has been reported (*20*).

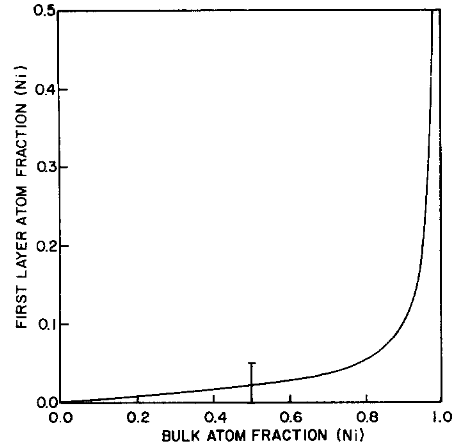

FIG. 4. Calculated values of first-layer atom fraction of Ni versus bulk atom fraction of Ni from Refs. (*12*) and (*13*).

ACKNOWLEDGMENT

The author would like to thank Michel Boudart for placing the facilities of his laboratory at the author's disposal and for stimulating discussions.

REFERENCES

1. SINFELT, J. H., CARTER, J. L., AND YATES, D. J. C., *J. Catal.* **24,** 283 (1972).

2. ERTL, G., AND KÜPPERS, J., *Surface Sci.* **24,** 104 (1971).

3. QUINTO, D. T., SUNDARAM, V. S., AND ROBERTSON, W. D., *Surface Sci.* **28,** 504 (1971).

4. NAKAYAMA, K., ONO, M., AND SHIMIZU, H., *J. Vac. Sci. Tech.* **9,** 749 (1972).

5. TAKASU, Y., AND SHIMIZU, H., *J. Catal.* **29,** 479 (1973).

6. ONO, M., TAKASU, Y., NAKAJAMA, K., AND YAMASHINA, T., *Surface Sci.* **26,** 313 (1971), AES studies of 60% Cu-40% Ni at ~100 eV. These authors observed a Cu-rich surface as in the present work; their resolution was too poor, however, to allow meaningful quantitative analysis.

7. WEBB, M. B., AND LAGALLY, M. G., *Solid State Physics* **28,** 302 (1973).

8. TRACY, J. C., *J. Vac. Sci. Tech.* **11,** 280 (1974).

9. LINDAU, I., AND SPICER, W. E., *J. Elect. Spect. Rel. Phen.* 3, 1 (1974).

10. BRUNDLE, C. R., *J. Vac. Sci. Tech.* **11,** 212 (1974).

11. VAN DER PLANK, P., AND SACHTLER, W. M. H., *J. Catal.* **7,** 300 (1967), and references contained therein.

12. WILLIAMS, F. L., AND NASON, D., *Surface Sci.* submitted.

13. WILLIAMS, F. L., Ph.D. dissertation, Stanford University, 1972.

14. COGHLAN, W. A., AND CLAUSING, R. E., ORNL-TM-3576 (1971).

15. CHUNG, M. F., AND JENKINS, L. H., *Surface Sci.* **22,** 479 (1970).

16. Accurate quantitative analysis by AES can only be done if the Auger second derivative spectra is integrated twice to obtain the total transition strength. The peak height ratios given here are only qualitative indications of the behavior described.

17. The Cu $L_3M_{2,3}M_{4,5}$ transition occurs at the same energy as does the Ni $L_3M_{4,5}M_{4,5}$ transition. It has been subtracted out following the procedure in Ref. (*2*).

18. The minimum detectable quantity is estimated to be 0.05.

19. TAKASU, Y., AND SHIMIZU, H., *J. Catal.* **29,** 479 (1973).

20. WILLIAMS, F. L., AND BOUDART, M., *J. Catal.* **30,** 438 (1973).

C. R. HELMS[2]

Stanford Electronics Laboratories and
Laboratory for the Study of
Adsorption and Catalysis
Stauffer III
Stanford University
Stanford, California 94305

Received April 9, 1974

[2] IBM Postdoctoral Fellow.