

Absolute Composition Depth Profile of a NiCu Alloy in a Surface Segregation Study

Yee S. Ng, T. T. Tsong, and S. B. McLane, Jr.

Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802

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Using the time-of-flight atom-probe field-ion microscope, we have obtained an absolute composition depth profile of a Ni-Cu(5%) alloy, with single-atomic-layer resolution. The first-layer Cu composition is found to be $(54.1 \pm 4.7)\%$ on the (111) plane at 550°C . The Cu concentration of the near-surface layers is slightly lower as compared to the bulk. The composition returns to bulk value in about 5 atomic layers. Comparison of our result with those from other macroscopic techniques and existing theoretical models is also presented.

It is well known that the unique catalytic properties of highly dispersed, supported alloy particles arise partly from a segregation of minority species to the alloy surfaces. A classical example of the surface segregation is the enrichment of Cu at the surface of NiCu alloys. Evidence of Cu enrichment has been derived from the measurement of catalytic activity,¹ from hydrogen adsorption,² from work-function changes,³ from Auger-electron spectroscopy (AES),^{4,5} from low-energy ion scattering (LEIS),^{6,7} and from ultraviolet photoemission spectroscopy (UPS).⁸ Although significant information has already been obtained with these macroscopic techniques, it is generally recognized that a truly quantitative composition depth profile has not yet been obtained.⁹ This is probably the reason why the depth profiles of NiCu alloys obtained by different techniques seem to give contradictory results.

An AES result⁵ indicates that the Cu enrichment extends beyond the top surface layer. The concentration of Cu for deeper layers decreases monotonically to the bulk value. A LEIS study indicates that the enrichment of Cu does not extend beyond the top surface layer.⁷ On the other hand, a UPS study⁸ concludes that the composition depth profile has at least one oscillation in the (011) plane.

We have to realize here that samples prepared by various macroscopic techniques are not well characterized on an atomic level. The derivation of the depth of probing and the calibration of signals to the composition of a sample is not yet reliable for each macroscopic technique. The spatial resolution in depth is also limited. It is therefore no surprise that results obtained from different techniques have not been consistent.

These limitations do not exist in atom-probe field-ion microscopy.^{10,11} Surfaces prepared by field evaporation are atomically flat. Characterization of a surface is not a problem. Field evaporation proceeds atom by atom from a plane edge,

and atomic layer by atomic layer. The field-ion emitter size, 200–600 Å, also corresponds well with the particle size in practical catalysis. We have demonstrated in a recent study that the absolute composition of surface layers can be obtained with atom-probe field-ion microscopy with single-atomic-layer resolution.^{12,13} We present here for the first time an absolute composition depth profile of (111) planes in a Ni-Cu(5%) alloy, with single-atomic-layer resolution.

The alloy tip was always developed by field evaporation to an atomically perfect surface. It was then annealed to $550 \pm 50^\circ\text{C}$ for 2 to 5 min in a vacuum of low 10^{-9} -Torr range in field-free condition to equilibrate the distribution of alloys species in the entire tip. The tip is then quenched to 78 K. The quenching rate is estimated to be larger than 10^4 °C/sec. A thermal endform is observed after each annealing, and the (111) poles develop into large facets. The Cu-enriched top surface layer gives a much dimmer field-ion image than other layers.¹⁴ A controlled, slow field evaporation was then started with the probe hole of the atom probe aiming at the edge of a top (111) layer. As the plane receded, the position of the probe hole was adjusted accordingly. Extreme care was taken not to mix up signals from different atomic layers. In Fig. 1, we show an example of the sequential arrival of Cu and Ni signals, with vertical lines partitioning each surface layer. To obtain a statistically reliable amount of data, the tip is annealed again to the same temperature, and the same procedures were then repeated. The atom-probe signals were sorted according to the depth of the surface layers. The absolute composition of each surface layer was then derived using a statistical analysis.¹² The data points are presented in Fig. 2 as circles with statistical errors indicated by a vertical bar.¹³ This composition depth profile is obtained by combining eight sets of data from four tips. The total number of signals detected for

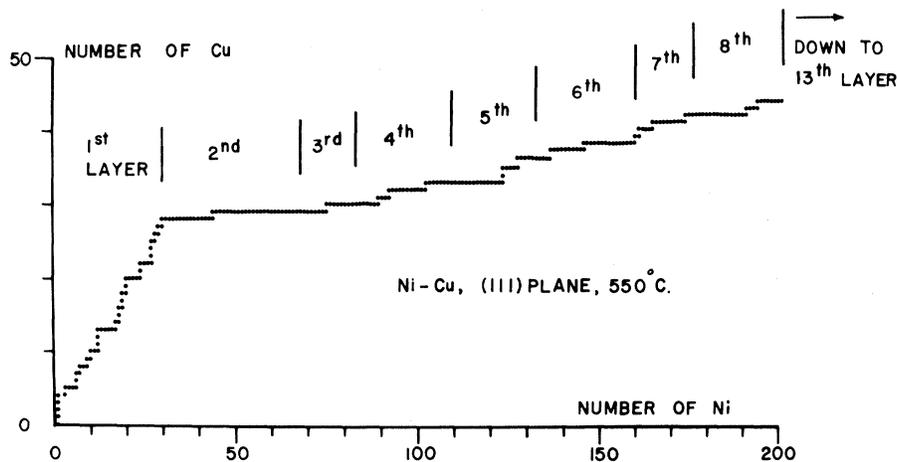


FIG. 1. Sequential plot of the number of Cu and Ni ions detected.

each near-surface layer ranges from 130 to 260.

The first-layer Cu concentration is found to be $(54.1 \pm 4.7)\%$. The Cu concentration decreases nonmonotonically into the bulk. In fact the second, third, and even the fourth layers are slight-

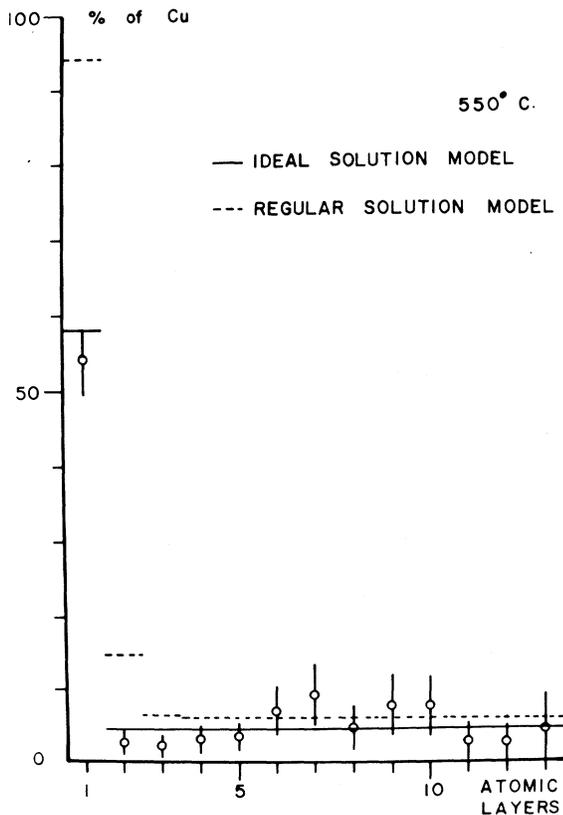


FIG. 2. Absolute composition depth profile of the (111) plane of a Ni-Cu (5%) alloy.

ly depleted in Cu as compared to the bulk. We did not find a strong enrichment of Cu in deeper surface layers as that found by UPS for the (110) plane.⁸

The reason that the annealing time was carried out at 2 and 5 min was to check whether a near thermodynamic equilibrium has been reached for the samples. Our data give the top-surface-layer Cu concentration of $(54 \pm 7)\%$ and $(55 \pm 7)\%$, respectively, for 2- and 5-min annealing periods at 550°C . We also found no enrichment of Cu in top surface layers for nonannealed samples. We estimate a root-mean-square displacement of $\sim 32 \text{ \AA}$ for Cu atoms in Ni matrix in 2 min at 550°C which corresponds to ~ 12 atomic layers.¹⁵ For 5 min, it is $\sim 51 \text{ \AA}$, or ~ 19 atomic layers. The fact that no significant difference in the Cu concentration is found for the two annealing periods suggests that a near thermodynamic equilibrium of the top surface layers has been achieved. Our preliminary computer study shows that unless a near thermodynamic equilibrium has been reached in both 2- and 5-min annealing time, the top-surface-layer concentration will differ significantly for the two annealing periods.¹⁵ Considerable blunting of tips after each annealing was also observed. We also estimate that during the quenching process, the root-mean-square displacement of Cu atoms is less than 0.2 \AA , about one tenth of an atomic layer. The quenching thus effectively freezes the distribution of species.¹⁵

A detailed comparison of our result with various theoretical models will be presented later.¹⁵ In this Letter we present some tentative explanations. An ideal-solution model¹⁶ gives the top-

TABLE I. Theoretical value of Cu concentration as a function of depth in (111) atomic layers.

Bulk conc. (%)	1st-layer conc. (%)	2nd-layer conc. (%)	3rd-layer conc. (%)	4th-layer conc. (%)
4	35.0	2.98	3.96	4.0
5	46.0	4.18	4.96	5.0
6	55.7	5.57	5.97	6.0
7	63.3	7.04	7.0	7.0
8	68.9	8.53	8.04	8.0
9	73.0	10.0	9.1	9.0
10	76.1	11.5	10.2	10.0
15	84.5	18.3	15.6	15.0
20	88.1	24.4	21.1	20.2
25	90.0	29.8	26.5	25.3
30	91.1	34.4	31.7	30.4

layer Cu concentration of 57.67% when a bulk Cu concentration of $(4.63 \pm 0.77)\%$ is used for the calculation. This value is the average of all the non-top-surface layers. Although this model agrees reasonably well with our experimental data, it does not account for the slight depletion of Cu observed in the near-surface layers.

A multilayer regular-solution model^{15,17} gives a much too high top-layer Cu concentration of 94.2% when the bulk concentration of Cu is taken to be $(5.82 \pm 1.11)\%$, the average of layers below the fifth layer. This model also predicts a Cu enrichment in the second and third layers as shown in Fig. 2, in contradiction to our result.

Our experimental result seems to fit best with the model of William and Nason,¹⁷ with an enthalpy relaxation parameter δ of 0.1686, that is to assume that all the bond enthalpy of atoms in the first layer will change by the same fraction by the presence of the surface. This model also predicts a slight depletion of Cu in the second and third layers within a certain range of bulk Cu concentration as shown in Table I. It is interesting to note that the experimental result of a recent LEIS study⁷ fits well with the model when $\delta = 0.16$ is used. In this case only the enthalpy of the lateral bonds in the surface is allowed to relax. We recognize here that a $\delta = 0.16$ seems to be unrealistically large.

The interesting findings of this study include the following: (1) The first successful absolute composition depth profile with single-atomic-layer resolution. (2) No enrichment of Cu beyond top layer (in contrast, enrichment of Cu beyond top layer has often been found by other macroscopic techniques). (3) A slight depletion of Cu

in the near-surface layers, which can be accounted for by a dynamic effect as discussed here, or by a kinetic effect.¹⁸

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¹P. Van der Plank and W. M. H. Sachtler, *J. Catal.* **12**, 35 (1968).

²J. H. Sinfelt, J. L. Carter, and D. J. C. Yates, *J. Catal.* **24**, 283 (1972).

³W. M. H. Sachtler and G. J. H. Dorgelo, *J. Catal.* **4**, 654 (1965).

⁴C. R. Helms and K. Y. Yu, *J. Vac. Sci. Technol.* **12**, 276-278 (1975).

⁵K. Watanabe, M. Hashiba, and T. Yamashina, *Surf. Sci.* **61**, 483 (1976).

⁶H. H. Brongersma and J. M. Buck, *Surf. Sci.* **53**, 649 (1975).

⁷H. H. Brongersma, M. J. Sparnaay, and T. M. Buck, *Surf. Sci.* **71**, 657 (1978).

⁸D. T. Ling, J. N. Miller, I. Lindau, W. E. Spicer, and P. M. Stefan, *Surf. Sci.* **74**, 612 (1978).

⁹S. H. Overburry, P. A. Bertrand, and G. A. Somorjai, *Chem. Rev.* **75**, 547 (1976).

¹⁰E. W. Müller, J. Panitz, and S. B. McLane, *Rev. Sci. Instrum.* **39**, 83 (1968).

¹¹E. W. Müller and S. V. Krishnaswamy, *Rev. Sci. Instrum.* **45**, 1053 (1974).

¹²T. T. Tsong, Yee S. Ng, and S. V. Krishnaswamy, *Appl. Phys. Lett.* **32**, 778 (1978).

¹³Yee S. Ng and T. T. Tsong, *Surf. Sci.* **78**, 419 (1978).

¹⁴T. T. Tsong and Yee S. Ng, in Proceedings of the Thirty-eighth Physical Electronic Conference, Gatling-

burg, Tennessee, 1978 (unpublished), and also Yee S. Ng, T. T. Tsong, and S. B. McLane, in Proceedings of the Twenty-fifth International Field Emission Symposium, 1978, Albuquerque, New Mexico (to be published).

¹⁵Yee S. Ng, T. T. Tsong, and S. B. McLane, to be published.

¹⁶J. J. Burton, E. Hyman and D. G. Fedak, *J. Catal.* **37**, 106-113 (1975).

¹⁷F. L. Williams and D. Nason, *Surf. Sci.* **45**, 377 (1974).

¹⁸S. Hofmann and J. Erlewein, *Surf. Sci.* **77**, 591 (1978).