December 1984

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Brief Reports

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Segregation of copper to the surface of copper-nickel alloys

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(Received 6 July 1984)

Copper segregation profiles at the surfaces of $Cu_{17}Ni_{83}(111)$ and $Cu_{17}Ni_{83}(100)$ have been calculated by a semiempirical procedure based upon previously published data. These profiles indicate that surface enrichment of copper is not limited only to the topmost layer but occurs for several layers away from the surface as well. A comparison of the calculated segregation profiles based upon the experimental results for the (100) and (111) surfaces of $Cu_{17}Ni_{83}$ do not agree with predictions based upon thermodynamic models of segregation.

Recently,[1] the segregation profile for chromium to the surface of a $Fe_{72}Cr_{28}(110)$ crystal has been determined using x-ray photoelectron spectroscopy. Model segregation profiles of chromium were employed to generate expected iron to chromium x-ray photoemission spectroscopy (XPS) signal ratios for the Fe and Cr $2p$ XPS core levels as well as for the Fe and Cr $3p$ XPS core levels. These models were then compared to the experimental results corrected for photoemission cross section and analyzer efficiency. This procedure, because of the different electron mean free paths for the $2p$ and $3p$ XPS signals, predicted chromium segregation profiles that were in good agreement with the profiles determined directly by Ar^+ ion bombardment experiments. Furthermore, these results indicated that a segregation profile of Gaussian or exponential shape occurs for equilibrium segregation at binary alloy surfaces.

Employing different photoemission take-off angles for a given XPS core level changes the electron mean free path perpendicular to the surface. By employing the Cu $2p_{3/2}$ to Ni$2p_{3/2}$ Al $K\alpha$ XPS signal ratios reported by Wendelt and Brundle,[2,3] copper segregation profiles at the surfaces of $Cu_{17}Ni_{83}(111)$ and $Cu_{17}Ni_{83}(100)$ may be calculated since the results were obtained for two different (45° and 75° off normal) emission angles. The nickel $2p_{3/2}$ signal, as a fraction of the total $2p_{3/2}$ signal from copper and nickel for model Gaussian and exponential segregation profiles, is approximately

$$C_{\mathrm{Ni}}=0.83\frac{\sum_{i=0}^{n}\{[1-S\exp(-id^2/G)]\exp(-id/\lambda_e)\}}{\sum_{i=0}^{n}\exp(-id/\lambda_e)}$$

and

$$C_{\mathrm{Ni}}=0.83\frac{\sum_{i=0}^{n}\{[1-S\exp(-id/G)]\exp(-id/\lambda_e)\}}{\sum_{i=0}^{n}\exp(-id/\lambda_e)},$$

respectively, where λ_e is the electron mean free path, d the crystal layer spacing, while S and G are parameters chosen for best agreement with experiment.[1,4] An "average" mean free path of 7.1 Å for 45° emission and 2.6 Å for 75° emission from the Cu and Ni $3p_{3/2}$ XPS photoelectrons may be assigned. Using these electron mean free paths, correcting for analyzer efficiency (assumed to increase with the reciprocal of energy), as well as photoemission cross section,[5] the published experimental XPS data,[3] shown in Table I, are consistent with the model segregation profiles shown in Fig. 1. These results assume equilibrium segregation occurred at ~800 K prior to taking the XPS measurements reported.[2,3]

The calculated segregation profiles shown differ from the predictions derived using theoretical models of surface segregation for copper in copper-nickel alloys.[6,7] Thermodynamic calculations only predict copper enrichment of the topmost layer or two. Clearly, the analysis of the data of Wandelt and Brundle, shown in the figure, indicates enrichment of copper occurs for as many as five layers. Thus,

TABLE I. Apparent fractional surface concentrations of copper and nickel in $Cu_{17}Ni_{83}$, as measured by XPS (Refs. 2 and 3), and corrected for analyzer efficiency and photoemission cross section. The crystal layer spacing is also indicated.

	C_{Ni}	C_{Cu}	d spacing (Å)
$Cu_{17}Ni_{83}(100)$ 45° emission	0.48	0.52	1.8
$Cu_{17}Ni_{83}(100)$ 75° emission	0.29	0.71	1.8
$Cu_{17}Ni_{83}(111)$ 45° emission	0.55	0.45	2.05
$Cu_{17}Ni_{83}(111)$ 75° emission	0.31	0.69	2.05

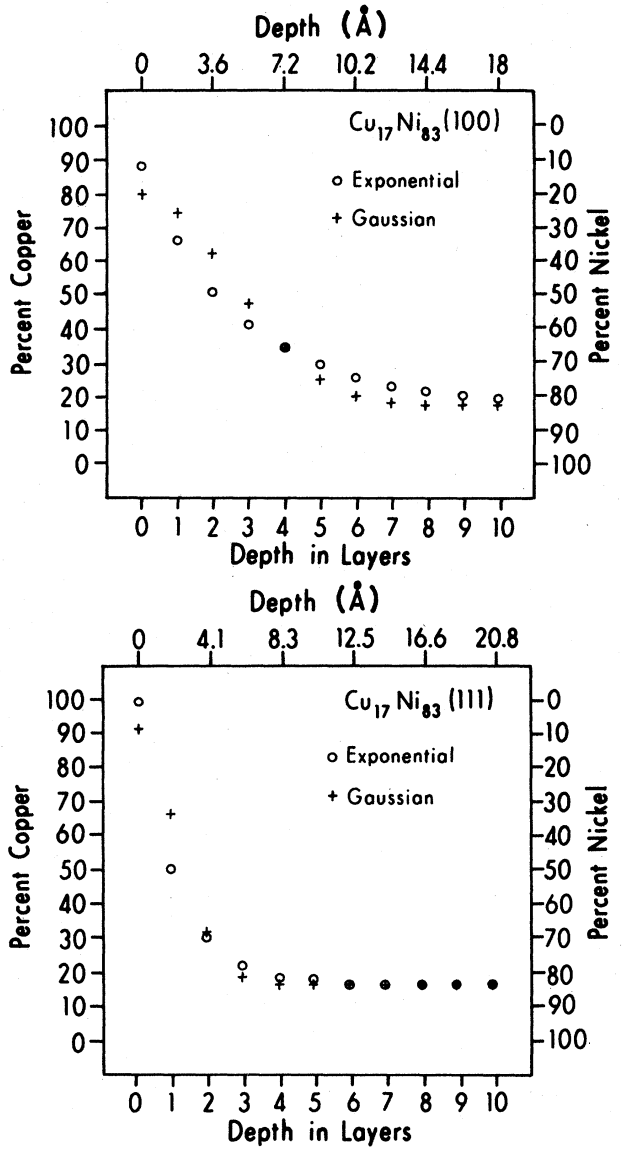

FIG. 1. Concentration profiles for copper and nickel calculated from the XPS $2p_{3/2}$ core-level signals reported by Wandelt and Brundle (Refs. 2 and 3) for 45° and 75° emission. The profile is assumed to have either Gaussian (+) or exponential (○) shape. The surface is placed at zero.

segregation in binary alloys does not appear to be limited to the top one or two layers as suggested by theoretical models. This result is consistent with the large selvedge enrichment found for chromium in $Fe_{72}Cr_{28}(110)$ for as many as 20 layers in depth from the surface.[1] Copper enrichment of more than the topmost surface layer has also been reported for Cu_5Ni_{95} alloys.[8]

For just the topmost surface layer alone, the calculated segregation profiles based upon the data of Wandelt *et al.*[2,3] for $Cu_{17}Ni_{83}(111)$ and $Cu_{17}Ni_{83}(100)$ are, in general, in good agreement with the theoretical surface concentration of copper at the surface layer. For equilibrium at 973 K, Kumar[7] has predicted that ~76% of the surface is copper for $Cu_{17}Ni_{83}(111)$. For equilibrium at 750 K, Donnelly and King[6] have predicted that for $Cu_{17}Ni_{83}(111)$, the topmost surface layer is ~85% copper and for $Cu_{17}Ni_{83}(100)$ the surface is 90% copper. The semiempirical calculated profiles derived here indicate 80% to 90% Cu at the $Cu_{17}Ni_{83}(100)$ surface and 90% to 100% at the $Cu_{17}Ni_{83}(111)$ surface (at ~800 K). Low-energy ion scattering results[9] also compare favorably, since the surface of the $Cu_{20}Ni_{80}$ alloy was found to be ~84% copper at 800 K. These results are summarized in Table II.

Generally,[3,6] one would expect more copper at the (100) surface as compared to the (111) surface for copper-nickel alloys. While the calculated copper segregation to the *surface region* is greater for the (100) surface than the (111) surface, unfortunately the surface concentration reported here for the *topmost layer* indicates that more copper segregation occurs on the (111) surface than the (100) surface. This defect in the semiempirical calculated segregation profiles is not as yet understood. Electron mean free paths may differ for each crystal face, though small changes in λ_e do not seriously alter the results shown in Fig. 1.

A better understanding of surface segregation both at the surface and the surface region must be sought. Despite the considerable attention paid to copper segregation in copper-nickel alloys, further work on selvedge enrichment, crystal face specificity in surface segregation, and electron mean free paths is required.

This work was initiated at the Fritz Haber Institut der Max Planck Gesellschaft. The author would like to thank Deutsche Forschungs Gemeinschaft (Sonderforschung Bereicht 6) and Syracuse University for their financial support. The author also acknowledges the useful suggestion of C. R. Brundle concerning the mean free path.

TABLE II. Estimated copper concentration at the surface and selvedge for copper-nickel alloys similar to $Cu_{17}Ni_{83}$.

Material	Method of determination	Temperature (K)	Percent Cu at surface	Substantial copper segregation in the selvedge	Reference
$Cu_{17}Ni_{83}(111)$	Theory	973	~76	No	7
$Cu_{17}Ni_{83}(111)$	Theory	750	~85	No	6
$Cu_{17}Ni_{83}(100)$	Theory	750	~90	No	6
$Cu_{20}Ni_{80}$	Ion scattering	800	84	. . .	9
$Cu_{17}Ni_{83}(111)$	Semiempirical	800	90–100	Yes	This work
$Cu_{17}Ni_{83}(100)$	Semiempirical	800	80–90	Yes	This work

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