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CHEMISORPTION INDUCED SURFACE SEGREGATION IN Cu-Ni ALLOYS

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Abstract
Surface segregation in Cu-Ni alloys, induced by ambient gases, has been studied using the time-of-flight atom-probe and Auger Electron Spectroscope. The study was made on the basis of the recent result that Ni atoms segregate to the surface in the Ni solute (below 16at.% Ni) alloys. Annealing in CO and O2 caused enhancement of Ni segregation but the degree of Ni enrichment depended on the bulk composition of the specimens. In the case of O2, the initial oxidation process was also investigated using the Ni solute alloys.

I. Introduction
There is no doubt that catalytic processes are critically dependent on the surface properties, such as the chemical composition, electronic states, atomic order, etc. Oxidation processes are also dependent on some of these same properties, especially surface composition. Therefore, a study of surface segregation should provide valuable information on the understanding of catalysis and of the initial stages of oxidation. Most of the studies of catalysis so far have been made by annealing the specimens in ultra-high vacuum, whereas catalysts are used in the presence of ambient gases or liquids. It is well known that the existence of adsorbates effectively changes the electronic states or the ordering of the surface atoms. Therefore, a study of surface segregation under real environmental conditions is warranted. In the present work, we introduced O2 and CO gases into the Cu-Ni binary alloy system during annealing the specimens to study the influence of these gases on oxidation and on segregation: the chemisorption induced surface segregation.

II. Experiments
The techniques employed in the present work are time-of-flight atom-probe FIM and conventional AES.
II-1. Atom-probe measurement I

One of the unique features of the atom-probe used in this study is the 100% detection efficiency achieved by the use of both a channel-plate and channeltron as signal detectors. This feature makes the instrument suited for the microscopic study of alloy surfaces. Further details of the instrument are described elsewhere/1,2/.

Cu-Ni alloys of various chemical compositions (1, 3.5, 16, 95.4 and 98at.%Ni) have been prepared from Cu(99.99%) and Ni(99.999%). They were pulled into fine wires of 0.1 mm diameter, and the specimen tips were prepared from the wires by electrochemical etching. The tip was spot-welded on a Mo wire of 0.1 mm diameter that could be attached to the sapphire/copper holder.

The field ion image of each specimen surface is observed through the viewing port of the main vacuum chamber. Hydrogen is usually used as the imaging gas. By applying higher voltages to the tip, the surface atoms field evaporate, and a clean surface may be obtained. The atomic order and the crystallographic orientations are observed from the image. Thus, the formation of oxides, precipitates, etc., may be studied in real space.

By flipping the channelplate out of the ion trajectory, the ions field evaporated from the surface may pass through the probe-hole and enter the Poschenrieder focusing lens, and be detected by the channeltron. By applying higher voltage pulses as triggers, the ions are evaporated from the surface, and the time of flight to reach the detector through the lens, is measured, and thus the mass-to-charge ratio of each ion is determined.

Annealing of the tip was carried out in-situ in the FIM chamber by heating the molybdenum supporting loop with an AC current (-1A). The tip temperature was monitored by an optical pyrometer with an accuracy of 20 K. The annealing temperatures were 823-923 K, and the time durations were 10-90 seconds. The tip could be quenched to 20 K at an estimated rate of 10⁴ degree/sec, which is sufficient to freeze the equilibrium compositions at the annealing temperatures.

Annealing in ambient gases was also carried out in-situ in the FIM chamber by introducing O₂ or CO gas in the range of 2x10⁻⁹ to 2x10⁻⁴ Torr. In these cases the base pressure was maintained below 4x10⁻¹⁰ Torr and the tip temperature was kept at 120 K in order to avoid condensation of the gases on the tip and the He liquefier. The chamber was degassed thoroughly to reach the base pressure before carrying out the AP measurement to avoid contamination.

II-2. AES measurement

AES measurements were carried out and the results were compared with those by the atom-probe. The AES system is a PHI model 11-500 with a single stage cylindrical mirror analyzer (CMA) model 10-155. The incident electrons were accelerated to 2 keV and the spectra were taken with the modulation frequency of 13 kHz and amplitude of 2 or 6 eV.

The specimens, Cu-9at.%Ni, were rolled to a foil of 0.2 mm thickness, cut into square pieces of 3 mm x 3 mm, and spot welded to a 0.05 mm thick Ta strip of 5mm width and 30 mm length. The specimen was cleaned by chemical etching in phosphoric acid solution followed by an ultrasonic cleaning in acetone for a few minutes immediately before putting into the AES system. Repetitive Ar ion sputterings and heatings at 1000 K were carried out in ultra-high vacuum until no contamination could be detected.

Annealing with or without ambient gases was carried out in-situ in the chamber by resistive heating of the Ta strip, and the temperature was measured by an optical pyrometer and an alumel-chromel thermocouple.

Oxygen exposures were in the range of 3x10⁻⁷ to 4x10⁻⁵ Torr at room temperature, 573 K and 893 K, for 3 to 1000 minutes.
II-3. Atom-probe measurement II

The second set of APFIM measurements were carried out using the Cu-9at.%Ni alloy used in the AES measurements. The tips were annealed at 473 K for 10 minutes in the presence of $10^{-3}$ to $10^{-2}$ Torr of oxygen gas. The annealing temperature has been calibrated from the electric current of the Mo loop with the aid of an infrared optical pyrometer.

III. Results and Discussion

The APFIM data show that in vacuum Cu segregates to the alloy surface in the case of the Ni-rich alloys of the Ni-Cu system/3/, in agreement with the literature. On the other hand, in the presence of either CO or O$_2$ the copper concentration in the surface region is substantially less. The topmost surface layer is 45% Cu after annealing in vacuum and only 5% after annealing in the presence of 3x$10^{-6}$ Torr CO in the case of the Cu-99at.%Ni alloy. The annealing conditions were 873 K for 30 seconds (Fig. 1). Similarly, the topmost surface layer is 40% Cu after annealing in vacuum and essentially zero percent (no Cu species detected) after annealing in 1x$10^{-5}$ Torr O$_2$ at 893 K for 30 s in the case of the (100) surface of the Cu-95.4at.%Ni alloy (Fig. 2). Cu was also deduced not to have been selectively oxidized from the surface since no oxide molecules or matching copper and oxygen species were detected. Thus, only if all of the oxide species had volatized, rather than condensed on the surface, which is unlikely, could selective oxidation have been a factor. These two results, therefore, can be taken to indicate that the O$_2$ and CO gases suppressed the copper segregation process.

The basic idea of the theory of chemisorption induced surface segregation by Tomanek et al./4/ is the modification of the heat of segregation in the Gibbsian formula by considering the difference of the chemisorption energies of the adsorbate with the two constituents of the binary alloys. In the present system, the modified heat of segregation, $Q_{\text{chemseg}}$, can be given as

$$Q_{\text{chemseg}} = Q_{\text{seg}} + \Theta(E_{\text{Cu}} - E_{\text{Ni}})$$

(1)

where $E_{\text{Cu}}$ and $E_{\text{Ni}}$ stand for the chemisorption energies of the adsorbate with Cu and Ni, respectively, and $\Theta$ stands for the adsorbate coverage ($\Theta = 1$ corresponds to one monolayer coverage). Using the values for $E$ ($E_{\text{Cu}} = 0.653$ and 3.099 for CO and O$_2$, respectively and $E_{\text{Ni}} = 1.306$ and 3.907 for CO and O$_2$, respectively in eV/mol), the modified heats of Cu segregation upon chemisorption of CO and O$_2$ are

$$Q_{\text{chemseg}}(\text{CO}) = 0.368 - 0.653\Theta \text{ (eV/mol)}$$

(2)

$$Q_{\text{chemseg}}(\text{O}_2) = 0.368 - 0.808\Theta$$

(3)

This indicates the suppression of Cu segregation with the existence of either CO or O$_2$ gas which is qualitatively in good agreement with the present results. This result may be understood, intuitively, as a situation in which the gas atoms have stronger bonding with the Ni atoms and thus attract the Ni atoms to the surface region.

Unfortunately, this theory does not hold in the case of the Cu-rich alloys containing less than 16at.%Ni for which nickel, rather than copper, segregates to the surface during vacuum annealing/3/. No enhancement of Ni segregation was observed after annealing in the presence of CO gas for the Cu-16at.%Ni or Cu-1at.%Ni specimens (Fig. 3). This is contradictory with the basic idea of Tomanek’s theory because the CO molecules are always likely to bond with Ni atoms. Therefore, the Ni solute (Ni concentration of less than 16%) alloys must be considered separately from Tomanek’s theory because the
absence of enhanced Ni segregation by CO cannot be explained from the Gibbsian formula.

The effect of O$_2$ gas on segregation in the Ni solute alloys has also been investigated. With a Cu-16at.%Ni specimen, thick layers of NiO were formed at the surface during annealing at 893 K in the presence of O$_2$ gas (Fig. 4). For this composition no segregation of either Cu or Ni was observed in vacuum/3/. With a Cu-3.5at.%Ni(111) specimen, there was no appreciable difference in the segregation behavior between the oxygen and vacuum annealing cases when the annealing time was less than 30 seconds (Fig. 5(a)). But as the duration of the annealing was extended over 30 seconds, the surface was found to be covered with 100% Ni, all in the form of NiO. This seems to agree with the results obtained by Ertl et al./5/ on the initial oxidation of the Cu-Ni(111). They reported, using AES, that the surface begins to form oxides with some latent period upon exposure to oxygen.

However, a different behavior was observed in the case of the (100) plane from that on the (111) plane of the Cu-3.5at.%Ni specimen exposed to oxygen at 893 K (Fig. 5(b)). Ni atoms segregated to the surface (up to 95%), but few of them were detected in the form of oxides, and the ratio of detected O and Ni atoms was far less than 1. The reasons for this fact are not trivial, but may be due to:

(1) the low oxidation rate of the (100) plane
(2) the large heat of segregation of the (100) plane
(3) the large evaporation field of the (100) plane which could result in dissociation of NiO.

In the AES experiment, Ni segregation was observed in the Ni solute alloys. By annealing a Cu-9at.%Ni specimen at 893 K for 3 to 1000 minutes in ultra high vacuum (pressure less than 10$^{-10}$ Torr), the peak height ratio of Ni (101 eV) and Cu (106 eV) indicated that the surface Ni concentration was enriched within the region of the escape length of these electrons, approximately 4 Å (Fig. 6), while the same ratio of the bulk signals of Ni (712 eV) and Cu (920 eV) remained nearly constant indicating no gross change in the total concentration within the depth of 15 Å.

In another AES experiment on Cu-9at.%Ni(111), 3x10$^{-7}$ to 4x10$^{-5}$ Torr O$_2$ gas was introduced to study the initial oxidation and/or chemisorption induced segregation. As the surface concentration of Ni is plotted against the amount of oxygen exposure measured in Langmuir (10$^{-6}$ Torr x sec), one can see the trend of Ni concentration decreasing at the surface as the oxygen exposure was increased (Fig. 7), which is rather contradictory to results obtained by the APFIM (Fig. 4). The possible causes of this discrepancy are the differences in exposure, pressure and duration time.

Measurements under various conditions are necessary to single out the dominant factor, but as a primitive one, 10$^{-3}$ to 10$^{-2}$ Torr oxygen was introduced for 10 minutes into the APFIM system in the third experiment. In this case both Cu and Ni oxides were found to form together with segregation of Ni amounting to 25% upon exposure for 10 minutes at 373 K. Analyzing the data in detail, however, one may recognize the different behaviors in oxide formation, such that, more Cu oxides were formed with higher pressures of oxygen (Table 1). The table shows the percentage of the total amount of elements detected and their oxides from the topmost layer (the left column) and from the next few layers (the right column).

From these results, the oxidation seems to first involve Ni, and then Cu oxidizes after Ni oxides have already formed. And there seems to be some enrichment of Ni accompanying this process.

Now the remaining problems are as follows:

(1) Why did the surface Ni concentration decrease with increasing O$_2$ exposure in the AES experiment?
Why did the surface Ni concentration increase to nearly 100% when annealed in $3 \times 10^{-7}$ to $4 \times 10^{-5}$ Torr $O_2$ at ~900 K for 10 minutes (Fig. 4), while it was only about 25% with $10^{-3}$ or $10^{-2}$ Torr $O_2$ at 373 K for 10 minutes (Table I)?

Some possible answers are considered:

1. In the AES experiment, the surface was covered with adsorbed oxygen so that the low energy Auger electrons from surface Ni atoms were "blocked", especially if oxygen atoms were adsorbed selectively on the Ni atoms rather than the Cu atoms.

2. Temperature and oxygen partial pressure play major roles in the different oxidation results. When the annealing temperature was 893 K, the decrease in nickel concentration (or increase in copper concentration) in the surface layer with increasing time could be the result of copper oxide overgrowing the nickel oxide, as suggested previously for compositional changes during the early stages of formation of bulk oxides on Cu-Ni alloys/6/. The lower surface nickel concentration under the lower temperature and/or higher oxygen pressure conditions is consistent with the formation of internal nickel oxides.

IV. Conclusions

Chemisorption induced surface segregation and the initial stage of oxidation in the Cu-Ni alloys were studied using an APFIM and AES with CO and $O_2$ gases. We have observed:

1) CO and $O_2$ gases both suppress the Cu segregation in the Cu solute alloys, in good agreement with the theory by Tomanek et al.
2) CO gas shows no influence on Ni segregation in the case of Ni solute alloys.
3) $O_2$ gas on Ni solute alloys enhances the Ni enrichment and oxide formation with a crystallographic orientation dependence;
   (a) The (111) surface showed the formation of Ni oxides after a sufficient duration of annealing.
   (b) The (100) surface showed strong Ni segregation with less Ni oxide formation compared to the (111) surface.
4) Ni segregation was also observed by AES.

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References

#Present Address: AT&T Bell Laboratories, Murray Hill, New Jersey 07974, U.S.A.
Table I Omidation of the Cu-9at.%Ni (111) plane annealed in the presence of $O_2$ at 373 K for 10 min.

<table>
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<th>OX/TOT</th>
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Next few layers

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</table>

Fig. 1. The cumulative number of Cu signals plotted against the total number of Cu and Ni signals detected with Cu-99%Ni (100), annealed at 873 K for 30 sec. in $3 \times 10^{-6}$ Torr CO.

Fig. 2. The cumulative number of Cu signals plotted against the total number of Cu and Ni signals detected with Cu-95.4%Ni (100), annealed at 893 K for 30 sec. in $1 \times 10^{-5}$ Torr $O_2$.

Fig. 3. The cumulative number of Ni signals plotted against the total number of Cu and Ni signals detected, showing no marked difference with Cu-16%Ni (111), annealed at 923 K for 10 sec. in $1 \times 10^{-4}$ Torr CO.

Fig. 4. The cumulative number of Cu, Ni and O signals plotted against the total number of signals detected, showing the formation of thick NiO-like layers formed with Cu-16%Ni (111), annealed at 823 K for 10 sec. in $2 \times 10^{-4}$ Torr $O_2$. 
Fig. 5. The cumulative number of Ni signals plotted against the total number of signals detected, showing no marked change with (a) Cu-3.5%Ni(111), annealed at 893 K for 30 sec. in 4x10^-7 Torr O_2 and (b) Cu-3.5%Ni(100), annealed at 893 K for 90 sec. in 5x10^-5 Torr O_2.

Fig. 6. The Ni concentration obtained by AES upon annealing Cu-9%Ni at 893 K in vacuum with Ni(101 eV) and Cu(106 eV) peaks, and Ni(712 eV) and Cu(920 eV) peaks.

Fig. 7. (a) The Ni concentration obtained by low energy Auger electrons and (b) the O concentration normalized by the total number of atoms within 15 A from the surface using the high energy Auger electron signals upon annealing Cu-9%Ni(111) in O_2.