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Relation Between Catalytic Activity Pattern and Surface Composition of Cu–Ni Alloy

An Application of Auger Electron Spectroscopy to the Study on Catalysis

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Changes in surface composition of copper–nickel alloy plates, with various pre-treatments were studied by means of Auger electron spectroscopy. The surface composition was found to be considerably changed from the bulk of alloy samples by the pre-treatments, namely the surfaces of the nickel-rich alloys are enriched with copper, while those of the copper-rich alloys are with nickel. Comparing the relations between the catalytic activity patterns of copper–nickel alloys and the pre-treatments of them which have been published by many authors, original activity pattern of the catalyst is estimated.

INTRODUCTION

Copper–nickel alloy catalysts have been studied by a number of authors, with a view to confirming the proposals of Dowden (*1*) relative to the influence of the electronic structure of solids on their catalytic activity. However, there have been pronounced discrepancies of the catalytic activity patterns in the experimental results reported for copper–nickel alloy catalysts. The most substantial problem on the discrepancy may be whether the alloy composition of the surface layers is the same as that of the bulk or not. However, very little has been reported on this problem.

Sachtler and his coworkers (*2*, *3*) have insisted that for copper–nickel alloys a miscibility gap exists, and that the observed solid solutions are metastable with respect to the two fixed alloy compositions. Finally they suggested that under certain conditions the outermost surface layers would consist of the copper-rich alloy throughout the miscibility gap range due to the greater diffusivity of copper than nickel. On the other hand, Hardy and Linnett (*4*) proposed from their study by means of an electron probe microanalysis that the surface composition was not appreciably different from the bulk of the copper–nickel alloy sheets. However, it seems still to be doubtful whether the method is suitable for the study on the outermost surface layers which take part in the catalytic reaction or not. On that point, Auger electron spectroscopy (AES) is a prominent technique for obtaining chemical species on solid surfaces. For the analysis of the surface compositions of copper–nickel alloy, the AES has been already applied by several investigators including Harris (*5*), Ertl and Küppers (*6*), Tarng and Wehner (*7*), and Quinto, Sundaram and Robertson (*8*).

Harris (*5*) obtained, in the first place, the Auger spectra of the copper–nickel alloy surfaces in the energy region of 700–1000 eV. Ertl and Küppers (*6*) have concluded that the surface composition of the copper–nickel alloy is the same as the bulk even after the annealing *in vacuo* in the study by use of a Constantan (55Cu–45Ni) single crystal. On the other hand, Tarng and Wehner (*7*) have indicated that the surface of Constantan was enriched with nickel by the argon ion-bombardment. Quinto and his coworkers (*8*) have also studied on the surface composition of copper–nickel alloys changing with the argon ion-bombardment by means of AES technique.

In these earlier works, however, a useful method of quantitative analysis on the surface composition of copper–nickel alloy has not satisfactorily been established.

The purpose of the present study is to attempt quantitative analysis of the surface composition of pre-treated copper–nickel alloy sheets and to discuss the catalytic activity pattern of this alloy system for the reaction of the hydrogenation or the exchange which have been published by many authors.

EXPERIMENTAL

A retarding field type analyzer with four spherical grids (*9*) was used to detect the Auger electrons.

Spectra were obtained in the form of the derivative of the secondary electron function reflected from the sample surface. After samples were set in the apparatus, the system was evacuated with an electro getter ion pump down the pressure of 3×10^{-9} Torr without baking out so as to avoid the effect of heating on surface composition of alloy samples. Analysis of the residual gases with a quadrupole mass-filter showed that water vapor was dominant. Pure nickel, copper and four copper–nickel alloys with compositions of 81, 62, 42 and 16 atomic per cent nickel were used. Each sample was 0.2 mm in thickness and 5×20 mm^2 in geometrical surface area. After polishing with emery papers in streaming of water, these samples were rinsed in distilled water and acetone (these samples were designated as N-T (non-treatment)).

To examine the surface composition of the usual powder catalyst of copper–nickel alloy, the N-T plate samples were oxidized and reduced with $P_{O_2} = 0.37$ Torr, 500°C, 1 min; $P_{H_2} = 21$ Torr, 300°C, 4 hr, respectively (these samples were designated as O-R (oxidation-reduction treatment)). The heating treatments (these samples were called as H-T) were made by an electric current passed directly through the samples. Temperatures were measured with a Pt-Pt·Rh thermocouple welded on the samples. The operating parameters in the Auger mode were as follows, beam energy 2000 eV, sensitivity of lock-in amplifier 100 μV, time constant $1 \sim 3$ sec and modulation voltage 20 V_{p-p}, 500 Hz.

RESULTS AND DISCUSSION

Auger Spectra and Calibration Curves (*10*)

Peaks of Auger electrons were observed at 54, 101, 712, 778 and 849 eV for nickel and 55, 105, 773, 842 and 922 eV for pure copper, respectively.

Figure 1 represents the derivative spectra of the N-T surface of pure nickel, pure copper and four copper–nickel alloys. The

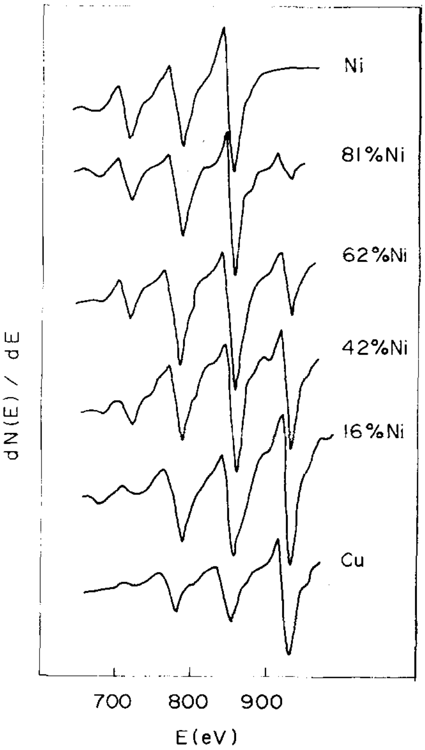

FIG. 1. AES spectra of the original surfaces of Cu–Ni alloys.

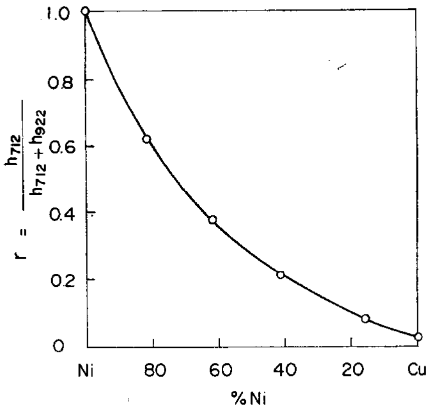

FIG. 2. Calibration curve of the surface composition of Cu–Ni alloys.

calibration curve for the quantitative analysis was made with a peak height of 712 eV which was normalized to the sum of the peak heights of Ni (712 eV) and Cu (922 eV). Assuming that the surface compositions of the N-T alloys are identical with the bulk, the calibration curve for the surface composition was obtained, as shown in Fig. 2.

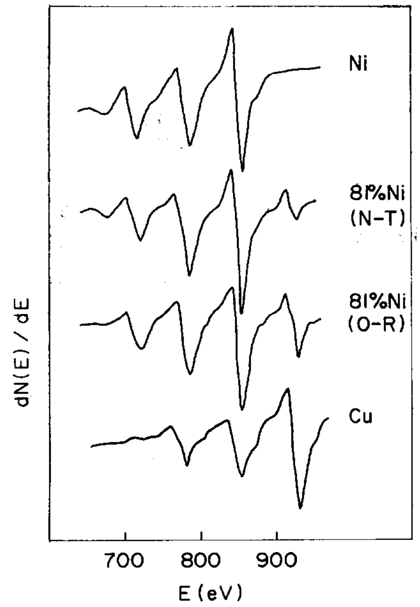

FIG. 3. AES spectrum of the 81% Ni alloy after the O-R treatment compared with the original spectra of the 81% Ni, pure Ni, and pure Cu.

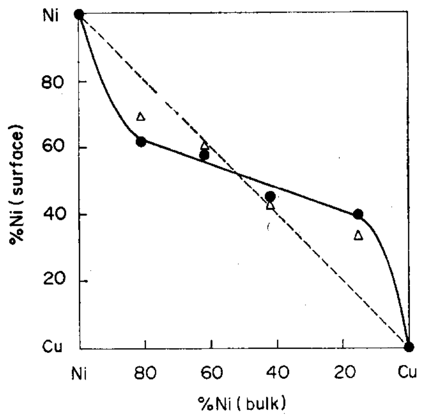

FIG. 4. Surface compositions of copper–nickel alloys after the O-R or the H-T treatment. (●, O-R treatment; △, H-T treatment.)

Various Surface Treatments

Figure 3 represents the Auger spectra from the O-R surface of 81% nickel alloy compared with those of nickel and copper. It is noted that after the O-R treatment the peak intensity at 712 eV became weaker, while the peak intensity at 922 eV became stronger. These facts give evidence that copper became more concentrated on the surface of the 81% nickel alloy after the O-R treatment. Using the calibration curve (Fig. 2), the surface composition of the copper–nickel alloys after the O-R treatment was derived and was plotted against the bulk composition of the alloys in Fig. 4. It is obvious that the surface compositions were considerably changed from the bulk compositions by the O-R treatment, namely the surfaces of the nickel-rich alloys were enriched with copper, while those of the copper-rich alloys were enriched with nickel.

Figure 5 shows the process of change in the surface composition of the 81% nickel alloy which was heated electrically for 10 min at each temperature up to 500°C. Auger analysis was carried out at room temperature after the heat treatment. It is to be noted that the surface was enriched rapidly with copper after only 10 min heating, and also the surface compositions were scarcely changed any more by further heating. The surface compositions of the

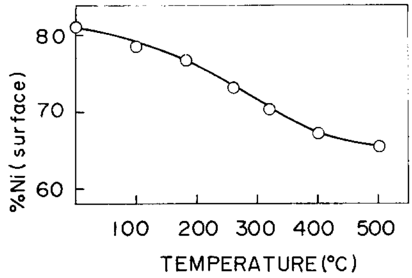

FIG. 5. Surface compositions of the 81% Ni alloy after the H-T treatments (heating cycle 10 min each).

copper–nickel alloys after the H-T treatment (300°C for 10 min *in vacuo*) were also plotted in Fig. 4 as the open triangle, and it is of much interest that the surface compositions after the H-T treatment showed almost same values as those after the O-R treatment.

Sachtler and his coworkers (*3*) suggested that the surface composition of these alloys was controlled by a miscibility gap dependent on the values of excess free energy of mixing. According to Kubaschewski and his coworkers (*11*), as shown in Fig. 6, copper–nickel alloy should have no miscibility gap at the temperature higher than 322°C. However, as seen obviously in Fig. 3, the surface composition was altered even above 400°C. Moreover, the surface composition of the 16% nickel alloy was also altered by heating even at 300°C. Considering these results shown in Figs. 4, 5 and 6, it would be concluded that the discrepancy of the surface composition to the bulk in these copper–nickel alloys might not be explained by the miscibility gap which is calculated with the thermodynamics of bulk.

The surface composition could be controlled by thermodynamic equilibrium of the surface layers; however, the lack of the information concerning surface layer makes the illustration about the equilibrated composition impossible at the present time.

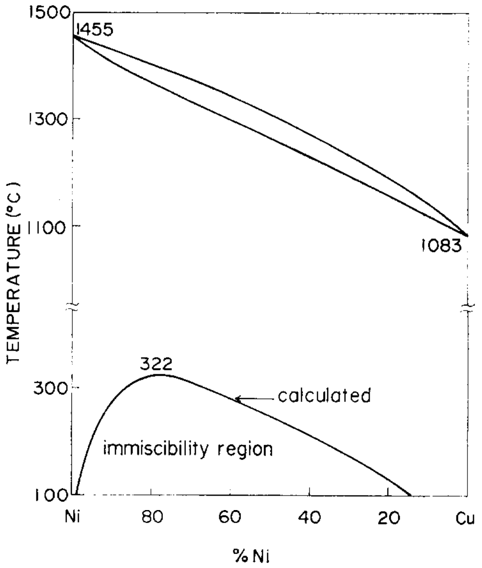

FIG. 6. Equilibrium diagram of Cu–Ni alloys obtained by Kubaschewski *et al.* (*11*).

Relation Between Catalytic Activity Pattern and Surface Composition

Considering the above facts, the catalytic activity patterns which have been drawn against the bulk composition of alloys reported by many workers should be reexamined. Therefore, we shall discuss this problem for the case of the hydrogenation reaction of ethylene, which has been studied extensively over copper–nickel alloy catalysts. The catalytic activity patterns can be classified in the following three types: α_1, α_2 and β as illustrated in Fig. 7. The α_1-type signifies the pattern for which the activity is governed by the content of nickel or it obeys the Dowden's forecast. The α_2-type has a nearly constant activity region over a wide

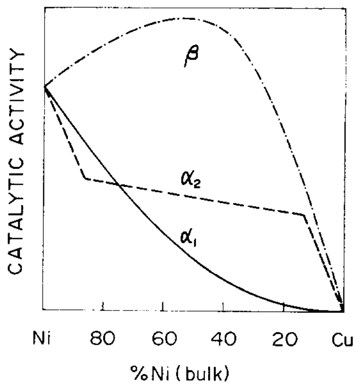

FIG. 7. Classification of the catalytic activity patterns on copper–nickel alloy catalysts.

range of composition, while the β-type has a maximum activity in alloy composition range. All of the catalytic activity data for the hydrogenation of ethylene which has been obtained so far at temperatures lower than 150°C on copper–nickel alloy catalysts are given in Table 1. The catalytic activity patterns for plate catalysts (a) reduced at 200°C belonged to the α_1-type. In this case, however, the corrected pattern in which the activities were drawn against the surface composition also belonged to the α_1-type.

As the catalysts (b) and (c) classified in the pattern of the α_2-type had been sufficiently annealed at each temperature, these catalysts can be regarded as the H-T samples. On the other hand, the catalysts (d) and (e) can be regarded as the O-R samples, since they had been prepared by the reduction of the powdery mixed oxide.

It is surprising to note that all the catalytic activity patterns of the catalysts which had been prepared by the H-T or the O-R treatment belonged to the α_2-type. Thus, if their values of the catalytic activities were drawn against their surface compositions, their corrected patterns must be expressed in the α_1-type, because their surface compositions could be altered by the treatments such as those shown in Fig. 4.

As has been described above, the catalytic activity patterns of the copper–nickel alloy catalysts have been shown to belong to the α_1-type. However, we must consider also the results in which a maximum activity was found in the alloy range, i.e., the β-type listed in the Table 1. Two features are found for catalysts classified in the β-type. The first is the surface inhomogeneity. Since the surfaces of (f) and (g) had been bombarded strongly by the argon ions from a glow discharge, a number of defects must have been present in the surface layers as described in these papers (*16*).

Similar considerations may apply in the case of (h). Because the films had been heated only to 30°C after deposition at −183°C, there may have been many defects present in the films. Yamashina (*16*) and others have claimed that lattice defects may act as catalytic sites. Therefore, these catalysts are not suitable for the investigation of the original catalytic activity pattern of copper–nickel alloys.

The second feature is the preadsorbed hydrogen. Namely, large amounts of hydrogen may have been sorbed by the catalysts (i), (j), (k) and (l), because they had been evaporated or cooled in the presence of hydrogen. Moreover, as pointed out by Hall (*21*), the alloy surfaces may be enriched in nickel on contact with hydrogen above 100°C and frozen in this condition on cooling to lower temperatures. Whatever the cause of catalytic activity in the copper–nickel alloy is enriched by

TABLE 1

CATALYTIC ACTIVITY PATTERNS OF HYDROGENATION OF ETHYLENE ON Cu–Ni ALLOY CATALYSTS

No.	Activity pattern	Form	Pretreatment	Condition of pretreatment	Reference
a	α_1	plate	reduction	200°C	12
b	α_2	plate	H-T	500°C	13
c	α_2	film	H-T	250°C	14
d	α_2	granular	O-R	200°C	12
e	α_2	granular	O-R	250 or 350°C	15
f	β	plate	Ar^+ glow discharge	500 eV 400 $\mu A/cm^2$	16
g	β	plate	Ar^+ glow discharge	500–600 eV	17
h	β	film	H-T	30°C	14
i	β	film	H-T in H_2	300–500°C	18
j	β	film	H-T in H_2	250–300°C	19
k	β	granular	O-R cooled in H_2	100°C	20
l	β	granular	O-R cooled in H_2	350°C	15

TABLE 2

Patterns of Heats of Adsorption of Hydrogen on Cu–Ni Alloy Catalysts

No.	Pattern	Form	Pretreatment	Condition of pretreatment	Reference
m	(α_2)	granular	O-R	200°C	12
n	(α_2)	granular	O-R	300°C	22

the preadsorbed hydrogen (*15*), and these results also do not seem to represent the original activity pattern of copper–nickel alloy. Considering the fact that all the catalysts classified in the β-type were related to either the first feature or the second, it can be asserted again that the original catalytic activity pattern of the hydrogenation of ethylene on copper–nickel belongs to the α_1-type. Similar reasoning can be applied to the case of the heats of adsorption of hydrogen and to the amount of hydrogen adsorbed on these alloys. In Tables 2 and 3, the dependencies on the alloy composition of the heats of hydrogen and on the amounts of hydrogen adsorbed are classified in the same way used for the catalytic activity patterns. Since all the catalysts in the tables had been prepared with the O-R or the H-T treatments, their surface compositions must have been altered as shown in Fig. 4, corresponding to the catalysts (b), (c), (d) and (e). Therefore, all the patterns for catalysts (m), (n), (o), (p), (q) and (r) could belong to the α_1-type if their values were drawn against the surface compositions of these alloy catalysts. Although only the hydrogenation of ethylene has been considered here, it is felt that the conclusion is of more general validity, provided that the reaction has not suffered from side effects such as the deposition of carbonaceous material from the reactant gases or from the surfaces impurities diffused from the bulk. As shown in Fig. 8, one of the authors (Y. T.) has found that both the catalytic activity patterns for the hydrogen–deuterium equilibrium reaction on the mechanically polished surfaces of copper–nickel alloy plates (*26*) and for the clean surfaces of known surface compositions (*27*) have belonged to the α_1-type. These results exactly correspond to the above conclusion, because the surface compositions of the mechanically polished plates of alloy might be almost same as the bulk composition. Also the catalytic activities of the clean surfaces have not been drawn against the bulk compositions, but have been drawn against the surface compositions which have been found by the Auger electron spectroscopy. From the facts described above, we should conclude again that the catalytic hydrogenation reaction of original copper–nickel alloy could be governed by the nickel content on the surface or by the factors proposed by Dowden. However, theoretical and experimental problems remain to be solved concerning the true factors which govern the activities of this alloy.

Finally, we have to point out that Sachtler *et al.* (*3*) have also illustrated catalytic activity patterns of the α_2-type, quoting a few results from the viewpoint that there must be constant surface com-

TABLE 3

Patterns of Amount of Hydrogen Adsorbed on Cu–Ni Alloy Catalysts

No.	Pattern	Form	Pretreatment	Condition of pretreatment	Reference
o	(α_2)	film	H-T	200–300°C	23
p	(α_2)	granular	O-R	350°C	24
q	(α_2)	granular	O-R	350°C	25
r	(α_2)	granular	O-R	200°C	12

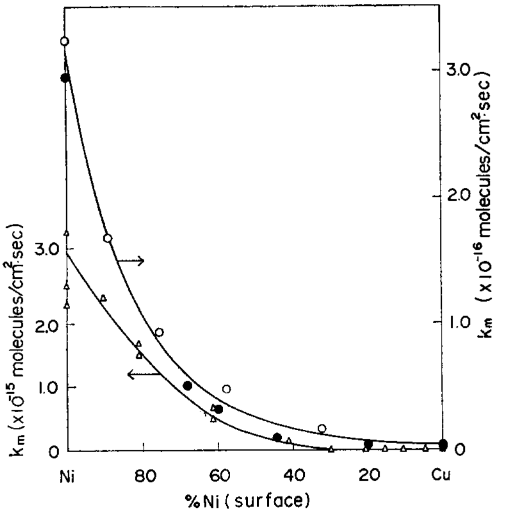

FIG. 8. Catalytic activities of the H_2–D_2 equilibrium on Cu–Ni alloy plates. Left scale: mechanically polished surfaces (*25*) (100°C, $P_{H_2+D_2} = 3.0$ Torr). Right scale: clean surfaces (*26*) (0°C, $P_{H_2+D_2} = 0.23$ Torr). ○, Argon ion beam bombardment (5 μA/cm² 100 min. 500 eV); ●, annealed 10 min after the argon ion beam bombardment.

position range in copper–nickel alloy heated at certain temperature range. This is not in contradiction with the views expressed herein.

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