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Changes in Surface Composition of Clean Copper-Nickel Alloys with Ion Bombardment and Annealing

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Abstract

Changes in the surface composition of clean Cu-Ni alloys with ion bombardment and annealing were investigated by Auger spectroscopy. The surface compositions were compared systematically for 8 Cu-Ni alloys by Auger spectra in the lower energies around 100 eV or thereabouts with the higher energies at 700～1000 eV.

It was found that the surface layers were considerably enriched with Cu atoms by annealing, but the Auger peak of Ni in a lower energy region did not disappear by high temperature annealing even at 600°C for all Cu-Ni alloys.

The configuration of component distribution in several atomic layers at the surface of Cu-Ni alloys was proposed by utilizing the difference in escape length of the Auger electrons from different transitions.

1. Introduction

Numerous studies have been carried out on Cu-Ni alloys in order to determine the fundamental basis of catalysis by alloys in connection with the electronic structure of the alloy surfaces. For Cu-Ni alloys, particular attention was paid to clarify whether the alloy composition of the surface layers is the same as that of the bulk or not. Nakayama, Ono and Shimizu[1,2,3] have reported changes in the surface composition of Cu-Ni alloys with ion bombardment and annealing by means of quantitative Auger analysis. We also have published several papers[4,5,6] on catalysis and surface composition of well-defined surfaces of Cu-Ni alloys.

Previously, we pointed out in Auger analysis that the Auger spectra in a rather lower energy region such as 100 eV or thereabouts should be of considerable important, since the lower energy spectra should be more sensitive to more surface layers, although the resolution was not sufficient to separate the peaks of Cu and Ni from the M_1 $M_{4,5}$ $M_{4,5}$ transitions[7]. Recently, Helms et al.[8,9,10] reported on the surface composition of clean surfaces of Cu-Ni alloys examined by Auger spectroscopy, in which they clearly separated both peaks in the lower energy region. They found significant deviation between the surface and the bulk compostions to be enriched drastically with Cu atoms by annealing. Remarkable deviation was also observed between the surface compositions determined by the lower energy spectra (around 100 eV) and those by the higher energy spectra (700～1000 eV). In their results, they found a very interested fact that the Ni peak (100 eV)

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disappeared completely by annealing at 300°C. On the other hand, in similar measurement mady by us[11] the Ni peak (101 eV) did not disappear by annealing even at 600°C.

The purpose of the present paper is to make systematic clarification of the effect of surface treatments by ion bombardment and annealing on the surface composition with a comparison of the lower and higher energy spectra by using clean surfaces of Cu-Ni alloys with ten different compositions in its entire range.

2. Experimental

Pure Cu (> 99.999%), Ni (> 99.99%) and eight Cu-Ni alloys with compositions of 90 weight percent Cu (89.3 atomic percent Cu), 80% Cu (78.7%), 70% Cu (68.3%), 50% Cu (48.0%), 30% Cu (28.4%), 20% Cu (18.8%) and 10% Cu (9.3%) were used in this experiment.

The dimensions of each specimen were 10 mm × 2.7 mm in a geometrical surface area and 0.5 mm in thickness. After mechanical polishing, these specimens were cleaned by ultrasonic washing with distilled water and acetone. Then all of the ten specimens were attached to a stainless steel sample holder of 15 mm × 10 mm × 10 mm for Auger measurement by which the specimens could be heated up to 1200°C by a tungsten heater installed in the sample holder.

A standard Auger spectroscopy system with a CMA optics (Varian) was used in this experiment. The Auger system was capable of evacuation to a pressure of 1×10^{-10} Torr. Clean surfaces of the alloys were prepared by sputtering of surface layers with argon ion-beam bombardment ($P_{Ar} = 5 \times 10^{-5}$ Torr, 2~3 $\mu A/cm^2$) during heating at 600°C. It generally required 25~30 hr to obtain an atomically clean surface as shown in Fig. 1. An electron beam of 5 μA and 2000 eV was used to excite the Auger transitions. The temperature of the specimens was measured by an alumel-chromel thermocouple attached immediately to the rear of the specimens.

3. Results and Discussion

An example of Auger spectra from the clean surfaces for 50% Cu alloy of the bulk composition is shown in Fig. 1, in which no impurity peaks such as oxygen, carbon and sulphur were detected in the spectra. In this figure, the spectra were compared on ion bombarded (at room temperature) and annealed surfaces after the cleaning treatment. As shown in Fig. 1, Auger peaks are seen around 100 eV as well as at 700~1000 eV. Peaks of Ni (M_1 $M_{4,5}$ $M_{4,5}$ at 101 eV) and Cu (M_1 $M_{4,5}$ $M_{4,5}$ at 106 eV) were obtained with a smaller modulation voltage (2 V) than in the ordinary case (20 V) of obtaining the entire spectrum within a range of 0~1000 eV in the figure. Comparing both spectra in Fig. 1, it is obvious that for the bombarded surface there was not a great difference in the peak height ratios Cu (106)/Ni (101) and Cu (920)/Ni (712), while for the annealed surface there was a considerable difference in the Cu (106)/Ni (101) and Cu (920)/Ni (712).

The Auger spectra in the lower energy region from all ten specimens were compared in the bombarded and the annealed surfaces, as shown in Fig. 2. It is clear in this figure that for the bombarded suarface the spectra changed gradually corresponding to the alloy composition of the bulk, while for the annealed surface (at 600°C) the peak height ratio Cu (106)/Ni (101) was observed to be much greater than that of the bombarded surface. It is also should be noted that in

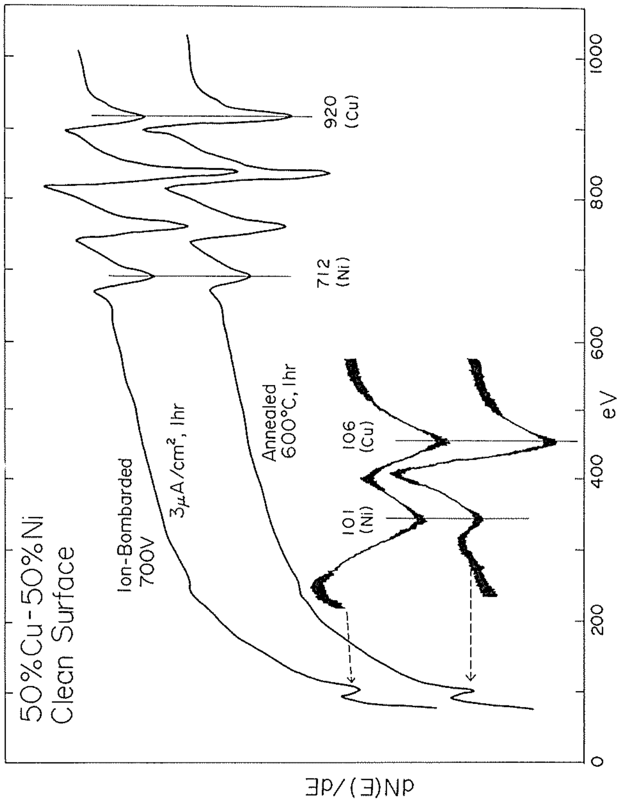

Fig. 1 Typical example of the derivative Auger specta from a clean surface of 50% Cu-Ni alloy, showing comparison of the bombarded and annealed surfaces, and the lower and higher energy spectra.

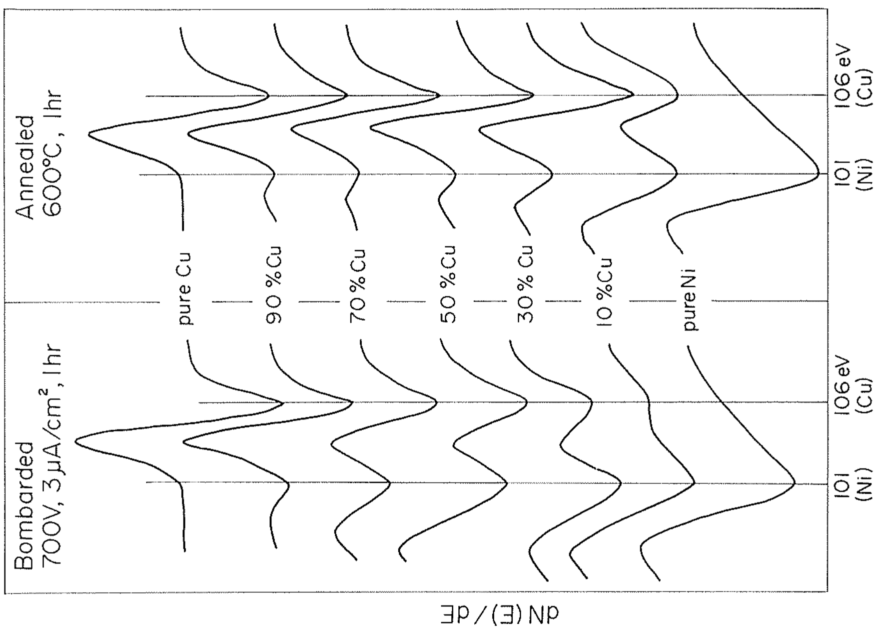

Fig. 2 The derivative Auger spectra at around 100 eV, from the bombarded and annealed surfaces of Cu-Ni alloys.

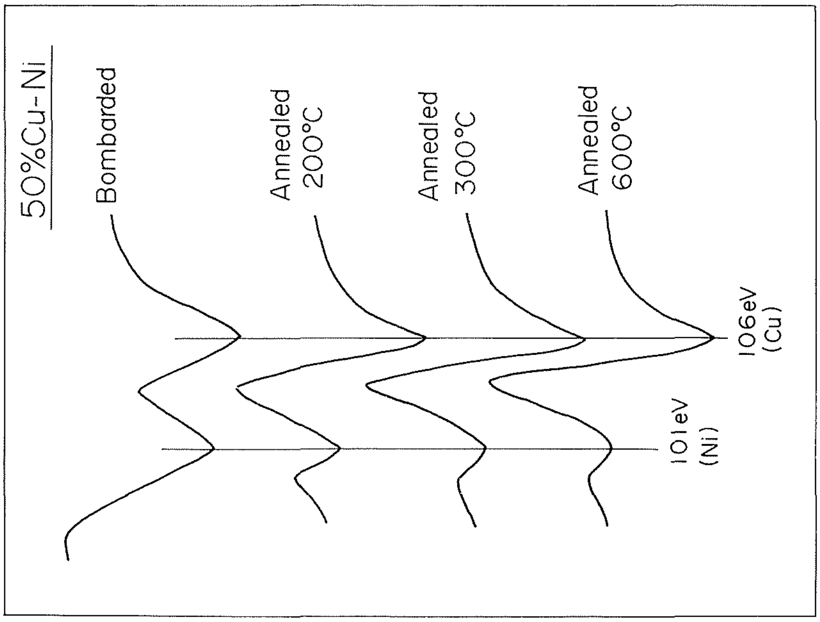

Fig. 3 Changes in the lower energy spectra with the annealing on the surface of 50% Cu-Ni alloy.

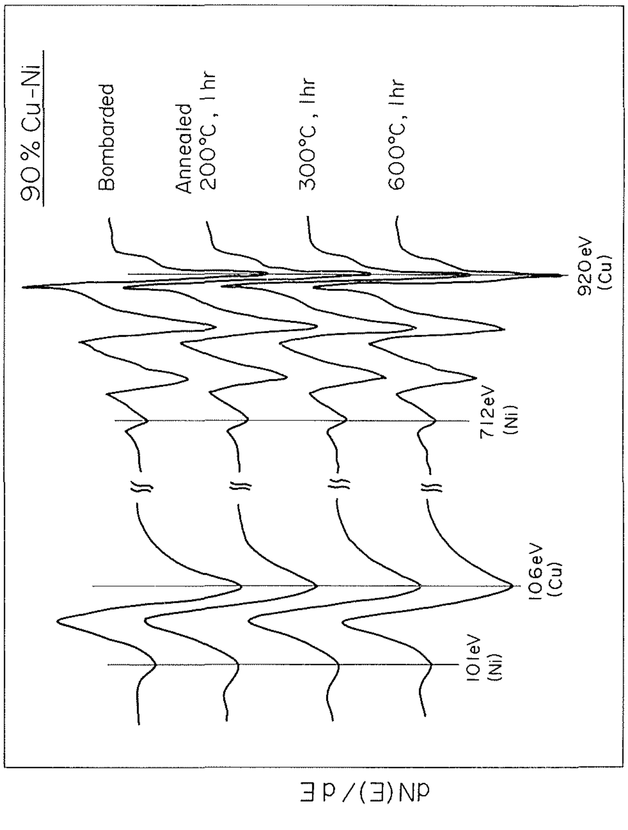

Fig. 4 Changes in the lower and higher energy spectra with the annealing on the surface of 90% Cu-Ni alloy.

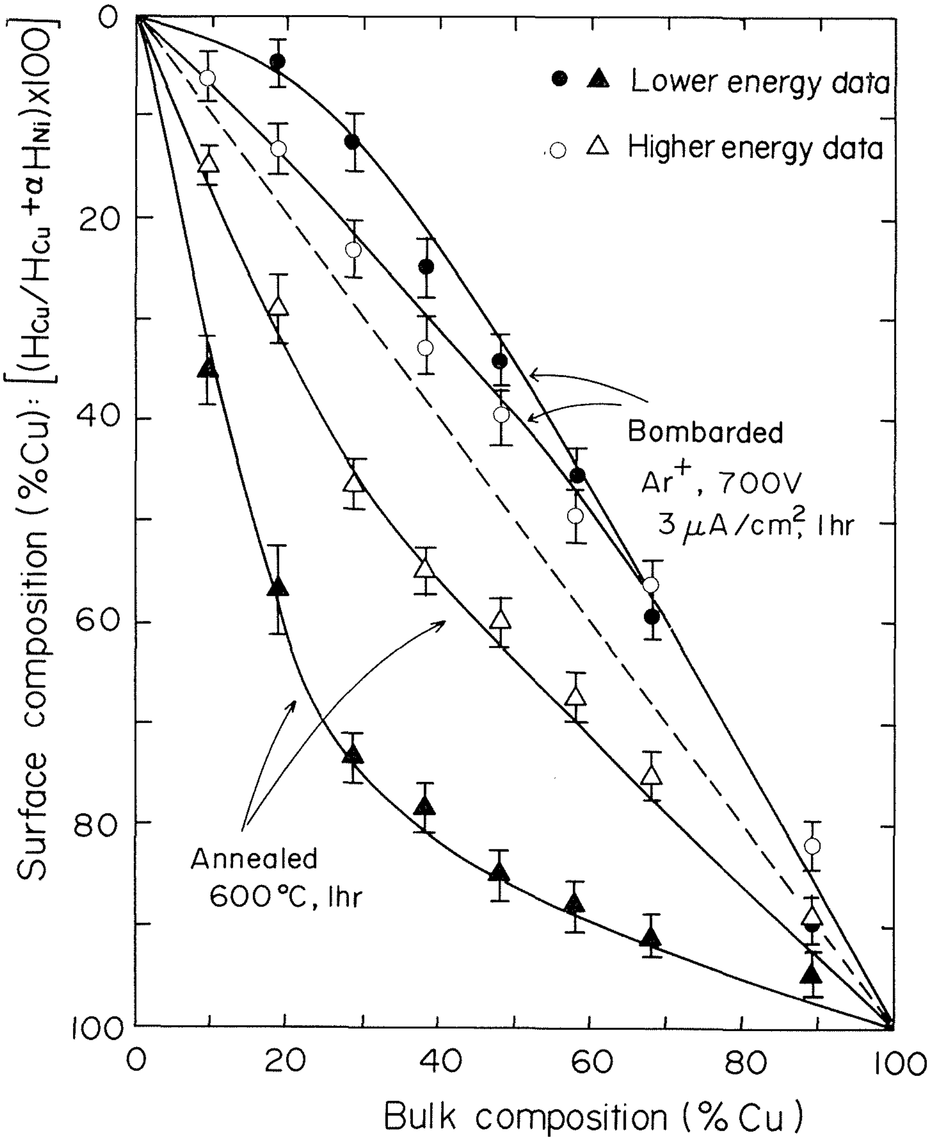

Fig. 5 The surface composition of the bombarded and annealed surfaces against the bulk composition.

any case of alloy specimens the Auger peak from Cu or Ni component did not disappear by both treatments of ion bombardment and annealing at 300°C even over 600°C.

According to Helms et al.[8,9,10] in their analysis of the Auger spectra in the lower energy region with the treatments of sputtering and annealing, the peak of Ni (100 eV) disappeared completely by heating at 300°C for the clean surface of 50% Cu alloy. They also observed on the clean surface of single crystal of the alloys that adsorption of oxygen at 300°C would cause drastical enrichment of Ni atoms on the uppermost surface layer.

We have attempted to obtain the lower energy spectra of clean surfaces of the alloys which changed with the annealing treatment. Some examples are represented in Fig. 3 and 4, in which 50% Cu and 90% Cu alloys were examined to run a comparison on the annealing effect. After the alloy surfaces were ion-bombarded for 1 hr at room temperature, they were annealed at each temperature for 1 hr under 2×10^{-10} Torr. As seen in these figures, the peak intensity of Ni was greatly decreased with increase of annealing temperature. However, Ni peak (101 eV) did not disappear even in the case of 90% Cu alloy. During annealing of samples at high temperatures (~600°C), no increase of peak intensity of impurity elements such as oxygen, carbon and sulphur was observed as shown in Fig. 1.

On the basis of the experimental results described above, the surface composition (atomic percent of Cu) was plotted against the bulk composition (atomic percent of Cu) with a comparison of the surface compositions determined from the lower and higher energy spectra as well as of those from the bombarded and annealed surfaces. In order to estimate the surface compositions the correction factor α was determined after the method of Pons et al[12]. which is based on an assumption that for an alloy composed of elements A, B, ..., N, the peak heights corresponding to a given element (H_A, H_B, ..., H_N) may be proportional to the atomic concentration of that element (C_A, C_B, ..., C_N). The correction factor α in $H_{Cu}/(H_{Cu}+\alpha H_{Ni})$ in the present study was determined as $\alpha_L=1.8\pm0.3$ (for the lower energy region) and $\alpha_H=2.6\pm0.2$ (for the higher energy region). As shown in Fig. 5, the surface composition changed considerably from the bulk composition by both treatments, i. e., the alloy surfaces were enriched with Ni atoms after ion bombardment,

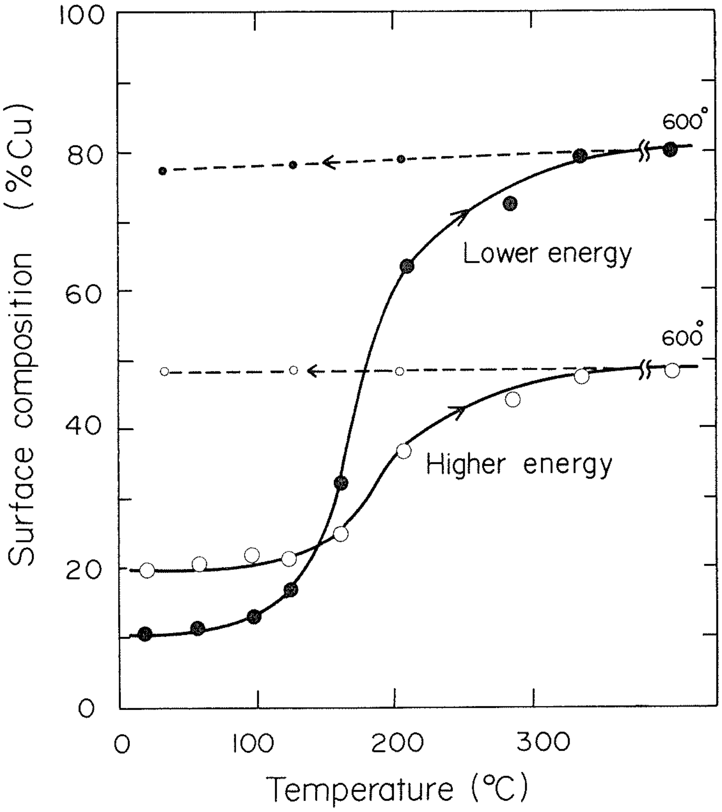

Fig. 6 Changing process of the surface composition with the annealing temperature, with the different energy regions.

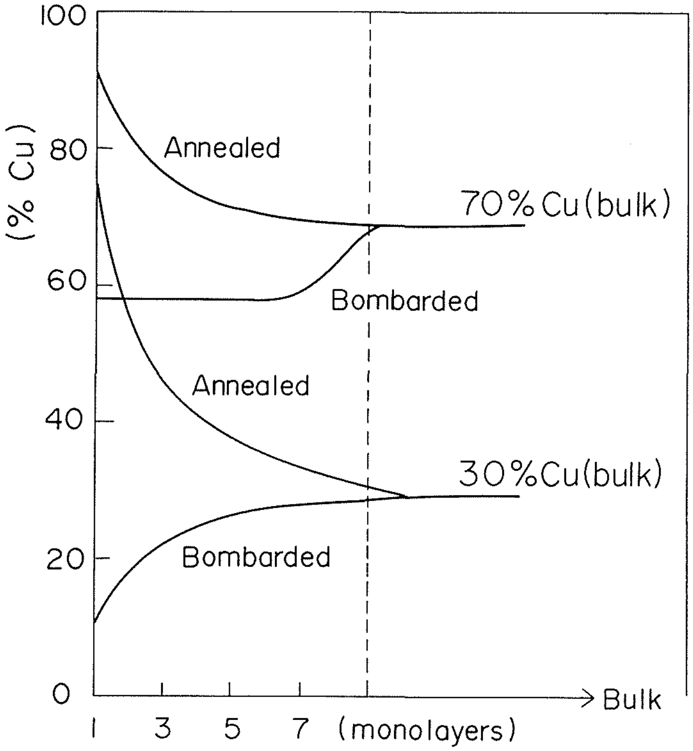

Fig. 7 An example of proposed depth profile of the composition in the surface layers of Cu-Ni alloys.

while with Cu atoms after annealing. Comparing the surface compositions determined by both spectra in the lower and higher energy regions, it is clear that the deviation of surface composition from the bulk due to annealing was much greater in the lower energy spectra than in the higher energy spectra.

The considerable enrichment with Cu atoms at the surface after annealing may be explained by thermodynamical calculations established by Williams et al[13,14]. and Burton et al.[15] which were based on a broken bond model and regular solution theory.

Fig. 6 shows an example of the process of change in the surface composition determined by both energy spectra as a function of annealing temperature for the bombarded surface of 20% Cu alloy. The surface composition was observed to attain a constant value after 10 or 20 minutes annealing at each temperature. It should be noted that the surface composition began to change drastically at temperatures over 150°C and the enrichment with Cu atoms was considerably greater in the upper surface layers than in the inner surface layers.

As described above, there may be differences in the escape length of the Auger electrons between the lower energies around 100 eV and the higher energies 700～1000 eV. Therefore by utilizing the difference in escape length of the electrons, we can draw a depth profile of alloy composition in several atomic layers at the surface. Examples of the depth profile are shown in Fig. 7 for 70% Cu and 30% Cu alloys (the bulk composition).

Further work is required to determine the exact values of the escape length of the Auger electrons with both energy regions.

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References

1) Nakayama, K., Ono, M. and Shimizu, H.: J. Vac. Sci. Technol., vol. 9, (1972), p. 749.
2) Ono, M., Shimizu, H., and Nakayama, K.: J. Vac. Sci. Technol., vol. 10, (1973), p. 566.
3) Shimizu, H., Ono, M. and Nakayama, K.: Surface Sci., Vol. 36, (1973), p. 817.
4) Takasu, Y. and Yamashina, T.: J. Catalysis, Vol. 28, (1973), p. 174.
5) Takasu, Y., Konno, H. and Yamashina T.,: Surface Sci., Vol.45, (1974), p. 321.
6) Takasu, Y. and Yamashina, T.: Proc. 2 nd Intern. Conf. on Solid Surfaces, Japan. J. Appl. Phys. Suppl. 2, pt. 2, (1974), p. 493.
7) Ono, M., Takasu, Y., Nakayama, K. and Yamashina, T.: Surface Sci., Vol. 26, (1971), p. 313.
8) Helms, C. R.: J. Catalysis, Vol. 36, (1975), p. 114.
9) Helms, C. R. and Yu, K. Y.: J. Vac. Sci. Technol., Vol. 12, (1975), p. 276.
10) Helms, C. R., Yu, K. Y. and Speicer, W. E.: Surface Sci., Vol. 52, (1975), p. 217.
11) Yamashina, T., Watanabe, K., Fukuda, Y. and Hashiba, M.: Surface Sci., Vol. 50, (1975), p. 591.
12) Pons, F., Héricy, J Le, and Lageron, J. P.: Surface Sci., Vol. 51, (1975), p. 336.
13) Williams, F. L., and Nason, D.: Surface Sci., Vol. 45, (1974), p. 377.
14) Williams, F. L.: Ph. D. Dissertation, Stanford University, (1972).
15) Burton,J.J.: Hyman, E., and Fedak, D. G.: J. Catalysis, Vol. 37, (1975), p. 106.