CHEMISTRY LETTERS, pp. 1343-1346, 1976. Published by the Chemical Society of Japan

AES-FDS SIMULTANEOUS MEASUREMENT FOR DECOMPOSITION OF FORMIC ACID OVER CLEAN SURFACE OF COPPER-NICKEL ALLOY

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A combined system of Auger spectroscopy (AES) and flash desorption spectroscopy (FDS) was utilized to reveal adsorption and decomposition processes of formic acid over clean surface of Cu-Ni alloy. It was found that the surface treatments of ion-bombardment and annealing brought about a great difference in decomposition process which could be attributed to change of the surface composition.

Flash desorption technique has been extensively used as a powerful method to reveal the mechanism of catalysis over solid surfaces, especially for the decomposition of formic acid on metallic catalysts.1),2)

In the present paper, we will report preliminarily the simultaneous measurement of Auger spectra and flash decomposition spectra applying to the decomposition of formic acid preadsorbed on the clean surface of Cu-Ni alloy.

A conventional AES system (CMA optics) equipped together with a secondary ion mass spectroscopy(SIMS) device was used in the present study. A Cu-Ni alloy specimen with plate form (20 x 6 x 0.5 mm^3) was mounted just in front of the CMA and a quadrupole mass spectrometer. The specimen could be electrically heated at any temperature between 300 and 1100 K as measured by a thermocouple (Tungsten-5%Rhenium vs. Tungsten-26%Rhenium, 0.12 mm in diameter and 40 cm in length) spot-welded to back of the specimen. Formic acid was dosed to the specimen from a tip of stainless-steel tube (1.5 mm diameter) placed 10 mm from the specimen surface. The dosing pressure was monitored by a B-A gauge. The surface composition of alloy was estimated by peak-to-peak height from the Auger transitions of $M_1M_{4,5}M_{4,5}$

at around 100 eV, and it could be varied by the surface treatments, e.g., ion-bombardment gave a Ni-rich surface and annealing gave a Cu-rich surface.[3)]

Figure 1 shows an example of AES-FDS simultaneous measurement for the decomposition of formic acid over a clean surface of 20%Cu-Ni alloy in the bulk composition which was annealed at 500°C for 1 hr in a vacuum of 2×10^{-10} Torr. The composition of this annealed surface was determined to be 60%Cu-Ni. After the specimen was exposed to formic acid at 1×10^{-7} Torr for 10 min at 25°C, the chamber was evacuated to 1×10^{-9} Torr at the same temperature and then sample temperature was raised linearly (approximately 4 K/sec) as shown in Fig. 1 to obtain desorption spectrum as well as the Auger spectrum. As seen in Fig. 1, the desorption spectrum of carbon dioxide exhibits a peak at about 480 K and a shoulder at about 420 K. The subsequent increase of CO_2^+ signal above 550 K in the desorption spectrum could be attributed to the desorption from the sample holder. During the flash decomposition, Auger signals from carbon and oxygen decreased gradually, showing similar tendency as desorption process of carbon dioxide and then disappeared completely at about 600 K. It indicates clearly that formic acid adsorbed over the alloy surface could be desorbed thoroughly after a flash experiment.

Figure 2(a) and (b) show the desorption spectra from an ion-bombarded and an annealed surfaces of 20%Cu-Ni alloy in the bulk composition. The conditions of the ion-bombardment were 700 eV, 3 $\mu A/cm^2$ for 1 hr which gave the surface composition of 5%Cu, while that of the annealing was 500°C for 1 hr in 2×10^{-10} Torr which gave the surface composition of 60%Cu. The conditions of adsorption of formic acid were same as above. The rate of temperature elevation was 18.2 K/sec by supplying 1.5 V and 65 Amp across the specimen. On the bombarded surface, it was found that the carbon monoxide spectrum has a peak at 440 K and a shoulder at 380 K. On the other hand, in case of the annealed surface, the desorption peaks were observed at about 450 K on the carbon dioxide and hydrogen spectra, while a peak at 445 K on the carbon monoxide spectrum. Much remarkable difference between both surfaces was on the FDS spectrum of carbon dioxide, that is, a characteristic peak was found at 380 K on the bombarded surface. It is also found that during a FDS measurement the surface composition was almost unchanged.

Making a comparison between both surfaces, one can see that carbon dioxide desorbed at 450 K on the annealed surface and at 380 K on the bombarded surface.

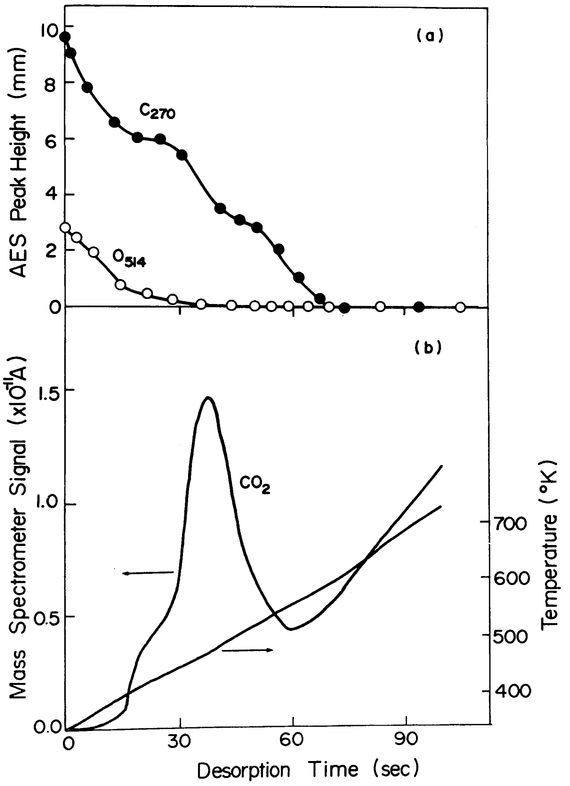

Fig. 1. Simutaneous measurement of AES-FDS for formic acid pre-adsorbed on the ion-bombarded surface of 20%Cu-Ni alloy in the bulk composition.

(a) Variation in the AES signal intensity of carbon and oxygen.

(b) Flash desorption spectrum of carbon dioxide and temperature elevation curve of the sample.

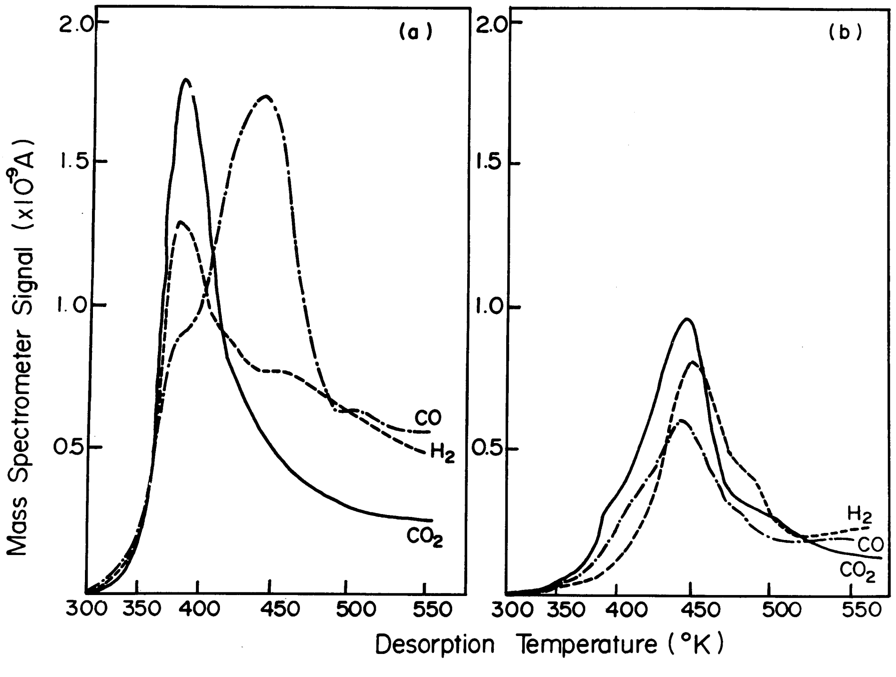

Fig. 2. Flash desorption spectra of carbon monoxide, carbon dioxide and hydrogen from the ion-bombarded(a) and the annealed(b) surfaces of 20%Cu-Ni (bulk) alloy after exposure of formic acid (1×10^{-7} Torr for 10 min).

By assuming the desorption of hydrogen and carbon dioxide obeys the first order kinetics with the frequency factor of 1 x 10^{13}/sec on both surfaces after the ion-bombardment and the annealing, the activation energy can be estimated from an equation $(E/RT_p^2) = (\nu/\beta)\exp(-E/RT_p)$, where ν is the frequency factor, β is the rate of the temperature elevation (β = 18.2 K/sec in the present study) and T_p is the peak temperature of desorption spectrum. The estimated activation energies are 22.3 kcal/mol for the lower temperature peak (380 K) and 26.9 kcal/mol for the higher temperature peak (455 K). It has been found that the activation energies of formic acid decomposition ($HCOOH \rightarrow H_2 + CO_2$) are 15 - 20 kcal/mol on Cu foils and/or films and 18 - 26 kcal/mol on Ni foils and/or films.4)-8) The activation energies of the decomposition over Cu-Ni alloys were observed to increase monotonically with increase of Cu content in the alloys.8)

Hence, it is considered that the difference in the FDS spectra for both surfaces might be attributed to the surface composition. However, there may be another possibilities to account for the difference in the FDS spectra, for example, ion-bombardment induces excess lattice defects which could be related to the catalytic properties of solid surfaces.

More detailed results will be reported shortly by using a combined system of the AES-SIMS-FDS measurement.

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(Received September 24, 1976)