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X-RAY PHOTOELECTRON SPECTRA OF EVAPORATED NICKEL EXPOSED TO O_2 AND H_2O

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Binding energies of $Ni2p_{3/2}$ and O1s electrons were measured by X-ray photoelectron spectrometer during the interaction of evaporated nickel with O_2 and H_2O. Two kinds of peaks were obtained for both oxygen and nickel of the surface species formed. On the reaction of the surface species with H_2O, electron transfer was observed.

X-ray photoelectron spectroscopy$^{1)}$ seems to be a useful tool for estimating the variation in the charge of the atoms in question during the reaction of solid surface. Application of the tool to the catalysis research has been reviewed recently.$^{2)}$ The interaction of oxygen with nickel is one of the most extensively studied metal-gas systems. With X-ray photoelectron spectroscopy, we investigated the surface species formed after the interaction to illustrate clearly the essential steps involved in a surface corrosion of a metal from the viewpoint of atomic charge. The electron transfer was also studied on the reaction of the surface species with H_2O.

Nickel sample was prepared by evaporating the metal onto the copper plate from tungstem filament at 10^{-5}-10^{-6} mm Hg pressure. After recording the spectrum of fresh nickel, the surface was exposed to the gases to be studied. After evacuation of the gases, photoelectron spectra were measured for the surface species formed. On recording the spectrum, the vacuum of photoemission chamber was maintained at 10^{-7} mm Hg. Spectra were measured on a KEC-X2000 electron spectrometer using Al $K\alpha_{1,2}$ X-ray radiation.

Binding energies of $Ni2p_{3/2}$ and O1s electrons were calculated from the kinetic energy of electrons ejected using value of 285.0 eV for the C1s electron binding energy observed as the background spectrum.

Figure 1 shows the $Ni2p_{3/2}$ and the O1s photoelectron lines from the evaporated nickel exposed to O_2. Case 1 is those from the evaporated fresh nickel. The Ni and the O peaks locate at 854.6 and 532.6 eV, respectively. (The Ni peak at 860.4 eV is due to $Ni2p_{1/2}$ electron ejected by Al $K\alpha_{3,4}$ radiation.) When the metal was exposed to O_2 (0.5 mm Hg pressure) for 10 sec, the genuine Ni peak was depressed and another peak appeared around 856.5 eV (case 2). The O1s peak increased in intensity and the second O1s peak was obtained at 530.2 eV; at lower binding energy than the first O peak. On oxygen treatment, electron counts of background were depressed over whole range of binding energy and the intensity discussion will be carried out by comparing the difference between the maximum and minimum counts of each peak or the peak areas. On subsequent exposure to O_2 (5 mm Hg) for 10 sec, the right (second) O peak became clearer (case 3). The metal was, again, treated with O_2 (100 mm Hg) for 30 min. The Ni peak around 856.5 eV was depressed and, instead, the peak at 857.6 eV appeared with well resolved profile (case 4). Following the changes in the Ni peaks, the left O1s peak was largely intensified, and the right O1s slightly.

The O1s peak was obtained on the fresh nickel. For the fresh iron, the O peak was also found at the same binding energy and with the comparable intensity.3) However, the peak with lower binding energy alone was intensified after the interaction of oxygen with iron unlike the case with nickel. The O1s and C1s background peaks were also observed in measurable intensity for prereduced Pt foil.2) The large part of O1s peak for the fresh nickel, therefore, can be assigned to the background oxygen rather than to the surface oxide-oxygen. The O peak for fresh nickel was subtracted graphically from each O1s spectrum and the resultant peaks are shown by dotted lines in the Figure. The dotted lines more properly represent the spectrum which is expected for surface oxide alone than the one obtained experimentally.

The above results will be discussed by a simple charge-chemical shift approach; the chemical shifts of the core binding energies are assumed to be related solely to the gross charge on the atoms in question. The intensity of the left O peak increases with the increase in that of the left Ni peak during the surface oxidation and these peaks are concluded to originate from the same oxide species. The chemical shift of the Ni peak is smaller than that for NiO (3.3 eV)2) and less oxidation is expected for the nickel atom of the surface oxide.

The interaction of oxygen with nickel has been studied by a number of workers and reviewed.4) At an oxygen pressure of 760 mm Hg, an oxide of the overall composition $NiO_{0.3}$ was suggested to be formed at 25°C.5) The surface oxide, giving the left Ni and O peaks, is likely to correspond to such an oxide.

The right O peak is correlated to the Ni peak around 856.5 eV on considering the change in intensities of the two peaks and the same behavior observed during the reaction with H_2O which will be described below. The shift of the Ni from genuine peak is 1.9 eV and is 1.1 eV less than that for the left Ni peak. If oxygen atom could bond to constant number of nickel atom during the oxidation, the more positive nickel would be correlated to the more negative oxygen. The observation is, however, not the case. Therefore, the oxygen giving the right O peak must bond to larger number of nickel atoms than that giving the left O peak and the bonding must be more ionic. The oxygen is, then, assigned to that forming the more highly oxygen-deficient oxide $NiO_m (m<0.3)$ or chemisorbed oxygen not being incorporated layer contacting to the bulk nickel, on the surface at the initial stage of oxidation and beneath the $NiO_m (m\approx 0.3)$ layer after further oxidation.

Figure 2 illustrates the effects of H_2O on the electronic states of the surface oxide. Case 1 shows the peaks from nickel treated with O_2 (5 mm Hg) for 5 sec. On addition of H_2O vapor (15 mm Hg) for 5 min (case 2) and, further, for 30 min (case 3), the right O1s peak was depressed in intensity and the left was enhanced. The Ni peak around 856.5 eV gradually changed its profile into the more distinguishable one with maximum at 857.6 eV. The intensity of genuine Ni peak did not change on the interaction with H_2O.

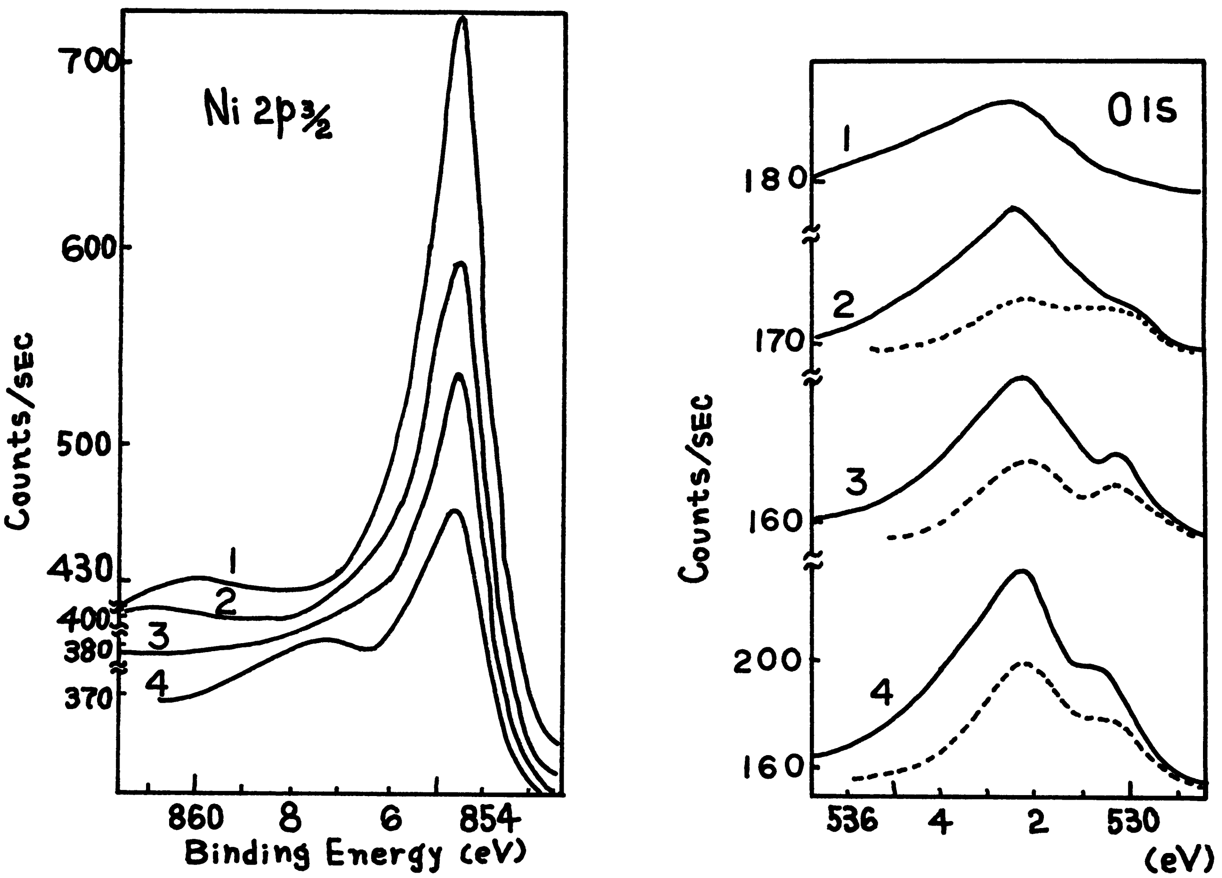

Figure 1. Ni($2p_{3/2}$) and O(1s) photoelectron lines from (1) evaporated nickel, (2) exposed to O_2 (0.5 mm Hg) for 10 sec, (3) to O_2 (5 mm Hg) for 10 sec, and (4) to O_2 (100 mm Hg) for 30 min in succession. Dotted lines were obtained by subtracting graphically the O1s spectrum for fresh nickel from each spectrum.

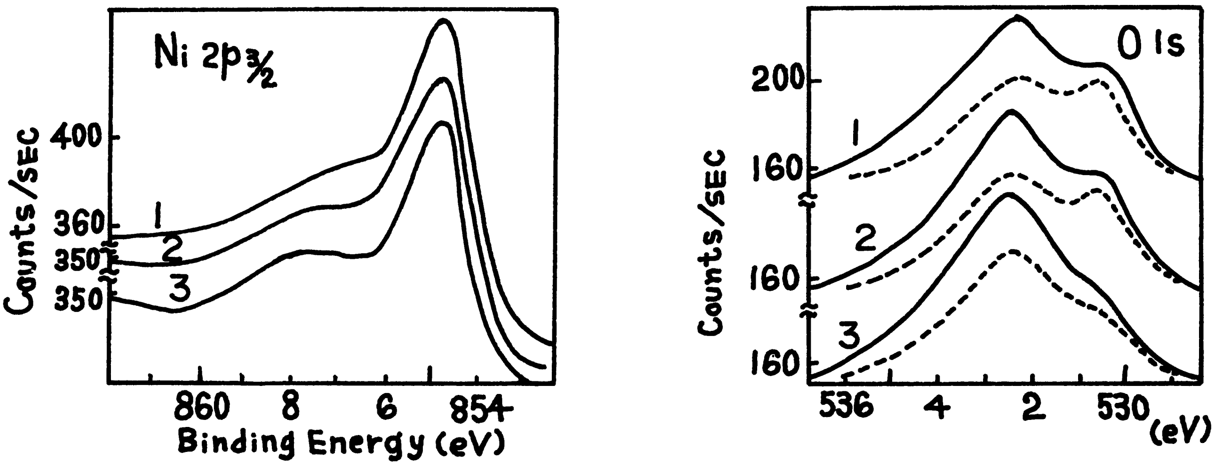

Figure 2. Ni($2p_{3/2}$) and O(1s) photoelectron lines from evaporated nickel exposed to (1) O_2 (5 mm Hg) for 5 sec, (2) H_2O (15 mm Hg) for 5 min, and (3) H_2O (15 mm Hg) for 30 min in succession.

This change in the O1s peaks indicates that the partial electron transfer occured from the oxygen of highly oxygen-deficient species, described above, to H_2O during the interaction. Hydrogen bonding is explained by the electron transfer from the proton accepting species to the antibonding orbital of, for example, O-H bond of the proton donating species.6) The above spectral change demonstrates the mechanism of the hydrogen bonding. The formation of hydroxide or hydroxide-like species is expected to result in. The latter species have, probably, the structure forming outer or inner complexes with H_2O. As shown by case 1 and 3 of Figure 2, the charge of nickel becomes higher, as the decrease in the negative charge of oxygen, on the reaction with H_2O. This indicates that the reaction induces the decrease in number of nickel atoms to which one oxygen atom is bonding or that the electron is also transfered from nickel to H_2O via oxide-oxygen.

The information about the reactivity of the oxide-oxygen, giving the left O peak, with H_2O is, however, not obtained clearly from spectral data since the O peak is at the same binding energy with that of the hydroxide or hydroxide-like species.

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