Time-evolution of oxidation states at the Ni(111) surface: O₂ incident translational energy dependence

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Abstract. Metallic Ni is expected to be a substitution candidate for Pt and Pd in catalytic materials. Generally speaking, catalytic reactions take place on a metal oxide layer. In this study, therefore, the oxidation states of the Ni(111) surface, which were made by irradiation with a supersonic O₂ molecular beam, were analyzed by soft x-ray photoemission spectroscopy with synchrotron radiation. The oxygen uptake curve and initial sticking rate were found to show remarkably strong dependence on the O₂ incident energy for energies of up to 2.3 eV. The intermediate plateau seen in the oxygen uptake curve for low incident energies was found to disappear with increasing incident energy due to a change of the dissociative adsorption mechanism from a two-dimensional island growth model to a direct activated adsorption model. Due to this activated adsorption, the formation rate of NiO and peroxide nickel increased as compared to backfilling oxidation by O₂ gas.

1. Introduction
The Ni(111) surface reacts with O₂ molecules to form a thin oxide layer on the surface at 147 K [1] showing a Langmuir-type oxygen uptake curve. When the clean Ni(111) surface is exposed to O₂ gas at higher temperatures, a plateau appears in an intermediate region of the oxygen uptake curve [1]. These characteristics are also observed in the oxidation of the Ni(001) surface [2]. This behaviour of the oxygen uptake curves can be explained by a two-dimensional (2D) oxide island growth model [2, 3]. Generally speaking, the surface chemical reaction rate of incident atoms and molecules depends also on their translational kinetic energy. Indeed, the oxygen uptake curve for Ni(111) oxidation by an O₂ molecular beam with a hyperthermal energy of 0.6 eV at a surface temperature of 300 K was observed to change from the 2D island growth model to the Langmuir type [4]. This implies that the kinetics of oxygen adsorption at the Ni(111) surface depends actually on the translational kinetic energy of the O₂ molecules, with higher energies allowing a direct activated adsorption mechanism [4]. Here the oxygen uptake showed an intermediate plateau of 0.2 monolayer (ML), and finally saturated at 3.0 ML [4] at 300 K. Translational kinetic energy effects have also been shown for the initial sticking coefficients of O₂ molecules on the Ni(111) surface [5]. Although a trapping-mediated adsorption mechanism was apparent at 123 K for incident energies lower than 0.05 eV, activated...
adsorption was found to take place in the higher incident energy region, with energies of up to 0.4 eV [5].

The incident energy of O\(_2\) molecules in a beam can be increased to 2.3 eV by using our supersonic molecular beam (SSMB) technique. Using this technique, the effects of incident energy on O\(_2\) adsorption at the Ni(111) surface have been studied using soft x-ray photoemission spectroscopic surface analysis with high brilliance and high energy-resolution synchrotron radiation (SR-PES). The surface chemistry experimental station (SUREAC2000) of BL23SU, one of Japan Atomic Energy Agency’s (JAEA) contract beamlines at the SPring-8 facility was used in these experiments [6,7]. Both an O\(_2\) SSMB and the soft x-ray monochromatic synchrotron radiation beam can be irradiated on a sample surface simultaneously at SUREAC2000. Real-time in-situ photoemission spectroscopic observations of chemical bonding states at the oxidized Ni(111) surface can be performed during O\(_2\) SSMB irradiation to elucidate changes in oxidation kinetics by the incidence of hyperthermal O\(_2\) molecules possessing translational energies larger than 0.6 eV. Furthermore, the incident energy dependence of the initial sticking rate can also be estimated from the initial slope of the oxygen uptake curve. In this work, the influence of the incident energy of O\(_2\) molecules on the oxidation of Ni(111) surface is discussed in the energy region up to 2.3 eV.

2. Experimental

All the experiments were conducted using the SUREAC2000 apparatus. The surface reaction analysis chamber of the SUREAC2000 is pumped by two turbo-molecular pumps in tandem fashion in conjunction with a titanium sublimation pump so that a base pressure less than 5x10\(^{-9}\) Pa is achieved. A hemispherical electron energy analyzer (Omicron EA125-5MCD) and a conventional twin anode (Al/Mg-K\(_{\alpha}\)) x-ray source are also available for photoemission experiments.

The O\(_2\) SSMB is continuously generated by the adiabatic expansion of a mixture of O\(_2\), He and Ar gas. The free expansion nozzle can be heated up to about 1400 K, corresponding to a calculated upper limit for the incident energy of O\(_2\) molecules of 2.3 eV. The incident energy is controllable by varying the gas mixing ratio and the nozzle temperature. Usually, the incident energy is changed by varying the gas mixing ratio keeping the nozzle temperature constant at 1400 K. The O\(_2\) SSMB was irradiated onto the sample surface with an incident angle of -10 deg with respect to the surface normal. The photoelectron detection was +30 deg. Incident energies less than 0.2 eV were achieved with a nozzle temperature of 300 K. A backfilling experiment (exposure to O\(_2\) gas) was also conducted to obtain data for an incident energy of 0.03 eV.

A clean Ni(111) surface was made by cyclic treatments of Ar\(^{+}\) ion sputtering (applied voltage; 1kV, ion current; 1\(\mu\)A) and thermal annealing (1273 K flashing followed by 923 K for 20 min). The cleanliness of the surface was confirmed by measuring an SR-PES wide spectrum and the observation of a 1x1 low energy electron diffraction (LEED) pattern.

After timed irradiation of the O\(_2\) SSMB onto the clean Ni(111) surface, Ni-2p, Ni-3p and O-1s core level photoemission spectra were recorded. Cycles of O\(_2\) SSMB irradiation and SR-PES measurements were repeated at each incident energy until saturation of the O-1s peak intensity. Oxygen uptake curves were obtained from the spectra. The surface temperature was kept at 300 K during both O\(_2\) SSMB irradiation and SR-PES measurements. SR energies of 680 eV and 1150 eV were used.

3. Results and discussion

3.1. Oxygen uptake curves

The time evolution of the O-1s photoemission spectra towards oxidation saturation is shown in figure 1 for incident O\(_2\) energies of 0.7 eV, 1.4 eV, and 2.3 eV, respectively. All O-1s photoemission spectra show a broad and asymmetric profile which changes with incident energy. The spectral profiles imply that the O-1s peak consists of several components. Figure 1 also demonstrates that the oxygen content at saturation also depends on incident energy.
If the area of an O-1s peak is assumed to be proportional to the oxygen content at the Ni(111) surface, an oxygen uptake curve can be obtained by plotting the areas of O-1s peaks as a function of O₂ dose. Figure 2 shows the incident O₂ energy dependence of the oxygen uptake curves. For low incident energy (e.g. 0.06 eV), the uptake curve shows an initial uptake (fast chemisorption stage), an intermediate plateau (oxide onset) followed by a re-increase (fast oxide growth stage) of oxygen coverage. These characteristics can be seen in previous reports [1-4]. The oxygen content at saturation has been reported to be 3 ML [4]. For a higher incident energy region than 0.6 eV, the intermediate plateau region shortened, and the oxygen coverage is higher in the intermediate O₂ dose region. For incident energies higher than 1.0 eV, the plateau almost disappeared as indicated in the 2.0 eV and 2.3 eV uptake curves in figure 2 and the oxygen content at saturation is about 5 ML, larger than that for an incident energy of 0.06 eV. This implies a change in the O₂ dissociative adsorption mechanism from a 2D island growth model to the Langmuir-type direct activated adsorption model. As mentioned below, the increase of oxygen saturation content can be attributed to the increase of the main components shown in figure 4. These are the NiₓOᵧ (x<y) peroxide component (c) and the nickel oxide component NiO (d).

3.2. Initial sticking rates of O₂ molecules
In order to investigate the influence of incident energy on the dissociative adsorption of O₂ molecules, the relative initial sticking rates for a clean Ni(111) surface were evaluated from the initial slope of each oxygen uptake curve. Figure 3 shows the relative initial sticking rates as a function of O₂ incident energy. The initial sticking rate increased gradually as incident energy increased, and reached a maximum at 1.0 eV. After that the sticking rate decreased slightly and a remarkable re-increase was observed in
the region around 2.3 eV. Such behavior is typical for quantum mechanical barrier penetration and over-barrier scattering. The first increase seen for incident energies below 1.0 eV implies that the activated dissociative adsorption of O\(_2\) molecules takes place by penetrating a potential energy barrier of 1.0 eV height. The abrupt increase around 2.3 eV implies that high speed O\(_2\) molecules adsorb by a mechanism which is distinctly different to that which occurs at energies of around 1.0 eV. That is, another potential energy barrier possessing a barrier height larger than 2.3 eV exists in a position closer to the surface than the first potential energy barrier.

3.3. Peak deconvolution of O-1s photoemission spectra

As seen in figure 1, the time-evolution of the O-1s peak profile is not monotonic at each incident energy. The variation of the peak profile during dosage of O\(_2\) molecules implies that the oxidation states of nickel change depending on oxygen coverage and incident energy. We assume here that the O-1s peak consists of six components. A typical peak deconvolution result is shown in figure 4. The main component is (d) NiO. The sub-oxide (f) Ni\(_x\)O\(_y\) (x>y) and the peroxide (c) Ni\(_x\)O\(_y\) (x<y) components are incorporated in the deconvolution in addition to (e) an oxygen chemisorption component, which corresponds to initially-chemisorbed oxygen atoms at a three-fold site on the top surface of Ni(111) [8]. The peak labelled (b) near 531 eV may be due to Ni(OH)\(_2\) generated from dissociative adsorption of residual H\(_2\)O gas molecules during the measurements. Residual H\(_2\)O gas molecules also adsorb gradually at the oxidized Ni(111) surface during experiments to form the H\(_2\)O component (a). Previous studies indicated that peaks related to H\(_2\)O- and OH- appear on the higher energy side of the main O-1s peak [9,10].

The peak deconvolution enables us to derive the time-evolution of each component during the growth of the oxide layers. The time-evolutions of the four major O-1s components are shown in figure 5. In the early oxidation stages, O\(_2\) chemisorption on the topmost Ni(111) surface initially takes place as the uptake of (e) O-chemisorption component occurs primarily, as shown in figure 5(a). Subsequent collisions of incident O\(_2\) molecules with the initially-formed O-chemisorbed local structures make the O-chemisorption sites change to nickel peroxides Ni\(_x\)O\(_y\) (x<y). If oxygen diffusion and migration occurs from the peroxide sites, NiO structures may be formed near the peroxide sites. The sub-oxide nickel should be formed in the interface region between the Ni(111) substrate and the oxide over-layer.

With increasing O\(_2\) incident energy, the rate of activated dissociative adsorption through the first potential energy barrier (1.0 eV height) also increases, leading to an abrupt appearance of the uptake of the peroxide component. The uptake of NiO also follows, as shown in figure 5(b). For incident energies higher than 1.0 eV, the NiO content becomes larger than the peroxide content, as shown in figure 5(c). This tendency is prominent at an incident energy of 2.3 eV, as shown in figure 5(d), where the second dissociative oxidation channel is opened through the second potential energy barrier. Collisions of high speed O\(_2\) molecules with the peroxide local structures or another nickel oxide local structure enhance the formation rate of NiO. According to prediction based on the Cabrera-Mott
model on the growth of NiO layer by O\(_2\) gas, potential barrier heights of 2.36 eV [11] and 2.56 eV [12] have been reported. Our experimental results are consistent with these theoretical predictions.

4. Conclusions

Oxidation processes of a clean Ni(111) surface with hyperthermal O\(_2\) molecular beams have been studied by using soft x-ray photoemission spectroscopy with synchrotron radiation. Oxygen uptake curves have been observed at various O\(_2\) incident energies, extending to energies higher than those of previous reports. The first plateau, which appears at an intermediate region of the oxygen uptake curve, was found to disappear with increasing O\(_2\) incident energy. Furthermore, an oxygen content at saturation of 5 ML was observed for an incident energy of 2.3 eV. This is 1.7 times higher than that observed for energies of 0.06 eV to 0.6 eV. These observations can be attributed to the influence of activated adsorption mechanisms. The initial sticking rate continued to increase as incident energy increased up to 1.0 eV, and a remarkable re-increase was observed in the region around 2.3 eV. The first increase is due to the activated dissociative adsorption of O\(_2\) molecules through a potential energy barrier of 1.0 eV, and the second increase around 2.3 eV implies that another potential energy barrier exists with a height larger than 2.3 eV. Higher O\(_2\) incident energy leads to higher formation rates and higher contents at saturation for the NiO component.

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