A Soft X-ray Appearance Potential Spectroscopy Study of the Oxidation of Nickel

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Variations of the electronic properties of nickel during the first stages of oxidation were studied by means of the soft x-ray appearance potential spectroscopy (APS). The spectra consist of a superposition of contributions from metallic nickel and from NiO and yield no evidence for a continuous change of the oxidation state of the Ni atoms. The binding energy of the $2p_{3/2}$-electrons in metallic nickel was found to be 851 eV and is increased in NiO by 1.4 eV. It is concluded from the shape of the APS peaks that with Ni above the Fermi level 3d- and 4s-bands are superimposed whereas with NiO these are separated in energy.

1. Introduction

The technique of soft x-ray appearance potential spectroscopy (APS)[1] may yield information about the binding energies of core electrons and about the densities of unfilled electronic states above the Fermi level of the solid. It therefore appears also to be suited to study variations of the electronic structure associated with chemical reactions of a solid. Characteristic changes of APS spectra after oxidation of a metal were reported for the first time by Park and Houston[2].

The principle of the method consists in measuring the intensity of the total x-ray radiation emitted from a solid which is bombarded by electrons of definite energy.

If by variation of the electron energy the threshold energy for excitation of a core electron to an unfilled state above the Fermi level E_F is reached a small but characteristic increase of the intensity of x-ray emission may result which is converted into photoelectrons and by means of electronic differentiation leads to the "appearance potential" spectra. If the energies of the primary electrons are below ~ 1000 eV their depth of penetration into metals is only of the order of < 20 Å which makes this method sensitive to the topmost atomic layers.

The present paper is concerned with the variation of the binding energies of Ni 2p-electrons ("chemical shift") and of the structure of empty electronic states during the first stages of oxidation up to the complete formation of NiO. APS spectra from clean[3—5] and oxidized nickel[3] were already reported

in the literature, however without any detailed interpretation of the results in the latter case which is tried in the present study on the basis of our knowledge about the electronic properties of NiO.

2. Experimental

The experiments were performed with an UHV system using an APS spectrometer as described by Musket and Taatjes[6]. Both mechanically polished Ni single crystal discs of about 2 mm thickness and a polycrystalline Ni-foil of 0.2 mm thickness served as samples which were mounted on a manipulator. The surfaces were cleaned by prolonged annealing and argon ion bombardment in vacuo. The cleanliness of the surfaces was checked by means of Auger electron spectroscopy (AES) using a retarding field analyzer as constructed in our laboratory[7]. Heating of the samples was performed by electron bombardment from the backside.

Continuous oxidation of the samples took place by exposing them for different times to an oxygen pressure of $2 \cdot 10^{-5}$ Torr at 500 °C (foil) or 600 or 700 °C (single crystals). The onset of oxidation was followed qualitatively by means of AES. Appearance potential spectra were taken after evacuation of the system. In order to suppress heating of the samples during the measurements as far as possible a primary electron current of only 0.5 mA was used, which nevertheless caused the surface temperature to rise to about 100 °C. However, only negligible variations of the state of the samples by the measuring procedure could be detected; the thermal decomposition of NiO only starts above 350 °C[8]. The spectra were recorded by means of a lock-in amplifier with high sensitivity (PAR 124 A) using rather high time constants between 10 and 30 sec.

It was demonstrated by control experiments that adsorption of oxygen at the photocathode has no noticeable influence on the shapes and intensities of the AP spectra. With residual gas pressures $> 10^{-7}$ Torr an increase of the noise was observed [9]. Variations of the work function of the sample by oxygen adsorption do not enter into the results. With the hot tungsten filament such effects may be excluded due to its high temperature.

3. Results

Figure 1 shows a series of spectra obtained from the foil sample and caused by the excitation of Ni 2p-electrons into empty states above the Fermi level. The spectrum from metallic nickel (curve a) agrees with already published data [3-5] and is characterized by two main peaks L_3 and L_2 according to excitation of $2p_{3/2}$ and $2p_{1/2}$ electrons. The recorded threshold potentials U_T do not represent directly the binding

Fig. 1. Appearance potential spectra of Ni 2p electrons of a clean and progressively oxidized Ni surface, showing a discontinuous increase of the binding energies of the Ni 2p electrons by 1.4 eV. The variations of peak shapes are in agreement with the bandstructure of NiO.

energies of the core levels but must be corrected for the work function of the tungsten filament and for a small contribution from the thermal spread of the energy of the primary electrons [4]:

$$E_B \approx e\,U_T + 4.5 \;[\text{eV}]\,. \tag{1}$$

The curves $b-g$ were obtained after successive oxidation at 500 °C. The oxygen exposures were in the range of up to 1350×10^{-3} Torr sec. The spectrum g represents the final stage of surface oxidation which could be identified as NiO by means of electron diffraction techniques. Although it is known that nickel may form a continuous series of oxides between NiO and Ni_2O_3 only negligible deviations from the stoichiometry of pure NiO is to be expected with the applied very low oxygen partial pressure [10]. Also, the appearance potential spectra yield no hint for the existence of other oxidation states of Ni. These spectra are characterized by the following general features:

i) The L_3-peak of metallic nickel is not shifted on the energy scale but with successive oxidation a new peak (L_3') emerges at a somewhat higher energy which finally replaces completely the original L_3-peak. The appearance potential of this new L_3'-peak is about 1.4 ± 0.2 eV larger than that of the L_3-peak. The L_3'-peak exhibits positive and negative dips of nearly equal size whereas the shape of the L_3-peak is highly asymmetric.

ii) Quite analogous variations are observed for the L_2-peak which is continuously replaced by a new one (L_2').

iii) The intensities of the satellites A and B in the spectrum of metallic nickel decrease continuously upon oxidation and are completely absent in the spectra from pure NiO. However two new peaks C and D are built up at 865 eV and 883 eV, respectively. The intensity of peak C finally even exceeds that of the L_2'-peak.

iv) Figure 2 shows the appearance potential spectrum of oxygen from NiO which is identical to that reported by Houston and Park [3]. The threshold potential is 531 eV. The multipeaked structure indicates the break-down of the simple one-electron picture. The energy separation between the peaks a and c is identical to that between the peaks b and d.

The following additional observations seem to be worthwhile to be mentioned:

The APS technique was found to be rather intensitive with respect to small amounts of adsorbed
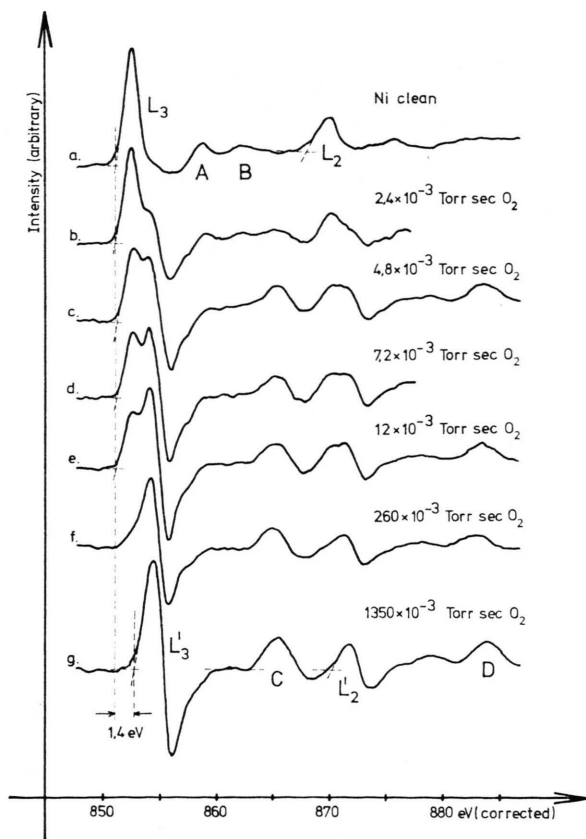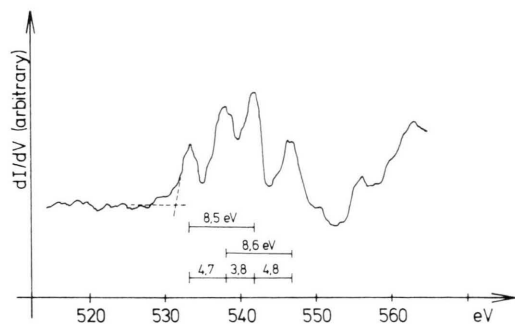
Fig. 2. Multipeaked AP spectrum of oxygen in NiO. The energy scale is corrected with respect to the work function of the tungsten filament.

oxygen. The Ni $L_{3,2}$-spectra changed only after strong interaction with oxygen. If a partially oxidized surface was annealed in vacuo for a longer period at temperatures above 200 °C the original clean nickel spectra reappeared, probably caused by the fact that oxygen diffuses into the bulk under these conditions [11].

4. Discussion

The first conclusion to be drawn from an inspection of Fig. 1 is that during the first stages of oxidation the AP spectra consist obviously of a superposition of the contributions from metallic nickel and from NiO. That means there is no continuous transition of the electronic properties of the nickel atoms but it has to be concluded that small crystallites of NiO are formed. The technique does not appear to be able to detect the variations of the electronic properties during adsorption of oxygen at the surface, i. e. prior to the onset of oxidation, as for example can be observed by means of ultraviolet photoelectron spectroscopy (UPS) [12].

Figure 3 a shows the densities of electronic states for Ni in the vicinity of the Fermi level E_F. The unfilled states above E_F are formed by a superposition of 3d and 4s states. The L_3- and L_2-peaks in the appearance potential spectrum (Fig. 1 a) arise from excitations of $2p_{3/2}$ and $2p_{1/2}$ electrons to these empty states. According to Eq. (1) the binding energies are evaluated from the threshold potentials. For the $2p_{3/2}$-electrons a value of 851 eV results which is in complete agreement with earlier APS results [4] and ESCA measurements [13, 14]. A somewhat larger value of 854.7 eV was tabulated by Bearden and Burr [15]. The spin-orbit splitting $L_3 - L_2$ = 17.1 eV is also in agreement with earlier data (17.3 eV) [4, 15].
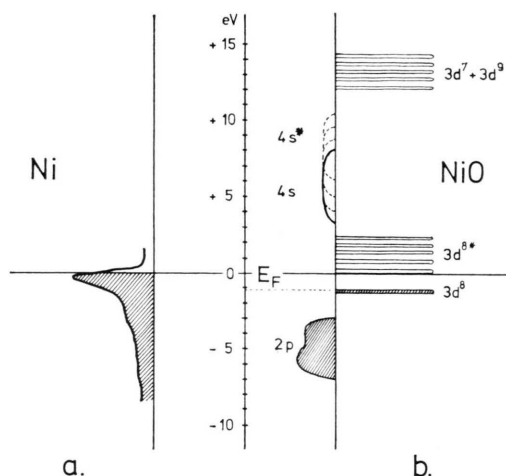

Fig. 3. Band structures of metallic nickel and nickel oxide.
a) Direct XPS valence band spectrum of Ni [a, b], b) Band-structure model for NiO from Adler and Feinleib [16]. Energy scale based on recent XPS results.
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The electronic structure of NiO was already the subject of numerous experimental and theoretical investigations [16, 17], but there are still discrepancies in understanding the electronic properties of this material. One of the main problems results from the fact that some of the valence states form normal itinerant energy bands which may be represented by the usual one-electron picture, whereas the 3d-states of the nickel ions are strongly localized. Since correlation effects play an important role, a one-electron representation will be no longer valid. Adler and Feinleib [16] therefore proposed a representation as reproduced in Fig. 3 b, where the states at the left side may be treated as ordinary one-electron (bandlike) states. The states on the right are quasi-particle states (which contribute to conduction only by means of thermally activated hopping). The Ni $-$ 3d^8 states are split by the influence of the crystal field. The position of the 3d^{8*} states corresponds to the excitation of an electron from a 3d^8 state and is mainly based on optical reflectivity and absorption measurements [18−21]. The lowest unfilled 3d^{8*} states are separated by 1.1 eV from the occupied 3d^8 ground state [22] whose width is smaller than 1 eV [16, 22, 23]. Between the O 2p- and the Ni 4s-bands exists an energy gap of 6.2 eV [24]. The 4s-band should have a width of several eV due to the highly delocalized character of its states. The states

indicated by $3d^7 3d^9$ correspond to the energy of excitation of an electron from a $3d^8$-state into a neighbouring Ni^{2+} ion, i. e. $d^8 + d^8 \rightarrow d^7 + d^9$. For a pair of free ions a value of 18 eV for this energy would result from the difference between the ionisation energies for Ni^{2+} and Ni^{3+} which is lowered in solid NiO to about 13 eV [16] resp. 9 ± 2 eV [25] and is used to explain the increase of optical absorption in this energy range [19]. The two energy scales for metallic nickel and for NiO are adjusted in Fig. 3 on the basis of recent photoelectron spectroscopic results, whereafter the maximum of the 2p-band in NiO is at about -5 eV and that of the $3d^8$-states at -1 eV with respect to the Fermi level E_F of metallic nickel [12, 22, 23]. As a consequence the lowest unfilled $3d^{8*}$-states of NiO should be located just above E_F.

From the foregoing discussion it becomes evident that the appearance potentials for the L_3, L_2 and L_3', L_2' peaks arise from excitations of electrons from $2p_{3/2}$- and $2p_{1/2}$-states in Ni and NiO, respectively, to E_F. The observed shift of 1.4 eV is therefore due to an increase of the binding energies of the core electrons in NiO. This value is in good agreement with that of ~ 2 eV as derived from ESCA measurements [13, 26]. Houston and Park [3] reported a separation $L_3' - L_3$ of only 0.8 ± 0.1 eV. Probably in these experiments the final stage of oxidation was not yet reached.

The origin of the satellite peaks observed in the spectra of Ni and of NiO is widely unknown. Threshold singularities due to the interaction of the core hole with single — particle or plasmon excitations of conduction electrons are probable events in APS [27] and certainly the multi-peaked structure of the oxygen spectrum of Fig. 2 is influenced by such processes. Surface and bulk plasmon excitation energies in Ni are 8.5 and 19 eV, respectively [28], but these values don't fit with any of the differences between the satellites and the main peaks in the APS spectra of Ni.

Possible explanations for the satellite peaks C and D in the NiO spectrum at an energy of $10 - 11$ eV above the main peaks may be given in terms of a direct transition of 2p electrons to the states indicated by $3d^7 d^9$ or in terms of a multiple excitation

including the transition $d^8 + d^8 \rightarrow d^7 + d^9$ besides the normal excitation of a core electron to the Fermi level. As can be derived from Fig. 3 b [16] both mechanisms should require excitation energies in the order of 13 eV and should differ by the energy gap between the filled $3d^8$ states and E_F of about 1 eV. Within the present results it is impossible to distinguish between these two cases.

In order to arrive at a qualitative interpretation of the shape of the main peaks of the AP spectra it is necessary to discuss briefly their mechanism of formation. The excitation probability of a core electron (and thereby to a first approximation the "extra"-intensity of x-ray emission) is proportional to the self-convolution of the density of empty states above E_F [29]:

$$T(E_B + E) \propto \int_0^E N(W) N(E - W) \, dW \quad (2)$$

where $E_B + E$ is the energy of the primary electrons and E_B the binding energy of the core electron. The shape of the appearance potential spectra should therefore to a first approximation be given by the first derivative of the above function. As can easily be seen noticeable APS signals are only to be expected in those cases where excitation occurs into levels with a high density of states, e. g. empty d-states. This is certainly the reason why with NiO no excitation into the 4s-band can be observed. As was shown in detail by Park and Houston [2] in the case of superimposed d- and s-bands the APS peaks should be asymmetric, i. e. the negative undershoot should be small, as is observed in the case of metallic nickel. If the excitation takes place in a separate d-band the positive and negative peaks should be of equal height as is fairly good fulfilled for NiO. This demonstrates that with NiO in fact the 3d- and 4s-bands are separated as demanded by the energy diagram of Figure 3 b.

The width of the APS peaks depends (among others) on the width of the unfilled bands into which excitation occurs. However in the present case this information is not directly accessible, since the instrumental resolution is only about 1.2 eV and because further broadening of the spectra takes place through the limited lifetime of the core hole [4].

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