Electron Spectroscopic Studies of the Oxidation of Ni/Pd Alloys

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The oxidation of polycrystalline samples of Ni/Pd-alloys at 600 °C and $2 \cdot 10^{-5}$ Torr O_2 has been investigated by means of Auger electron spectroscopy and soft x-ray appearance potential spectroscopy. The clean surfaces are enriched by Pd; and with increasing Pd content the binding energy of the Ni 2p-core levels was found to decrease continuously by 0.7 eV. After completion of the oxidation identical overlayers were formed on all samples (except on pure Pd!) which were identified to consist of NiO. Within the depth probed by the applied techniques ($\lesssim 20$ Å) the rate of oxidation was found to increase with increasing Pd content, which is in contrast to the behaviour to be expected for the growth of thick oxide layers after the formation of a coherent NiO overlayer.

1. Introduction

Although the suggestion that the addition of a nobler metal might improve the oxidation resistance of a base metal is misleading the use of a noble metal like palladium or platinum which itself is not attacked by oxygen is considered as being of considerable importance for the understanding of the mechanism of oxidation of alloys [1]. The rate of oxidation of alloys of this type was treated theoretically by Wagner [2] who selected the system Ni/Pt as a suitable example, but quite similar conclusions are to be expected for a series of Ni/Pd alloys. It was assumed that the only stable oxide to be formed is NiO, the mechanism of oxidation to be the same for nickel as well as for the alloys.

Whereas "bulk" oxidation processes were studied extensively in the past the investigation of the initial stages at clean metal surfaces became only accessible after the introduction of ultrahigh vacuum techniques and of electron spectroscopic methods probing the outmost atomic layers of a solid. The present work was devoted to a study of the variation of the compositions as well as of the electronic properties of the surface regions of Ni/Pd alloys interacting with oxygen at 600 °C. The results were obtained by means of Auger electron spectroscopy (AES) and of soft x-ray appearance potential spectroscopy (APS). The surface-sensitivity of both techniques are based on the fact that the mean free paths of the low energy electrons ($E < 1000$ eV) involved in the processes are smaller than about 20 Å [3]. AES is used to determine the elemental composition whereas APS yields information on the core level binding energies as well as on the empty electron states above the Fermi level [3, 4]. Variations of these properties by oxidation were already observed by APS in the case of chromium [5], nickel [6, 7, 23], iron [8, 9] and Fe/Ni alloys [10].

2. Experimental

The experiments were performed within a stainless-steel UHV system (base pressure $5 \cdot 10^{-10}$ Torr) which was equipped with a four grids retarding field analyzer and a glancing angle electron gun for AES and with an APS spectrometer of the type as described by Musket and Taatjes [11]. Details of this apparatus were described elsewhere [12]. The samples consisted of ten foils (area 1 cm², thickness 0.2 mm, purity 99.999%) of varying composition (including the pure components) and were mounted on the axis of a manipulator. They could be treated and analysed separately. Cleaning of the surfaces was performed by alternating heating (by electron bombardment from the backside to 800 – 900 °C) and argon ion bombardment (400 – 600 eV, 10 μA) cycles. The state of cleanliness was continuously controlled by means of AES.

In agreement with previous investigations [13] it was never possible to record APS spectra from Pd in the interesting energy range (< 1000 eV). Compositions of the surface regions were therefore derived from the peak heights of the Ni-Auger signals at 850 eV since the energy (and therefore the information depth) of these Auger electrons is nearly identical to that of the electrons involved in the creation of the Ni L_3-appearance potential spectra which were used for the analysis of the electronic properties.

Oxidation was performed by exposing the corresponding sample at 600 °C to an O_2 partial pressure of $2 \cdot 10^{-5}$ Torr for different periods of time. Spectra were taken subsequently after evacuation of the chamber and after cooling of the sample. During recording APS spectra the sample temperature rose to about 100 °C due to the relatively high intensity of primary electrons (0.5 mA at about 850 eV) but without affecting the measured surface composition to any noticeable extent.

By control experiments it was demonstrated that oxygen exposure of the APS-photocathode did not affect the shapes or the intensities of the appearance potential spectra. Work function changes of the sample do not influence the results [13].

3. Results

3.1 *Clean alloy surfaces*

Some interesting observations were made on variations of the surface region during the cleaning procedure. Such effects were however not the primary aim of this work and were therefore not studied in detail.

The most prominent Auger signals occur at 330 eV for Pd and at 850 eV for Ni. The peak height of the latter was used to determine the composition of the volume detected by AES. With well-annealed clean samples these compositions agreed usually with the nominal bulk concentrations to within a few percent. However both elements exhibit also Auger transitions at 42 (Pd) and 60 eV (Ni) which are in an energy range where the escape depth of the electrons is only about 4 – 6 Å. Therefore these peaks are indicative for the composition of the topmost 2 – 3 atomic layers.

After mounting the samples into the vacuum system they were annealed for about 2 hours at 900 °C. The Auger spectrum exhibited then large amounts of sulfur at the surface besides the constituents of the alloy. Argon ion sputtering leads to the removal of the impurities but also to a continuous decrease of the Pd content of the surface, i. e. Ni (the lighter element) is more effectively sputtered. Subsequent annealing at 600 °C causes diffusion of Pd atoms to the surface. This effect is demonstrated by Fig. 1 which shows the variations of the ratios of the relative Auger peak heights from Ni and Pd for an alloy containing 50% Pd as a function of the annealing time. If there were no concentration gradients normal to the surface both curves were predicted to level-off at 1.0, provided that backscattering effects etc. of the Auger electrons may be neglected. It is evident that the topmost atomic layers contain more Pd and less Ni than the bulk. Such a behaviour is to be expected on the fact that the heat of sublimation of Pd (90 kcal/mole) is smaller than that of Ni (103 kcal/mole) [14]. Following a theory of Williams and Nason [15] the element with the lower heat of vaporization is predicted to be enriched (with respect to its bulk atom fraction) at the surface of an alloy.

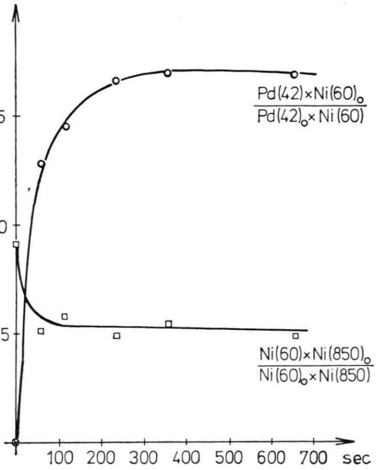

Fig. 1. Variation of the surface composition of a freshly sputtered Ni/Pd alloy (bulk composition 1:1) with the annealing time ($T \approx 600$ °C). Pd(42), Ni(60) and Ni(850) denote the peak heights of Auger transitions at 42, 60 and 850 eV arising from Pd and Ni, respectively. The subscript ○ denotes the respective quantity for the pure component.

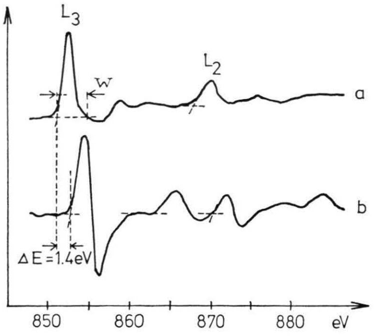

Fig. 2. Ni-$L_{3,2}$-appearance potential spectrum from metallic nickel (curve a) and from NiO (curve b). W defines the peak width and ΔE the "chemical" shift due to oxidation.

The $L_{2,3}$ appearance potential spectrum of pure Ni has already been published several times [6, 16–18] and is reproduced in Fig. 2 (curve a). It is characterized by two pronounced peaks (L_3 and L_2) corresponding to excitations of electrons from $2p_{3/2}$ and $2p_{1/2}$-states, respectively, their appearance potentials being 850.9 and 867.8 eV. Additional features of these spectra are the asymmetric shapes of the peaks (i. e. without a negative dip) and several satellites which are interpreted as being caused by characteristic energy losses.

With pure Pt it was not possible to detect any APS peaks in the accessible energy range ($\leqq 1000$ eV) even with the highest sensitivity of the spectrometer. This fact is in agreement with previous findings [13] and has so far not yet found a completely satisfactory explanation. Admission for several hours of 10^{-3} Torr H_2 at room temperature as well as of $2 \cdot 10^{-5}$ Torr O_2 at 850 °C had no detectable influence on the appearance potential spectrum of palladium.

In the case of the Ni/Pd alloy series again no peaks attributable to Pd atoms could be discovered. The Ni-$L_{2,3}$ spectra from the alloys are not reproduced since their general shapes were identical to those from pure nickel, the peaks however exhibiting varying intensities and threshold potentials. Within the simple one-electron picture of the mechanism of APS the height H of an APS peak is proportional to the square of the (local) densities of states at the Fermi level $N(E_F)$ of the corresponding element, provided that $N(E)$ has its maximum at the Fermi level E_F [17–19]. Figure 3 shows a plot of $\sqrt{\nu_{Ni} H_{Ni}/{}^0H_{Ni}}$ for the Ni L_3-peak as a function of the alloy composition, where ν_{Ni} is the atom fraction of Ni and ${}^0H_{Ni}$ the height of the L_3 peak with pure Ni. This quantity varies linearily with the composition which is to be expected to a first approximation for an alloy of this type consisting of isoelectronic elements [20].

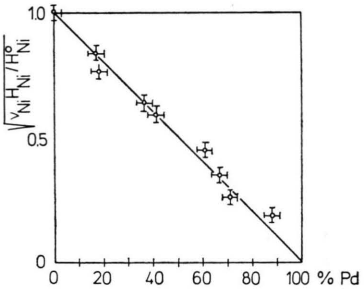

Fig. 3. Variation of $\sqrt{v_{Ni} H_{Ni}/H^0_{Ni}}$ with the alloy composition. (Explanation see text.)

The difference between the Ni L_3- and L_2-appearance potentials (indicating the energy of the spin-orbit splitting) remains unchanged over the whole series of alloys, however the absolute values of the appearance potentials are altered. Figure 4 shows a plot of the Ni L_3-appearance potential as a function of the alloy composition which accordingly varies linearily by 0.7 eV. In addition also the width W of the Ni L_3-peak as defined in Fig. 3 decreases from 2.6 eV (pure Ni) to about 2.1 eV (12% Ni). Since the latter quantity is markedly influenced by core-hole lifetime broadening [16] an interpretation of this effect appears to be rather problematic. Shifts of the Ni appearance potentials by alloying were also observed with the systems Ni/Cu [12] and Ni/Fe [21] and had tentatively been interpreted in terms of local intra-atomic reorganization processes of the Ni valence electrons. Since other data on the electronic properties of Ni/Pd alloys are rather scarce no more specific explanation can be offered in the present case.

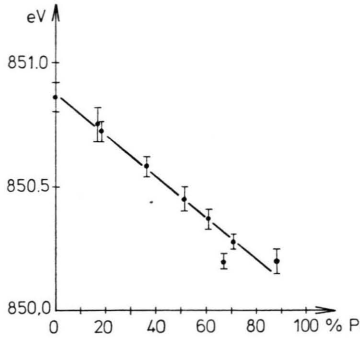

Fig. 4. Variation of the Ni L_3-appearance potential with the alloy composition (clean surfaces).

3.2 Oxidized samples

Figure 5 represents a series of Auger spectra for three alloys at different stages of oxidation at 600 °C. In all cases an O_2 exposure of $3-4 \times 10^4$ L [1 Langmuir (L) $= 10^{-6}$ Torr × sec] is sufficient to remove Pd completely from the surface region ($\lesssim 10$ Å) as can be seen from the gradual disappearance of the Pd Auger signal at 330 eV. The final state of oxidation is always characterized by Auger peaks merely arising from Ni and O. The alloy containing only 12% Ni was an exception in so far as this was the only case where after an oxygen exposure of $4 \cdot 10^4$ L still a weak Auger signal from Pd was visible. One might speculate that with alloys containing only small Ni concentrations after oxidation a part of the Pd atoms is still "embedded" into a NiO matrix.

Curve b of Fig. 2 represents the $L_{3,2}$ appearance potential spectrum from nickel in NiO as described

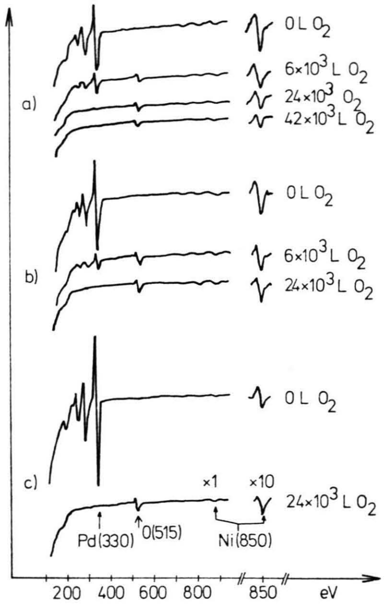

Fig. 5. Auger electron spectra from three alloy samples at different stages of oxidation. Bulk compositions: a) 83% Ni; b) 58% Ni; c) 29% Ni.

previously[6]. The main differences as compared with the spectral features from clean Ni are the following:

a) The L_3 and L_2 peaks now exhibit positive and negative parts of nearly equal size.
b) The satellites are replaced by two maxima at 865 and 883 eV, i. e. at about 11 eV above the L_3 and L_2 appearance potentials.
c) The latter are located at energies 1.4 ± 0.2 eV higher than with metallic nickel ('chemical' shift ΔE).

Ni-L_3 appearance potential spectra from different alloys at various stages of oxidation are reproduced in Figure 6. After an O_2 exposure of 2.4×10^4 L the spectral features were completely identical to those of NiO as produced by the oxidation of pure Ni and did not change upon further oxygen treatment. That means that exposures of this order of magnitude were sufficient to build-up an oxide layer which was thicker than the mean free path of the 850 eV-electrons involved in the APS process. The heights of the L_3 peaks from the completely oxidized samples as well as the appearance potentials themselves (see below) were identical to within a few percent indicating identical densities and electronic properties of the Ni atoms in the oxide overlayers of all samples containing initially 12 to 100% Ni in the metallic bulk. The lattice constant of the oxide layer was determined by means of high energy electron diffraction (RHEED) to be 4.15 ± 0.04 Å which is (within the limits of error) identical to that of NiO (4.17 Å [22]).

Figure 7 shows a plot of the Ni L_3-appearance potentials after complete oxidation as a function of

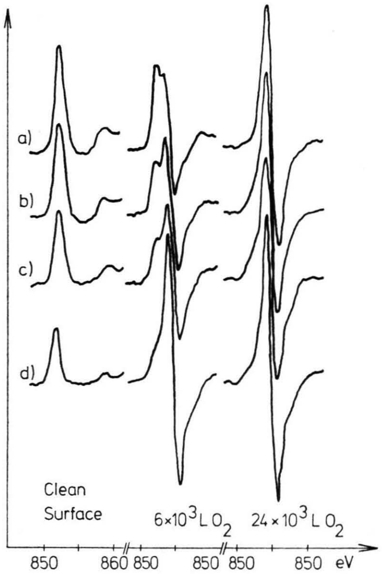

Fig. 6. Ni L_3-appearance potential spectra from four alloy samples at different stages of oxidation. Bulk compositions: a) 82% Ni, b) 64% Ni, c) 58% Ni, d) 33% Ni.

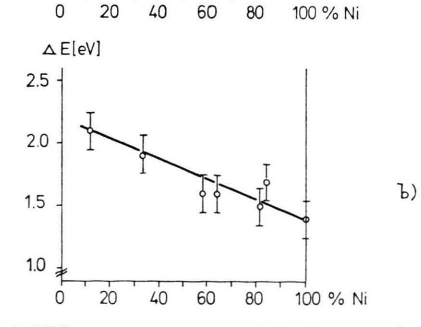

Fig. 7. a) Ni L_3-appearance potentials after complete oxidation as a function of the initial alloy composition. b) Chemical shift ΔE of the Ni L_3-appearance potentials due to oxidation as a function of the initial alloy composition.

the initial alloy composition as well as the 'chemical' shift ΔE as compared with the corresponding data prior to the oxygen treatment. The latter quantity varies between 1.4 eV (100% Ni) and 2.1 eV (12% Ni) which is due to the fact that with the metallic alloys the Ni L_3 appearance potential changes again by 0.7 eV over this concentration range as becomes evident from Figure 4.

As can be seen furthermore from Fig. 6 after an exposure of $6 \cdot 10^3$ L oxygen the spectra may be considered as being composed of *two* peaks. This effect had already been studied in some detail with the oxidation of pure Ni[6] and is ascribed to a superposition of contributions from metallic and oxidized Ni atoms within the probing depth of APS, the latter exhibiting the higher binding energy (i. e. appearance potential) due to the positive atomic charge. As can be seen from Fig. 6 $6 \cdot 10^3$ L oxygen are sufficient to oxidize the sample containing only 30% Ni nearly completely whereas the Ni atoms in the 90% Ni alloy are still predominantly in the metallic state after such a treatment. This effect continues to pure nickel, where the formation of the oxide layer was found to be complete only after an O_2 exposure exceeding $26 \cdot 10^4$ L. We thus reach at the interesting conclusion that the initial rate of NiO formation *increases* with decreasing Ni content of the NiPd alloys.

4. Discussion

Variations of the appearance potential spectrum of pure Ni due to oxidation were observed for the first time by Park and Houston[23] and studied later in some detail by Ertl and Wandelt[6]. The formation of the negative dip at the high-energy side of the $L_{3,2}$-peaks upon oxidation is interpreted as being due to the energetical separation of the empty 3d- and 4s-bands in NiO whereas these are superimposed with metallic Ni. The variation of the L_3 appearance potential by 1.4 eV is caused by a corresponding increase of the binding energy of the Ni 2p-level as was confirmed by XPS measurements by Kim and Winograd[24].

Under the chosen experimental conditions palladium is not expected to form a stable three-dimensional compound with oxygen which was confirmed recently by experiments using ultraviolet photoelectron spectroscopy (UPS)[25]. For simple thermodynamic reasons it appears therefore to be evident that during oxidation of the alloys nickel is enriched at the surface until a continuous layer of NiO grows.

With a series of Fe/Ni alloys APS was able to demonstrate after oxidation a continuous variation of the electronic properties of the Ni atoms with the alloy composition[10]. In this case both constituents may be oxidized and it was found that alloys containing more than 70% Ni were covered with a mixed oxide layer which was identified with a spinel structure. In the present case after completion of the oxidation the Auger spectra as well as the AP spectra were found to be identical for the whole series of alloys with the spectral features of oxidized nickel. The formation of NiO in all cases is thus evident and is further confirmed by the determination of the lattice constant of the oxide overlayer as mentioned in Section 3.2.

The kinetics of the early stages of oxidation of clean Ni single crystal surfaces was recently studied by Holloway and Hudson[26], mainly by using AES. They found that the reaction proceeded by the initial formation of chemisorbed oxygen phases, followed by nucleation of NiO islands which grew laterally across the surface at a thickness of only about 2 monolayers. The third stage consisted in a slow thickening of the oxide. A three-step model of this kind had also been proposed by Fehlner and Mott[27]. In the present work the applied techniques probe a depth of the solid sample which is estimated to correspond to the beginning of the third stage of the oxidation process. On the other hand this layer appears to be still too thin for the applicability of Wagner's theory of oxidations[2] which assumes that the mechanism of the formation of (thick) oxide layers proceeds via diffusion of Ni^{2+} cations over vacant lattice sites of the coherent NiO layer. In this case of course a decrease of the oxidation rate with increasing concentration of the noble metal is to be expected which was also observed experimentally with Ni/Pt-alloys[28]. In contrast the present results as represented by Fig. 6 suggest that in the early stages of oxidation (i. e. before a coherent NiO layer has been formed) the rate increases with increasing content of the noble metal. Similar observations were already reported nearly 4 decades ago for Ni/Au alloys[29] where it was shown that the NiO layer was porous. Since the lattice constant of Ni/Pd-alloys increases continuously with increasing Pd content it is probable that this effect is mainly responsible for the enhanced reactivity. Another possibility lies probably in the altered electronic properties as demonstrated by the variation of the Ni $L_{3,2}$-appearance potentials. Clearly more detailed experiments are necessary in order to reach at any definite conclusions.

Acknowledgement

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