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Electron Spectroscopy and the Study of Chemical Reactions on the Surfaces of Metals

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The experimental technique and the physical principles of the fundamental electron spectroscopic methods are examined: X-ray electron spectroscopy (XES), Auger electron spectroscopy (AES), and ultraviolet photoelectron spectroscopy (UPES). Their advantages and disadvantages are compared. The application of electron spectroscopic methods in the study of chemical reactions on the surfaces of metals is considered in relation to the investigation of the oxidation of metals and alloys in both the vapour-gas phase and in aqueous electrolytes. In addition, studies on the application of XES and AES to the investigation of corrosion processes at the metal-electrolyte interface are discussed.
The bibliography includes 76 references.

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I. INTRODUCTION

The chemical reactions occurring on the surfaces of solids have been the subject of studies in many independent branches of physical chemistry† such as catalysis, electrochemistry, metal corrosion, etc. As a rule, the interaction of the surface of a solid with the components of the surrounding medium involves a chemical modification of the surface itself. Investigation of such "modification" by methods of electron spectroscopy makes it possible to obtain qualitative and quantitative information about the nature of the interactions on the surface of the solid, which range from adsorption interaction to a significant alteration of the chemical composition of a surface region with a thickness up to 10^{-5}–10^{-4} cm.

The set of methods referred to as "electron spectroscopy" includes X-ray electron spectroscopy (XES)#, Auger electron spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPES), the spectroscopy of characteristic losses (SCL) (or electron energy loss spectroscopy), and many other methods.

†The techniques for the physicochemical study of chemical reactions on the surface is considered in A.Adamson's monograph "The Physical Chemistry of Surfaces" (Translated into Russian), Izd.Mir, Moscow, 1979.

#This method has been referred to as ESCA (electronic spectroscopy for chemical analysis) by the authors—a team of Swedish scientists working under the supervision of K.Siegbahn[1].

This review deals mainly with the first three methods, since they have found most extensive applications in studies on the chemical composition of the surfaces of solids. A common feature of all the methods under consideration is that the spectrum of electrons is subjected to final analysis. The physical principles of the excitation of the spectrum of electrons are described in the next section.

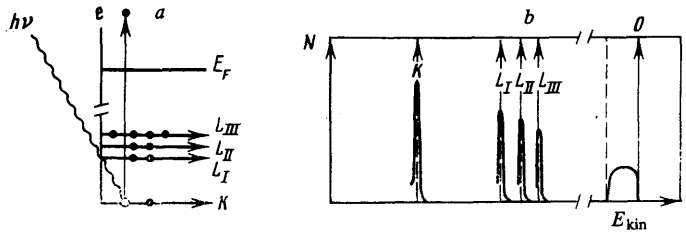


Figure 1. Schematic illustration of the electronic levels in a metal with ionisation of the K level (a) and the corresponding electron spectrum[1] (b): E_F = Fermi level; e = free electron; N = number of photoelectrons; E_b = binding energy of electrons; E_{kin} = kinetic energy of photoelectrons.

II. PHYSICAL PRINCIPLES AND ANALYTICAL POSSIBILITIES OF ELECTRON SPECTROSCOPIC METHODS

Fig. 1a [1] illustrates the diagrams of electronic levels in a metal. The action of a quantum of known energy on the K shell leads to its ionisation; if the energy of the electrons is sufficiently high, the latter leave the metal and become free. By detecting the free electrons emerging from the metal under the influence of radiation, it is possible to obtain the electron spectrum illustrated in Fig. 1b. Evidently the electron spectrum corresponds to the energy level diagram in Fig. 1a. The accuracy of the measurement of the energy of the free electron is determined by the natural width of the ionised level and the accuracy of the measurement of the wavelength of the incident radiation. The spectrum illustrated in Fig. 1b is also referred to as the photoelectron spectrum and is the main object of study in XES and UPES, in contrast to the spectra of Auger electrons obtained in AES.

The mechanism of the formation of Auger electrons can be described as follows. When a vacancy is produced in one of the inner electronic levels due to its ionisation under the influence of a particular type of radiation, there is also a possibility of another type of emergence of an electron from the solid. Such a vacancy can be filled by an electron in one of the outer levels and the energy of this transition can be evolved in the form of a quantum of electromagnetic radiation or can be transferred to one of the electrons in the outer

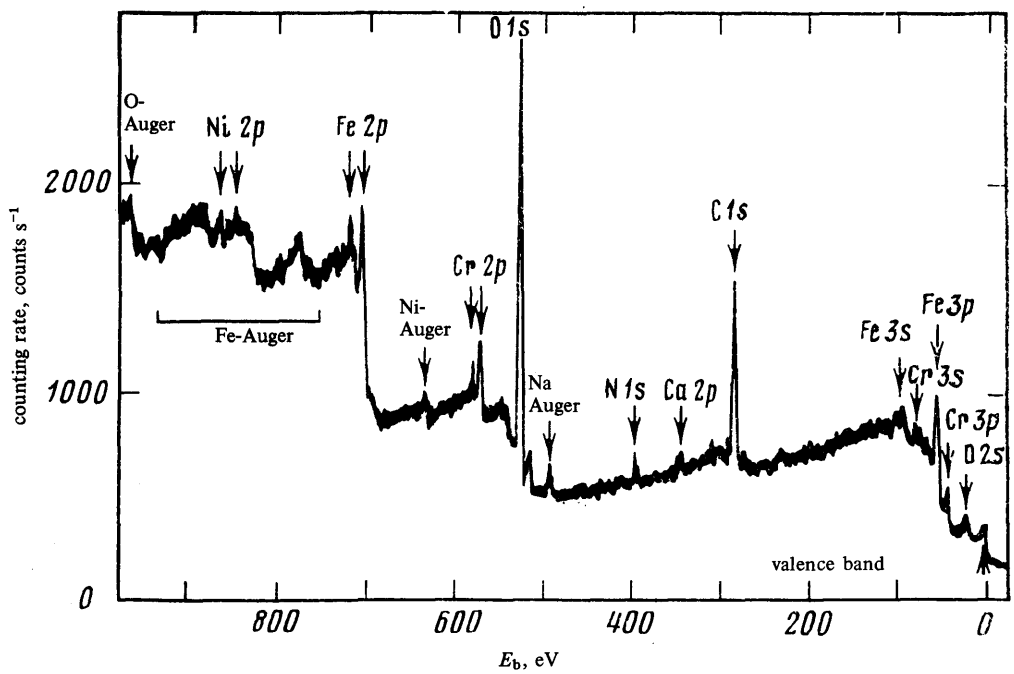


Figure 2. Electron spectrum of the surface of the Kh18N10T steel oxidised in air at 20 °C.[4]

levels, which is then ejected from the specimens. This process is referred to as the Auger effect and the ejected electrons are called Auger electrons§. The probability of the Auger process increases with decrease of the atomic number of the element, while the yield of X-ray fluorescence diminishes with decrease of the atomic number of the element. Because of this, it is possible to investigate, by analysing the spectra of Auger electrons, the surfaces of solids in order to detect light elements on the latter.

Thus, when ionising radiation acts on a metal surface, it is possible to obtain both photoelectron spectra associated with a simple one-electron process and Auger spectra associated with many-electron transitions. However, the approaches used in the analysis of the electron spectra (of both photoelectrons and Auger electrons) are very similar.

Indeed the fundamental equation of the external photoeffect is the Einstein equation:

$$h\nu = E_f - E_i + E_{kin}, \quad (1)$$

where $h\nu$ is the energy of the photons, E_f the energy of the system in the final state after the ejection of an electron from the K shell, E_i the overall initial energy of the atom or the molecule, and E_{kin} the kinetic energy of the dislodged electron. By defining the binding energy of the electrons E_b^F as the energy necessary to remove the electron from the K level to infinity (where $E_{kin} = 0$), it is possible to formulate Eqn.(1) as follows:

$$E_b^f = h\nu - E_{kin} - \varphi, \quad (2)$$

where E_b^F is the binding energy of the electrons of the metallic specimen measured relative to the Fermi level of the spectrometer and ϕ is the electron work function of the metal of the spectrometer. The equation relating the kinetic energy of the Auger electrons E'_{kin} to the energies of the levels of the given element is[2]

$$E'_{kin} = E_K - E_L - E_L^{z+1}; \quad (3)$$

where $E_{K(L)}$ is the energy of the $K(L)$ level of the element under consideration and E_L^{z+1} is the energy of the L level of the element having an atomic number one greater than the element of the specimen.

The determination of E_b permits the elemental analysis of the specimens, because there is a specific energy spectrum of electronic levels corresponding to each element. Fig.2 [4] illustrates the electronic spectrum obtained on irradiation of the surface of the Kh18N10T alloy oxidised in air at room temperature; the aluminium K_α line was used to obtain the X-radiation. It follows from Fig.2 that the electronic spectrum exhibits lines corresponding to photoelectrons and Auger electrons. Examination of the energies of the lines permits a qualitative analysis of the surface layer¶. The first studies by Siegbahn et al.[1] showed that the energies of the X-ray electron and Auger electron lines depend on the oxidation state of the atom of the test element. As a rule an increase of the degree of oxidation increases the shift of the binding energy of the electron (ΔE_b) relative to E_b in the zero oxidation state. Consequently, one can infer not only the elemental composition of the surface of metals but also the oxidation state of the elements. This can be illustrated by the data in Fig.3,[1] which illustrates the X-ray electron spectra of the beryllium 1s line. A structure consisting of two peaks corresponds to beryllium sputtered *in vacuo* (Fig.3*a*). According to the XES theory[1-3], the low-energy (relative to E_b) peak should be attributed to metallic beryllium and the high-energy peak is due to beryllium oxide BeO. Evidently the X-ray electron spectrum of beryllium oxidised at a high temperature (Fig.3*b*) contains only the high-energy peak, which confirms the validity of the assignment of this peak to beryllium in the +2 oxidation state.

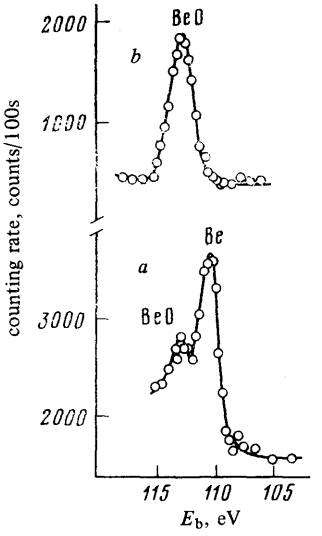


Figure 3. Electron spectra of beryllium[1] obtained by vacuum vaporisation after reduction with zirconium (*a*) and of the specimen after heat treatment in air (*b*).

It is noteworthy that the X-ray electron spectra† can carry information relating not only to the nature of the atom under investigation itself but also to its environment. A change in the charge distribution in the valence shell, occurring when the valence state of the atom is altered, influences also all the inner electrons and is therefore manifested in the electron spectra. This situation can be illustrated by the spectra of beryllium and its compounds shown in Fig.4.[1] Evidently, when beryllium is oxidised, E_b for the inner 1s electron of beryllium increases by 2.9 eV. Beryllium in BeF_2 has an even higher positive charge than in BeO [although the oxidation state is the same (+2)] as a result of the high electronegativity of fluorine, since the binding energy of the 1s electrons of beryllium in BeF_2 is greater than in BeO. In the general case the chemical shifts of the maxima in the X-ray electron spectra increase with increase of the amount of ionic character of the bond.

§For a more detailed description of the physical principles of the Auger process, see "Methods for the Analysis of Surfaces" (Edited by A.Zaderna) (Translated into Russian), Izd.Mir, Moscow, 1979.

¶Problems concerning the thickness of this layer will be considered below.

†Only the information obtained from the XES is considered, since allowance for the effects of collective interactions is extremely difficult for the two-electron Auger process.

In compounds where the test element exists in different oxidation states but is surrounded by identical atoms E_b varies approximately linearly with the degree of oxidation, which has been shown[3] in relation to nitrogen and chlorine oxides.

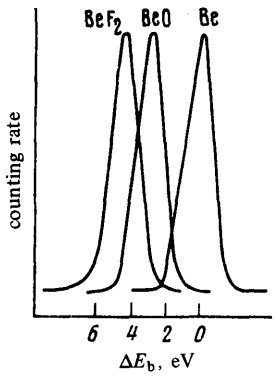


Figure 4. The positions of the lines due to metallic beryllium, beryllium oxide, and beryllium fluoride in the electron spectrum[1]; ΔE_b = change in binding energy.

For elements of a single Period, the line shift in the electron spectrum varies linearly with the total number of valence electrons and with the formal degree of oxidation[5,6].

According to the estimates of Siegbahn et al.[1], the photoelectrons abstracted from the surface carry information about a surface layer not thicker than 100 Å. Later studies showed that this layer can be even thinner. Thus the investigation of gold coated by a thin layer of graphite showed[7] that, when the electron energy changes from 1169 to 920 eV, the thickness of the layer of graphite which absorbs 95% of the electrons changes from 55 to 43 Å. By selecting the energy of the exciting radiation, E_b, and the angle of the path of the electrons between the surface and the spectrometer slit, it is possible to increase the thickness of the layer investigated to ~10 Å.[3] Fraser et al.[8] arrived at the same figure by considering the mean free path of the electron in non-elastic scattering in close-packed solids. According to Nemoshkalenko and Aleshin[2], when the energies of the primary electrons are suitably selected, AES can carry information about 2–3 monolayers of the test substance.

We shall consider the scope of the quantitative analysis by electron spectroscopy. The data given below refer to photoelectron spectra and primarily to XES, since a complete quantitative theory of analysis with the aid of AES is still being established.

Having assumed that the intensity of the beam of X-ray photons does not undergo appreciable changes in the surface region 100 Å thick, the intensity I of a stream of photo electrons with a specified energy can be expressed[2] by

$$dI = F\sigma Nk \exp(-x/\lambda)\,dx, \qquad (4)$$

where F is the intensity of the stream of X-ray photons, σ the photoionisation cross-section for the given energy of the photons and the atomic level under consideration, N the number of electrons of the given kind per unit volume of the substance, k the constant for the given spectrometer, x the distance which the electron traverses in the substance, and λ the effective depth from which electrons emerge, determined by the length of the free path of the electron in the test substance.

Using Eqn.(4), the following expression can be written for the intensity of the stream of photoelectrons which have emerged from a massive specimen:

$$I = F\sigma_1 N_1 k\lambda_1 [1 - \exp(-d/\lambda_1)], \qquad (5)$$

where d is the thickness of the layer which the photoelectrons have traversed. It follows from Eqn.(5) that the intensity is linearly related to the number of atoms in the test substance N_1 and this constitutes a basis of the quantitative analysis. Indeed, using Eqn.(5) to determine the relative increments in the concentrations of the components of the surface, the following simple expression can be obtained when the λ_i of the components are equal:

$$I_A/I_B = \sigma_A N_A (\sigma_B N_B)^{-1}. \qquad (6)$$

Here subscripts A and B refer to components A and B. The values of σ are known for virtually all chemical elements from the results of a number of studies[9,10]; although the accuracy of the tabulated σ is low (~10%), the availability of known values of σ makes it possible to employ Eqn.(6) and hence XES for quantitative analysis. One should not forget that Eqn.(6) was derived taking into account a number of simplifying postulates and therefore in each specific case one must estimate its applicability.

A more rigorous theory of photoelectron emission[11], developed taking into account the difference between the probabilities of excitation from states with different symmetries and the differences between the effects associated with the scattering of the electron wave in the crystal and on its surface, leads to much more complex expressions than Eqns.(4)–(6). However, practical experience has shown that the use of Eqns.(4)–(6) is in most cases justified.

In applying the XES method to quantitative analysis, one should remember that the existing apparatus has a maximum absolute sensitivity of ~10^{-10} g.[12,13] However, the relative sensitivity of the XES method does not exceed ~0.1% and it is therefore irrational to employ, for example, XES when the content of the given alloy component on the surface is less than 1% relative to the base.

It is of interest to compare the XES, UPES, and AES methods. The fundamental advantages of the UPES method are shown in the study of the changes of the energies of the electronic levels close to the valence band. This is due to the comparatively small range of the energies of the emitted electrons associated with the comparatively low energy of the exciting light quanta when a helium discharge lamp is used as the source of radiation. At the same time, the resolution of the UPES method can be to within 0.05 eV, which is more than an order of magnitude better than the resolution of the best X-ray electronic spectrometers. This feature of the UPES makes it possible to investigate fine effects such as the change in the structure of the valence band following a change in the concentration of one of the alloy components or the role of π,σ interactions in the adsorption of molecules, including hydrocarbons[14], on the surfaces of metals. The possibilities of UPES in the study of surfaces have been described in greater detail in another review[15].

It follows from Eqn.(3) that the measurements of the kinetic energies of the Auger electrons of atoms in different compounds should yield virtually the same information about the nature of the chemical bond as the values of E_b. In certain cases the Auger spectra have a definite advantage over the photoelectron spectra. In particular, the depth from which electrons in the substance emerge depends on the kinetic energy of the electron; therefore, knowing the distribution

of Auger electrons, it is possible to estimate the thickness of the surface layer investigated. The shift of the lines due to Auger electrons can be greater than the shift of the line due to photoelectrons[16]. Furthermore, owing to the greater efficiency of the liberation of the Auger electron and the possibility of creating fairly powerful beams of primary exciting electrons, the rate of accumulation of Auger spectra can exceed by a factor of 10^2 the rate of accumulation of X-ray electron spectra. However, a number of studies have shown that the effect of a beam of primary electrons can lead to a series of irreversible changes in the surface. These effects are associated both with the desorption of the adsorbed molecules from the surface under the influence of the electron beam[17] and with the surface dissociation and subsequent diffusion of the components of the specimen into the bulk of the specimen[18]. A recent detailed analysis of the "beam effects"[19] enabled the authors to conclude that the AES should be used as an auxiliary method in the quantitative study of the surface. AES should then naturally be regarded as an extremely effective means of the elemental analysis of the surface.

Compared with the excitation of the spectrum by a beam of electrons, used in Auger spectroscopy at the present time, the excitation by X-ray quanta is characterised by smaller cross-sections of the desorption of the adsorbed substances and a weaker secondary electron background. The relatively small intrinsic width of the lines due to the photoelectrons emitted from the inner shells greatly improves the accuracy of the measurement of the "chemical shift" of the spectral lines. The interpretation of the spectra of inner electrons is simpler than that of the results of the many-electron Auger process. The sensitivity of the photoelectron spectra excited by X-rays to substances adsorbed on the surface can be increased by selecting the corresponding angles between the ejected electrons and the surface of the specimen[20].

In many instances it is possible to achieve a sensitivity equivalent to ~0.01 of the monolayer in the study of adsorption by XES. Such sensitivity has been reached in practice in the study of the adsorption of CO, CO_2, and O_2 on platinum[13]. A direct comparison of the sensitivity of the XES (ESCA) and AES methods has been carried out in a study[21] where X-ray electronic and Auger spectra of 54 elements (ranging from lithium as the lightest element to technetium as the heaviest element) were obtained under the same conditions on the same specimens. The sensitivities of the methods were compared[21] in terms of the signal/noise ratio under the optimum conditions for the detection of the element. The results of the above study showed that the XES method is more sensitive for 10 elements (Na, Cr, Mn, Kr, Cd, Sb, Xe, W, and Th), while for the remainder the AES method is more sensitive.

Thus the XES method is at present the most universal for analytical purposes. On the other hand, in the study of each specific object one should bear in mind the advantages and disadvantages of each of the methods described and, in investigating an object which had not been studied previously, it may prove extremely useful to compare the Auger and photoelectron spectra.

III. EXPERIMENTAL TECHNIQUE

The fundamental design of the electron spectrometer used to obtain electron spectra, which is involved in virtually all modern models of electron spectrometers, combines all three methods: UPES, AES, and XES. The presence of three excitation sources makes it possible to obtain with the maximum efficiency the electron spectra considered in these methods, while a single system can be used to detect the electrons.

Ultraviolet light and X-ray generators and electron guns are used as sources of exciting radiation. Ultraviolet light is generated mainly by capillary discharge lamps filled with helium at a pressure of ~1 mmHg. The resonance line at a wavelength of 584 Å (21.21 eV) predominates in the discharge. The emission is collimated with the aid of a capillary tube. The sources of X-rays consist of both the usual X-ray tubes and of tubes with a rotating anode (to decrease the local over-heating of the anode). The material of the anode is usually aluminium and magnesium and rarely copper and chromium. The radiation is made monochromatic to increase the resolution of the spectrometers.

In modern X-ray spectrometers there are two types of analysers: magnetic and electrostatic. In magnetic spectrometers the electrons are focussed with the aid of a magnetic field. Apparatus with double magnetic focussing has been described[1]. In almost all commercial spectrometers electrostatic focussing is used nowadays; in this case the requirements for the compensation of the Earth's magnetic field are much less stringent. The scanning of the spectrum with respect to energy is achieved by a retarding electrostatic field applied as a rule between the spectrometer and the source. In the best modern electron spectrometers provision is made for highly efficient systems designed to generate an ultrahigh vacuum. The residual pressure after evacuation with heating at ~200° is $\sim 10^{-10}$ mmHg. The maximum pressure of the gas (vapour) in the specimen chamber depends on the excitation source employed but does not exceed 10^{-5} mmHg.

After passing through the analyser, the electrons are detected by a radiation receiver. In the first spectrometers of Siegbahn's group[1] photographic plates were used for detection. Nowadays electrons are counted with the aid of proportional counters or electron multipliers.

Although the fundamental design of the electron spectrometers has not changed, the measuring technique continues to improve. Thus a method has been described[22] for eliminating the interfering background signal which is superimposed on the Auger spectra in the region of low electron energies and depends strongly on the energy. The method consists in modulating the intensity of the electron beam with a continuous alteration of the modulation amplitude as the electron energy is varied, which causes a corresponding change in the sensitivity of the spectrometer as a function of the energy. This method made it possible to detect many intense closely spaced peaks for low electron energies, i.e. under conditions where the fine structure is usually lost.

One should note that in the industrial production of electron spectrometers a tendency has arisen very recently to manufacture two types of instruments. The first type consists of high-speed spectrometers designed for the rapid analysis of several specimens immersed in the vacuum chamber simultaneously (sometimes up to 20), which can consist of a combination of two complex instruments. Thus "Physical Electronics Industrials"# has manufactured an instrument which is a combination of X-ray electron and scanning Auger spectrometers; 12 specimens can be fixed simultaneously in the cassette of the apparatus. However, despite its considerable analytical possibilities, this device, designed for large series of routine measurements (necessary, for example, in the manufacture of the elements of integrated circuits), cannot replace the instruments of the second type, designed for scientific research. In these instruments (for example, in the ESCA-3 electron spectrometer)[2] the time required to obtain the spectra of a series of specimens is much longer.

#See "Handbook for Electron Spectroscopy", PEI, N.Y., 1978.

However, the instrument has a chamber for the preliminary treatment of the specimen, separated from the analyser chamber by a vacuum lock. In this device the metallic specimen can be etched by an ion beam in order to obtain a clean surface. The specimen can be heated (using an electron gun) to 1800 °C or cooled to the temperature of liquid nitrogen. In the preliminary treatment chamber the metal can be sputtered. The provision of metering taps in the chamber makes it possible to treat the specimen in a specified atmosphere. The content of the components of the atmosphere is controlled by a quadrupole mass-spectrometer, the sensor of which is mounted directly in the preliminary treatment chamber. This auxiliary equipment significantly extends the scope of the experiment.

IV. OXIDATION OF METALS

The oxidation of metals, particularly at temperatures close to 300 K, which leads to the formation of very thin oxide films, is one of the most "natural" processes investigated with the aid of electron spectroscopy. This is why the first studies on the oxide films on metals, arising when oxygen interacts with the surface, were carried out almost simultaneously with the development of the method of electron spectroscopy itself[1]. The early studies of the oxidation of metal surfaces have been briefly reviewed[3,23]. We shall examine below the fundamental results of a series of investigations which not only made it possible to understand more deeply the mechanism of the initial stages of the oxidation but also in many instances led to the discovery of hitherto unknown effects.

The considerable practical value of iron and its alloys have apparently been the cause of the extensive research carried out in different countries into oxidised surfaces of iron (and iron alloys) with the aid of XES and AES. In the first study where XES was used to investigate the oxidation of iron in atmospheres of oxygen and water vapour[24] it was shown that the shift of the Fe $2p_{3/2}$ level, observed in the oxidation of iron by oxygen, depends significantly on the duration of exposure to oxygen and the pressure of the latter. The range of oxygen pressures was 10^{-2}–10^{2} mmHg. Shifts of the binding energy (ΔE_b) of the electrons of the Fe $2p_{3/2}$ level of 3.2 and 4.2 eV corresponded to the minimum and maximum pressures respectively. These results[24] show that, depending on the oxidant pressure, the relative contents of Fe^{2+} and Fe^{3+} ions in the surface layer of the oxide can be significantly altered.

On the other hand, the presence of two states of oxygen on the iron surface has been observed[24] (the O 1*s* line consisted of two peaks); the relative contribution of each state also depends on the oxygen pressure and the duration of exposure. The authors[24] explained the existence of a doublet in the structure of the O 1*s* line by the presence on the surface of two forms of oxygen—in the chemisorbed state and the form corresponding to the oxygen in the iron oxide. The latest conclusions by the above investigators[24] are in clear conflict with the results of a study[25] where it was observed with the aid of AES that, for nearly monolayer coverages, the oxygen forms with the surface bonds analogous to those in Fe_2O_3 and the "chemisorption" component of oxygen is therefore negligibly small.

The combination of AES with mass spectrometry[26] and slow-electron diffraction[7] yields extremely important information about the interaction of the surfaces of an iron single crystal with oxygen and water vapour in the very initial stages. But it has been shown[27] that the oxidation of the (100) and (110) faces leads to an increase of the lattice parameters and to a change of symmetry from cubic to hexagonal. It has been noted[26] that, for surface coverages less than a monolayer, the adhesion coefficient is close to 0.2. This quantity persists up to the accumulation of oxygen on the surface in an amount of $\sim 1.6 \times 10^{15}$ cm^2. This quantity of oxygen corresponds satisfactorily to the surface density of the Fe atoms on the (110) face. Next the adhesion coefficient falls to less than 10^{-2}. These data are correlated with the results of a study[28] where it was shown that the oxygen adsorbed on the iron surface (the oxygen–surface bond energy is 9 kcal mol^{-1}) gives rise to a surface superstructure, which leads in its turn to a sharp decrease of the adhesion coefficient. On saturation with oxygen, this superstructure rearranges to two-dimensional FeO crystals. Further adsorption of oxygen leads to the formation of a three-dimensional oxide film. An equally detailed study of the oxidation of iron by water vapour was made by Dwyer et al.[29] In determining the kinetic parameters of the adsorption of oxidant molecules on iron, the authors of the above studies did not consider the kinetics of the growth of the three-dimensional oxide. Such a study with the aid of XES was made by Akimov et al.[30], who investigated the oxidation of polycrystalline iron in oxygen and water vapour; the range of oxidant pressures was 10^{-5}–10^{-7} mmHg. Much attention has been devoted to the purity of the initial surface and the oxidants§. The purity of the oxygen and water vapour was followed with the aid of a quadrupole mass-spectrometer combined with the preliminary treatment chamber of the X-ray electron spectrometer. A gun for the etching of the surface of the specimen with Ar^+ ions was mounted on this chamber. The surface of the specimen was regarded as "clean" when the ratio of the integral intensities of the iron and oxygen signals was ~100. Approximate calculation showed that this intensity ratio corresponds to the adsorption of ~0.1 of a monolayer of oxygen on the surface. Figs.5*a* and 5*b* [30] present the X-ray electron spectra of the Fe $2p_{3/2}$ lines for oxidation with oxygen and water vapour. Figs.5*c* and 5*d* illustrate the X-ray electron spectra of the O 1*s* line also for oxidation with oxygen and water vapour respectively. Analysis of the data presented in Fig.5 permitted the following conclusions.

1. After exposure of iron to oxygen (duration of exposure ≥ 10 *L*¶), an oxide film having the composition Fe_3O_4 is formed on its surface. This conclusion is based on the measurement of ΔE_b for the Fe $2p_{3/2}$ line in the oxidation process, which amounted to -3.6 ± 0.1 eV, and on the stoichiometric ratio Fe/O, calculated from measurements of the integral intensities of the Fe $2p_{3/2}$ and O 1*s* lines. For comparison, one should note that ΔE_b amounts to 4.2 and ~1.0 eV for Fe_2O_3 and FeO respectively. The smaller value of ΔE_b for Fe_3O_4 compared with Fe_2O_3 is associated with the presence of iron ions in the +2 oxidation state. Ertl and Wandelt arrived at the same conclusion[32].

2. The exposure of iron to water vapour does not lead to the formation of a three-dimensional oxide film on the iron surface, as shown by the comparatively small changes in the intensity of the Fe $2p_{3/2}$ line (Fig.5*b*) and the absence of the oxide component of this line.

3. The symmetry of the O 1*s* peak, its small half-width, and the value of E_b for the oxidation of iron with oxygen show that the oxygen adsorbed on the iron immediately forms bonds analogous to the Fe–O bonds in the oxide. The clear asymmetry of the O 1*s* peak in the oxidation of iron by water vapour and the results of the Fourier resolution of this peak

§It has been shown[31] that the presence of impurities on the surface can inhibit (sulphur) or significantly accelerate (carbon) the oxidation.

¶Here *L* denotes a Langmuir (10^{-6} mmHg s).

show that oxygen exists on the surface in two states: the oxygen involved in the Fe–O bond on the surface oxide and the oxygen of the hydroxide ion—the high-energy component of the O 1s doublet.

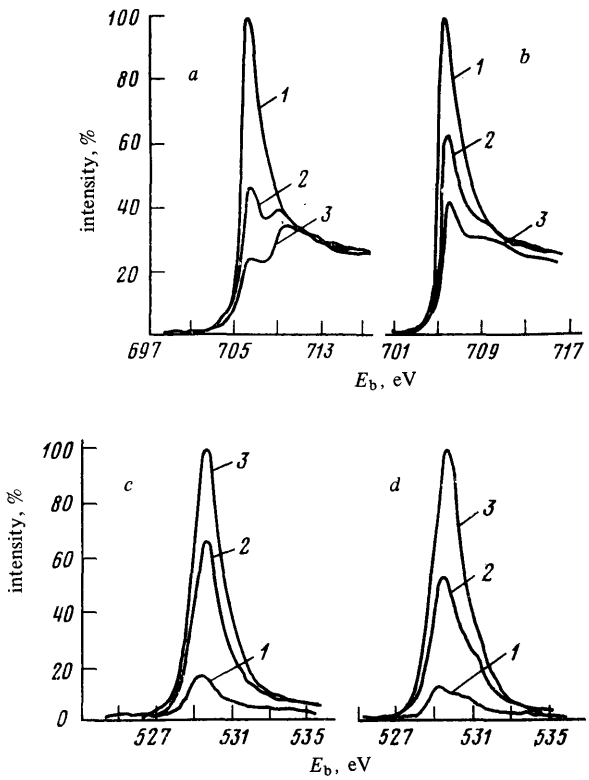


Figure 5. X-Ray electron spectra of the Fe $2p_{3/2}$ (*a* and *b*) and O 1s (*c* and *d*) lines for the Fe + O_2 (*a* and *c*) and Fe + H_2O (vapour) (*b* and *d*) systems; exposure (in Langmuirs): 1*a*)–1*d*) 0; 2*a*) and 2*c*) 5; 2*b*) 2.4×10^4; 2*d*) 2.4×10^3; 3*a*) and 3*c*) 10^3; 3*b*) 5×10^4; 3*d*) 5×10^3.

By analysing the dependence of the intensities of the X-ray electron lines of the elements on the duration of exposure in an atmosphere of the oxidant, it was possible to establish[30] certain kinetic relations for the initial stages of the interaction of iron with oxygen and water vapour. In the initial stage of the oxidation, where the peak in the X-ray electron spectrum of the Fe $2p_{3/2}$ line, corresponding to iron in the oxidised state, is not visible because it is overlapped by a high-intensity background caused by the scattering of the electrons dislodged from the Fe $2p_{3/2}$ level, it is difficult to infer the growth of the oxide film from the decrease of the intensity of the Fe $2p_{3/2}$ peak. Its intensity depends on the thickness of the surface film, in the given case an oxide, in the following manner[2]:

$$I=I_0\exp\left[-d/(\lambda\cos\alpha)\right], \qquad (7)$$

where α is the angle between the normal to the plane of the specimen and the spectrometer slit, I the intensity of the Fe $2p_{3/2}$ line for a given exposure, I_0 the intensity of the signal due to the clean surface, d the thickness of the film, and $\lambda = 15$ Å the depth from which electrons are emitted with a given kinetic energy[33]. Eqn.(7) is valid when the values of λ for the clean and oxidised metal surfaces are constant, which can be assumed to a first approximation.

The dependence of the thickness of the oxide film d on the duration of exposure to O_2, calculated from Eqn.(7), is illustrated in Fig.6.[30] It follows from the data in Fig.6 that, up to a thickness of ~5 Å, the oxide film grows in accordance with a linear law; for greater thicknesses, a logarithmic law governs the growth of the oxide film, corresponding formally to the model of the growth of the oxide surface put forward by Hauffe and Ilschner[23]. This shows that the transfer of charged species in the surface oxide begins to limit the rate of growth of the oxide only after the attainment of a film thickness of ~5 Å, which corresponds to two oxide monolayers.

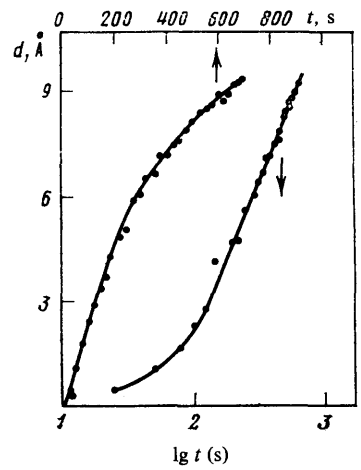


Figure 6. Dependence of the oxide film thickness (d) on the time of exposure t of iron to O_2.

The slight changes in the intensity of the Fe $2p_{3/2}$ peak following the absorption of H_2O vapour on the surface of the specimen (Fig.5*b*) suggest that this entails only the absorption of the products of the interaction between the adsorbate and the adsorbent. The degree of the adsorbent surface coverage θ can be estimated by modifying Eqn.(7) somewhat. If the thickness of the adsorbed layer does not change with θ, the modified equation relating the intensity of the Fe $2p_{3/2}$ peak to θ, can be written thus:

$$I=I_0(1-\theta)+I_0\theta\exp(-\Delta/\lambda). \qquad (8)$$

where Δ is the thickness of the adsorbed layer. On the basis of the known radii of the O^- and OH^- ions as well as the geometrical structure of the H_2O molecule, one can adopt $\Delta \cong 2.5$ Å. Having adopted, as before, $\lambda = 15$ Å, we obtain

$$I=I_0(1-\theta+0.85\theta)=I_0(1-0.15\theta), \qquad (9)$$

whence

$$\theta=6.7(1-I/I_0). \qquad (10)$$

The dependence of θ on the duration of exposure of the specimen to water vapour, calculated from Eqn.(10) for a water vapour pressure of 10^{-8} mmHg, is presented in Fig.7.[30] An estimate of the contamination of the surface by O, C, N,

and Ar atoms after bombarding it with a stream of Ar^+ ions leads to an initial surface coverage $\theta_i < 0.1$. This value of θ_i was adopted as the starting point for the θ readings in Fig.7.

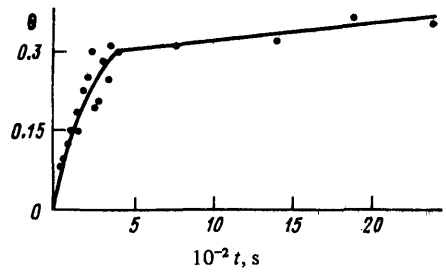


Figure 7. Dependence of the degree of surface coverage θ of iron on the exposure time t in H_2O vapour.

The data in Fig.7 show that, in the adsorption of the dissociation products of water molecules, $\theta = 0.3$ is attained fairly rapidly after which the rate of surface coverage decreases significantly and that, for an exposure of iron to water vapour $>10^4$ *L*, no growth of the oxide film is observed[30]. The low values of θ for which a significant inhibition of adsorption is attained demonstrate, in our view, a strong interaction of the adsorbed species on the surface.

Numerous studies have been made of the oxidation of nickel (and particularly of the adsorption of oxygen and other oxidants) by electron spectroscopy. In the first of these[34] the X-ray electron spectra of nickel were obtained before and after its treatment with oxygen and water vapour. It was also shown that the oxide film on nickel consists of NiO. Other workers arrived at the same conclusion[35]. The surface of nickel has been investigated[36,37] by XES for very low exposures in oxygen (exposure <2 *L*).[37] For such small exposures, a bulk-phase oxide film was not formed on the surface and the chemisorption of oxygen on the nickel surface was investigated.

The X-ray electron spectra of the nickel surface with chemisorbed oxygen served as the basis for a quantum-mechanical model of the formation of the Ni_5O cluster, put forward by Batra and Pobaux[37]. The model of the NiO_6^{10-} cluster has been calculated[38] on the basis of data obtained in the study of the interaction of the (111) face of nickel with oxygen by ultraviolet electronic spectroscopy and low energy electron diffraction.

The results of a detailed investigation of the oxidation of Ni single crystals [(111), (110), and (100) faces] and polycrystalline nickel in the range 30–70 °C with the aid of UPES and XES have been described[39]. It was observed that the initial stage of the interaction with oxygen constitutes dissociative chemisorption for all four types of surface. For a coverage equivalent to ~0.2 of a monolayer, the chemisorption structure comprises adsorbed oxygen atoms distributed on the surface of the nickel support. With increase in the degree of surface coverage to 0.8 of a monolayer, the oxygen atoms are arranged at the lattice sites between the surface nickel atoms. With increase of exposure, the oxygen atoms penetrate into the bulk of the nickel specimen and form a three-dimensional oxide with an average thickness of ~18 Å. This oxide layer is a non-stoichiometric nickel oxide NiO.

The oxidation of nickel was investigated also by the authors of the present review[40]. The results are fully correlated with the conclusion[39] that the oxidation of nickel proceeds via a chemisorption stage. Furthermore, it has been shown[40] that the chemisorbed oxygen on the surface of nickel exists together with the three-dimensional oxide. This is indicated by the data in Fig.8.[40] The figure shows that the X-ray electron spectra of the O 1s line, corresponding to oxygen on the surface of nickel (at 20 °C), undergo a significant change not only in intensity but also in form with increase of exposure. If, after etching with Ar^+ ions the surface gives rise to a low-intensity peak with a maximum at 531 eV (curve *1*) corresponding to a small amount of oxygen, then exposure to oxygen, equal to 20 *L* (curve *2*), does not increase significantly the intensity of the peak, but causes its appreciable broadening. Fourier analysis of this structure yields two peaks with $E_b = 529.5$ and 531 eV. An increase of exposure (curves *3* and *4*) leads to an increase of the intensity of the O 1*s* peak and to a change of the intensity ratio of the two peak components. According to some investigators[35,39], E_b for electrons corresponding to the O 1*s* line of NiO is 529.5 eV. On the other hand, according to Joyner and Robertson[41], the presence of adsorbed oxygen increases E_b by 1.5 eV, which yields 531 eV in our case.

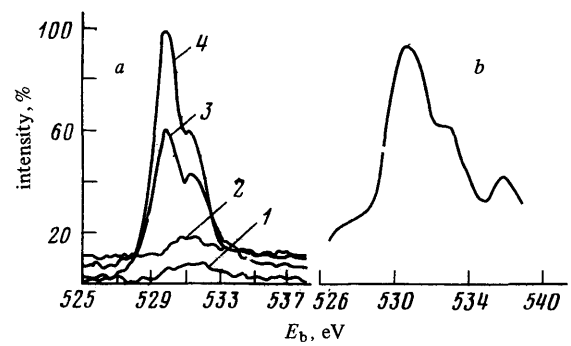


Figure 8. *a*) X-Ray electron spectra of the O 1*s* line on exposure of nickel to O_2 at 20 °C [exposure (in Langmuirs): 1) 0; 2) 2; 3) 10^3; 4) 10^5]; *b*) X-ray electron spectra of the O 1s line on heating an oxidised nickel surface in a vacuum of $\sim 10^{-10}$ mmHg at 100 °C.

Thus the change in the structure of the O 1*s* peak on interaction of nickel with oxygen indicates the existence of only adsorbed oxygen on the nickel surface in the initial stage of the interaction and the existence of oxygen in two states—adsorbed and "oxide"†—in subsequent stages of the oxidation. Heating of the oxidised nickel *in vacuo* ($\sim 10^{-10}$ mmHg) to 100 °C diminishes somewhat the oxide component and the O 1*s* doublet is better resolved (Fig.8*b*).

The oxidation of aluminium was investigated by AES and layer-by-layer etching of the oxide by a beam of Ar^+ ions in a study[42] which is largely of methodological importance. A study[43] of the kinetics of the adsorption and oxidation of aluminium, magnesium, and manganese, and chromium is of considerable interest, the oxidation of aluminium and magnesium having been investigated in greatest detail. The

†A state analogous to that of oxygen in the nickel oxide NiO.

information obtained[43] is of extreme interest also because the interactions of metals with oxygen and water vapour were studied simultaneously by two methods: XES and the method of piezoquartz weighing. The quartz resonator was mounted directly in the preliminary treatment chamber of the electron spectrometer. Data were obtained[43] for both the chemical composition of the surfaces of the oxides and for the dependence of the adhesion coefficient of the oxidant molecules on the exposure and hence on the chemical composition of the surface. The experimental demonstration of the direct proportionality between the change in the intensity of the peak of the O 1s line and the amount of adsorbed oxygen on the above metals must be regarded as an important result of the investigation[43]. The possibility of the formation of both the oxide MgO and the hydroxide $Mg(OH)_2$ on the surface of magnesium when it interacts with water vapour was demonstrated[43]. ΔE_b for these compounds amounted under these conditions to 2.5 eV according to the data of the above investigation. The oxidation of magnesium has been studied in greater detail by Akimov et al.[44], who obtained the electron spectra of the O 1s line, confirming the conclusion[43] that a mixed oxide, consisting of magnesium oxide and hydroxide, is formed on the magnesium surface on interaction with water vapour (Fig.9). This is indicated both by the values of E_b corresponding to the O 1s doublet and by the ΔE_b for these peaks. With increase of the exposure of the magnesium surface in water vapour, the relative amount of $Mg(OH)_2$ also increases. The ratio of the amount of magnesium hydroxide to that of the oxide is stabilised for an exposure of 20–30 *L* and amounts to 0.45; the overall thickness of the oxide film is then also stabilised.

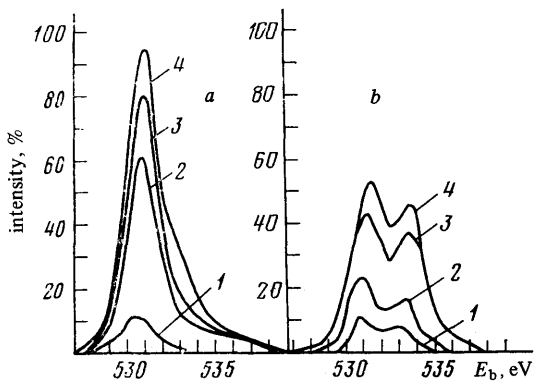


Figure 9. X-Ray electron spectra of the O 1s line on exposure of magnesium to O_2 (*a*) and to H_2O vapour (*b*); exposure (in Langmuirs): *a*: 1) 0.75; 2) 8; 3) 25; 4) 3100; *b*: 1) 5; 2) 10; 3) 25; 4) 10^4.

The oxidation of titanium has been studied by XES.[45–48] An investigation[45] of the electrons corresponding to the Ti $2p_{3/2}$ line for an oxidised titanium surface and titanium oxides showed that the ΔE_b for the Ti $2p_{3/2}$ electrons in TiO and TiO_2 amount to 1.9 and 5.4 eV respectively (relative to the same line for titanium in the zero oxidation state). These data differ from the values of ΔE_b for TiO and TiO_2 published previously[46] (1.0 and 4.9 eV). However, the results of Grant et al.[47] and additional data[48], also published by Simon et al.[45], demonstrate the validity of the values obtained by the latter workers[45]. The value of the study by Simon et al.[48] also lies in the fact that these workers elucidated the composition of the surface in the oxidation of titanium as a function of temperature at an oxygen pressure of ~10^{-5} mmHg. Furthermore, Simon et al.[48] established the values of ΔE_b for titanium compounds such as the carbide, nitride, and hydride, which are respectively 1.8 ± 0.2, 2.2 ± 0.2, and 0.6 ± 0.2 eV.

A study of the oxidation of alloys showed that certain effects can be observed only with the aid of electron spectroscopic methods. Thus a study[49] of the composition of the surface of Au–Ni alloys showed that, when oxygen was adsorbed, the concentration of gold on the surface increased by a factor of 100 compared with the bulk phase and, conversely, the adsorption of hydrogen caused an enrichment of the surface in nickel. The enrichment of the surface in indium on Au–In alloys has been observed with the aid of AES.[50]

The enrichment of the surface in tin following the oxidation of an Ag–Sn alloy has been observed[51] by XES, its extent increasing on heating the alloy. A study of the oxidation of Ni–Al alloys[52] containing between 10 and 30% of nickel, in air at temperatures in the range 20–450 °C showed that aluminium predominates on the surface and determines the behaviour of the alloy on oxidation, even after treatment with alkali, which tends to remove aluminium from the surface. A significant change in the composition of the surface of the alloy has been observed in a study[53] where the oxidation of platinum–rhodium alloys was investigated in air at temperatures up to 1000 °C with the aid of XES and the mass spectrometry of secondary ions. The authors[53] found a significant enrichment of the surface in rhodium at alloy oxidation temperatures close to 1000 °C.

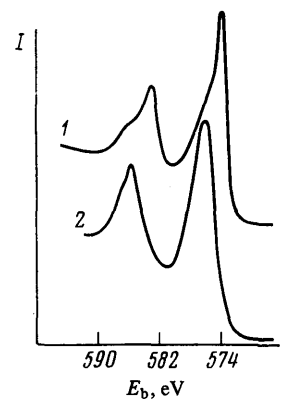


Figure 10. X-Ray electron spectra of the Cr 2p line obtained on oxidation of massive chromium (curve *1*) and the 86% Fe + 14% Cr alloy (curve *2*).

The dependence of the surface concentration of chromium in the $Fe_{0.84}Cr_{0.16}$ single crystal on the oxygen pressure has been investigated[54]. The authors concluded that the change in the ratio of the concentrations of chromium and iron on the surface is associated with the difference between the free surface energies and oxygen affinities of chromium and iron. The oxidation of Fe–Cr alloys in oxygen and water vapour has also been studied by Akimov et al.[55] at ~300 K and oxygen and water vapour pressures in the range 10^{-7}–10^{-5} mmHg.

They investigated the kinetics of the oxidation of these alloys and determined the compositions of the oxide films formed on their surfaces. It was found that the oxide films consist of a mixture of Fe_3O_4 and Cr_2O_3. Comparison of the X-ray electron spectra (Fig.10) of the Cr 2*p* line for the oxidised surface of chromium (curve *1*) and the oxidised surface of an alloy of 86% of iron and 14% of chromium (curve *2*) shows that chromium in the massive state and in the alloy is not oxidised in the same way. Indeed, the chromium in the massive state is oxidised at low oxygen pressures to give a stable oxide film with a thickness equivalent to 2–3 monolayers[10], which is manifested by a slight "bulge" on the Cr $2p_{3/2}$ peak on the high-energy side. The chromium in the alloy with iron is wholly oxidised to Cr_2O_3 for the same exposures, which follows from the shift of the E_b for the Cr $2p_{3/2}$ peak (curve *2*). This difference in the oxidation of chromium in the alloy and in the massive state can be accounted for by the absence of kinetic control in the oxidation of chromium in the alloy, which shows in its turn the absence of aggregates made up of chromium atoms from the oxide film, i.e. the oxide film consists of a solid solution of Cr_2O_3 in Fe_3O_4.

V. ELECTROCHEMICAL PROCESSES AND METAL CORROSION

The electrochemical reactions occurring at the metal–electrolyte interface can lead to a significant change of the chemical composition of the surface of the metallic electrode. These changes are very often localised in a thin surface layer ~100 Å thick. In this case a quantitative analysis of the changes in the chemical composition of the electrode surface can be performed only by electron spectroscopic methods. Here one should recall that such analysis cannot be performed *in situ* and in each specific case one must therefore estimate the possibility of undetectable changes in the chemical composition of the surface associated with the removal of the electrode from the electrochemical cell.

One of the first studies of the application of XES in the investigation of the changes in the chemical composition of the metal as a result of chemical and electrochemical reactions in a metal–electrolyte system was one[56] where the composition of the surface of the platinum electrode was determined (indicated in weight percentages in the Table below) in the course of its treatment in concentrated nitric acid and electrochemical oxidation in 1 *N* $HClO_4$.

The composition of the platinum electrode surface.

Surface compound	HNO_3	Potential in 1.0 *N* $HClO_4$		
		0.7 V	1.2 V	2.2 V
Pt	41	56	39	34
PtO (ads.)	39	39	37	24
PtO	14	5	24	22
PtO_2	6	0	0	20

The tabulated data could not be obtained by any other method and, although the absolute values obtained in the above study[56] give rise to doubts[57], the value of this investigation consists primarily in the fact that the scope of XES in the study of the metal–electrolyte interface was demonstrated.

The electrochemical oxidation of platinum and gold in sulphuric acid has been studied[57] with the aid of XES. It was shown that the oxide layers on platinum begin to be formed at potentials in the range 0.6–0.7 V# (in the same solution); PtO_2 appears at potentials of 1.2–1.3 V. The oxide film on gold consists of Au_2O_3. The thickness of the oxide layers and the true electrode surface areas have been estimated[57]. An important result is the observation[57] of the reduction of platinum and gold oxide under the influence of X-rays; this fact, which was disregarded by Kim et al.[56], can have a significant effect on the results of X-ray electron spectroscopic studies.

The modifications of a tin oxide surface of the electrode formed on adsorption of aminopropylethoxysilane $(C_2H_5O)Si.(CH_2)_3NH_2$ on the latter have been investigated[58] with the aid of XES. It was shown that the adsorption of this substance leads to the formation of covalent –Sn–O–Si– bonds on the electrode surface. The results of the analysis of the X-ray electron spectra are in good agreement with those obtained in the measurement of the impedance in the electrode–electrolyte system.

The surface films arising on a gold electrode in the electrochemical reduction of the Cr^{6+} ion have been studied in an investigation[59] where the gold electrode was polarised in 1 M chromic acid mixture and a mixture of 1 M chromic acid and 0.01 M sulphuric acid. The dependence of the chemical composition of the surface on that of the solution and the electrode potential has been investigated[59] by XES; furthermore, the changes in the thickness of the surface layer, formed on gold following the adsorption of various complexes arising as a consequence of the electrochemical reduction of Cr^{6+} ions, have been studied by analysing X-ray electron spectra.

The chemical composition of the surface of an iron electrode ("Armco") has been investigated[60] by XES in a neutral solution to which a series of oxo-anions, used as corrosion inhibitors, were added. The following salts were studied: Na_2WO_4, Na_2MoO_4, Na_3VO_4, $NaVO_3$, and Na_2CrO_4. The salt concentrations in the electrolyte corresponded to the protective concentrations found as a result of separate experiments. The results[60] permit the following conclusions.

1. All the oxo-anions investigated are strongly chemisorbed on the iron surface, behaving at the same time as acceptors, which follows from the somewhat higher values of E_b for the Fe $2p_{3/2}$ electrons compared with E_b for the Fe $2p_{3/2}$ electrons in the case of Fe_2O_3.
2. On chemisorption, the oxidation state of all the oxo-anions, except the chromate anions, remain unchanged.
3. The entire chemisorbed chromate is reduced, undergoing a transition from the +6 oxidation state to the +3 oxidation state.
4. On chemisorption of the oxo-anions (with the exception of chromate), the oxide Fe_2O_3, in which part of the oxygen has been substituted by the oxo-anions, is present on the surface.
5. The anomalously high protective capacity of chromate compared with other oxo-anions can apparently be accounted for by the existence of a stable complex, the formation of which is probably associated with the reduction of the CrO_4^{2-} anion on the surface of iron.

The study of the interaction of organic inhibitors with the surfaces of metals and alloys is of considerable interest. The interaction of metal ions with the inhibitor results in the formation of complexes whose solubility is fairly low and which are deposited on the surface of the metal. These complexes can in fact enter into the composition of the protective surface layer, which prevents the oxidation of the metal.

#Here and henceforth the potential is given relative to the normal hydrogen electrode.

Despite certain difficulties, particularly the necessity to remove the specimen from the working solution and to transfer it through the atmosphere (although the latter can be eliminated by employing a preliminary chamber filled with nitrogen or another inert gas), promising data have been recently obtained with the aid of XES.[61,62]

For example, surface layers formed as a result of the interaction of benzotriazole with copper (benzotriazole inhibits the corrosion of copper in chloride solutions) have been studied[61]. It has been shown that the protective film consists mainly of the copper(I) complex of benzotriazole. These data were compared with the results obtained with the aid of infrared reflection spectroscopy and the authors[61] were able to estimate the thickness of the surface film as a function of the method of treatment of the specimen.

In the study of the interaction of the surface of iron with organic molecules containing amino- and cyano-groups, it was shown that the interaction of iron with the amino-group results in a considerable decrease in the positive charge on the iron atom and an increase of the positive charge on the nitrogen atom as a result of the formation of the Fe ← N coordinate bond.

However, one should note that there have been as yet no studies of the interaction of the metal surfaces with inhibitors. Furthermore, studies of the interaction of metal surfaces with volatile inhibitors, in which one could carry out experiments in the spectrometer chamber without contact of the specimen with the atmosphere, are apparently of interest.

The interest in the problem of the passivity of metals led to a number of investigations involving the study by electron spectroscopic methods of passive oxide films on the surfaces of metals, in the first place iron and its alloys. The passive films on an iron electrode in neutral borate solutions have been studied[63,64]. Auger spectra have been obtained[63] with layer-by-layer etching of the passivating oxide film on iron with Ar^+ ions, which was formed in the anodic oxidation of an iron electrode in a borate buffer (pH 8.4); its thickness did not exceed 50 Å according to the authors[63], who concluded that a two-layer model is suitable for the oxide film on the iron surface, the inner and outer layers consisting of Fe_3O_4 and γ-Fe_2O_3 respectively.

Different oxide phases, formed on iron under different oxidation conditions, have been studied[64] by AES. The authors[64] were able to distinguish different oxide phases on iron: FeO, Fe_3O_4, Fe_2O_3, and FeOOH. However, the conclusions reached in the above studies[63,64] can hardly be regarded as unambiguous. Apart from the disadvantages of the AES in quantitative analysis described above, this is also indicated[65] by studies of the degradation of the passivating film on iron when the specimen is heated *in vacuo*[65]. According to Revie et al.[65] heating of the specimen leads to irreversible changes in the oxide film associated with the decomposition of OH^- ions. The exposure of the oxide film to a beam of primary electrons, used to generate Auger electrons, can lead to analogous results.

The X-ray electron spectra of chrome and chrome-nickel steels in $1N\ H_2SO_4$ have been obtained[66] and interpreted over a wide range of potentials. It was shown that, depending on the electrode potential, the surface can be enriched in iron or chromium, i.e. the possibility of the selective dissolution of chrome steels was confirmed. It was observed[66] that the surface of steel electrodes exposed at a potential of −0.4 V (the potential corresponding to the maximum rate of anodic dissolution of chromium) is significantly enriched in iron; the opposite behaviour is observed when the electrodes are maintained at −0.15 V. At this electrode potential, which corresponds to the maximum rate of the anodic dissolution of iron, the surface is enriched in chromium. The enrichment of the surface in nickel was not observed.

The influence of silicon on the electrochemical behaviour of Ni–Si alloys (silicon concentration from 0.1 to 3.3 wt.%) in $2N\ H_2SO_4$ has been studied[67]. The silicon concentration on the surface was determined by XES. It was shown[67] that the introduction of silicon into the alloy increases the repassivation currents by two orders of magnitude. Chemical analysis of the surface showed that this effect is associated with a change in the surface concentration of silicon when the electrode potential is altered. It was found that the silicon is present on the surface in two oxidation states (+2 and +4).

The states of the surface of a nickel electrode in the active and passive regions have been studied by different methods[68], including XES (the electrolyte was $1N\ H_2SO_4$). The X-ray electron spectra obtained confirmed that, at potentials more positive than 0.6 V, films of the nickel oxide Ni_2O_3 are formed on the nickel surface. The formation of this oxide terminates at potentials of ~1.0 V. At potentials more negative than 0.6 V (but corresponding to the passive region) an NiO film is present on the nickel surface.

The dependence of the composition (atomic ratio of magnesium and aluminium) of the surface of aluminium bronze in seawater on the electrode potential has been studied by XES.[69] The relation obtained is satisfactorily consistent with the electrochemical idea that the layer near the electrode becomes more alkaline in the cathodic range of potentials and more acid in the anodic range.

The joint application of the technique involving the etching of the surface with a beam of Ar^+ ion and the XES method permitted a layer-by-layer analysis of the passive films formed on chrome steels[70,71]. The surface layer formed on binary Fe–Cr alloys $\{40 \leq [Cr] \leq 30$ wt.%$\}$ following the exposure of the specimens to doubly distilled water freed from oxygen has been investigated at 25° and 70 °C.[70] It was shown that in all cases the concentration of chromium in the surface layer of the oxide increases near the oxide–medium interface; the concentration of chromium on the surface varies linearly with its volume concentration, but dc_S/dc_V increases with temperature (c_S and c_V are the surface and volume concentrations of chromium in the alloy). The passive layer consists of a two-layer film, in which the outer layer consists of chromium hydroxide $Cr(OH)_3$, while the mixed oxide $Fe_{1+x}Cr_{2-x}O_4$ is located closer to the metal. A model of the interaction of steel with water has been proposed[68].

The influence of the same medium and temperatures as in the study of Olefjord and Fischmeister[70] on a chrome-nickel steel (18/8 steel) has been investigated[63]. Castle and Clayton[71] were able to achieve a milder etching of the surface by Ar^+ ions and to obtain a larger number of points on the concentration profiles, which makes their result more reliable. The thickness of the oxide films was 15–30 Å. The composition of the surface oxide includes Cr^{3+}, Fe^{2+}, and Fe^{3+} bound to OH^- or O^{2-} ions. The authors[71] believe that the selective oxidation or dissolution of the components of the steels is ruled out.

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The above examples of the application of the XES, AES, and UPES methods in the study of the interaction of the surfaces of metals and alloys with the external medium show that, with their aid, it is possible to obtain very valuable and sometimes unique information about the nature of the chemical interactions occurring on the surfaces and in the surface layers of solids. Application of electron spectroscopic methods in combination with mass-spectrometric and diffraction methods yields a fully quantitative picture of the complex chemical processes occurring on the surfaces of metals when the latter interact with various media and makes it possible

to identify reliably the chemical transformations already in the chemisorption stage when the degree of surface coverage is much less than a monolayer.

Naturally, the analytical possibilities of the above methods are not of interest solely to specialists working in the field of oxidation, corrosion, and electrochemistry, although the examples of the application of the methods refer to these particular fields. One should note that a number of reports containing extensive data on the application of XES, AES, and UPES in the study of adsorption and catalytic processes have now been published[72-75]; furthermore, a collection of reports[76], published in Russian translation in 1979, is extremely useful to investigators becoming acquainted with the applications of electron spectroscopic methods.

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