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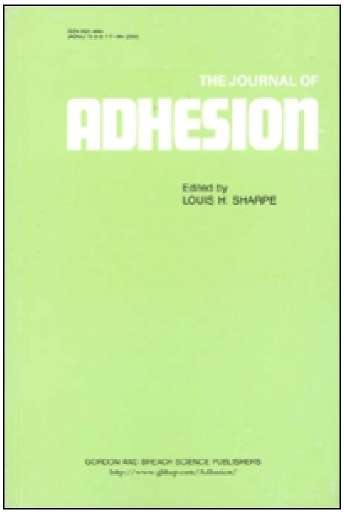

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The Composition of Metal Surfaces After Atmospheric Exposure: An Historical Perspective

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The Composition of Metal Surfaces After Atmospheric Exposure: An Historical Perspective

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This brief review describes the understanding of the surface chemistry of metals that was gained in the first ten years of the use of surface analytical techniques: the period 1968–1978. The work undertaken during this period established what we still recognise as a basic description of the technological surface with which the coating and adhesive industry has to deal. Since that time the same analytical techniques have been developed greatly, giving more information in shorter times and having a much greater sensitivity. This has enabled subsequent studies of bonding types and their relation to good adhesion. Nevertheless, it is hoped that this review of the early work and its systematic study of the hierarchy of layers that form on metallic surfaces will be of use for students and researchers entering the field of adhesion science.

Keywords: Adhesion to metals; Environmental interactions of metallic surfaces; Surface preparation; Technological surfaces; Weak boundary layers; XPS analysis

INTRODUCTION

Organic coatings and adhesives are normally applied to "technological surfaces", that is surfaces which have been treated by relatively simple techniques and then exposed to the atmosphere before and during the application of the organic material. Forty years ago this was a topic of intense debate which yielded an understanding which was remarkable, since it pre-dated the availability of the techniques which we now regard as indispensable for analysis of such surfaces: XPS, commercially available in 1970; auger electron spectroscopy (AES),

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available from *ca.* 1969; and secondary ion spectroscopy (SIMS), available from about 1974. The understanding of the 1960's was developed by means of the classical methods of surface chemistry, *e.g.*, adsorption and desorption measurements using gravimetric and volumetric methods to obtain surface free energy as a function of coverage, or wetting and spreading measurements using contact angles. Research by Girifalco and Good [1] and by Fowkes [2] was establishing the thermodynamic basis of adhesion. At the end of this period, in a symposium sponsored by General Motors (Detroit, MI, USA) on "Interface Conversion for Polymer Coatings", Eirich [3] and Bolger and Michaels [4] described the then understanding of the hierarchy of layers by which the surface of a metal becomes terminated after a period of atmospheric exposure. Figure 1, from the summing-up of the presentations at the meeting by Eirich, summarizes the problem of coating in a manner that many will recognize as a fundamental requirement of good practice in adhesion for today's world.

In a brief introduction to the potential value of the then new surface analysis techniques given at a NATO school on coatings in 1972, Sparnaay [5] cited the three "unanswerable questions" which defined surface problems up to the end of the 1960s:

(1) Is the surface clean, *i.e.*, free from foreign atoms?
(2) What is the exact position of the surface atoms?
(3) What is the physical nature of the surface structures?

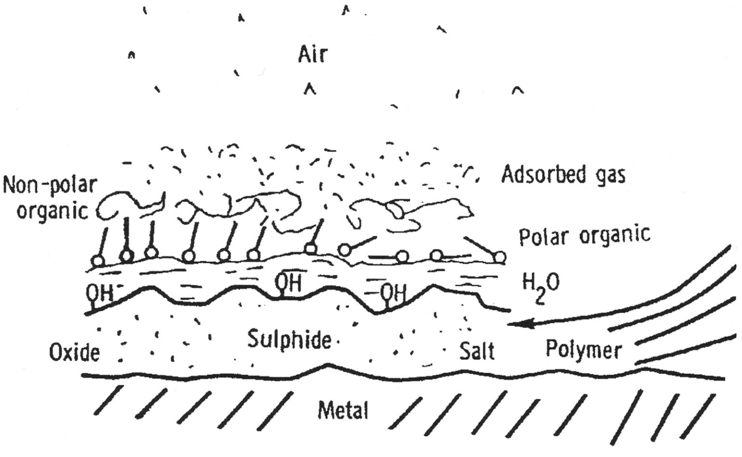


FIGURE 1 The surface layers on a technological surface as depicted in 1968 by Eirich [3].

At the time of Sparnaay's review, the techniques to answer such questions were beginning to appear but it was then usual, prior to surface analysis, to remove the "surface contamination" by ion etching in order to obtain a clean metal surface. Thus, whilst the passage of time had allowed the perfection of measurements made on clean surfaces, the study of the surface layers represented in Fig. 1 came about much more slowly. Towards the end of the 1970's I contributed lectures to a graduate course on coating of metals and in the first of these I tried to summarize what was known of the technological surface after the first decade in which XPS and AES had been available. The lecture formed the basis of a talk given in 1978 at the symposium on "Corrosion Control by Coatings" [6] – just ten years after the General Motors Symposium. The present article is again based on my notes from this period, as taken from my files, and though not updated is offered as a guide, to students and researchers, on the manner in which the sequence of changes to a surface can be reconstructed using surface analysis. It is perhaps a fitting contribution to this particular volume which marks the start of Professor John Watts' period as President of the Adhesion Society. Watt's outstanding work on the science of adhesion was built from this point in time, using the newly available technology to add direct evidence on what is missing from Fig. 1, *i.e.*, the nature of bonding between the pre-treated metal and the polymer.

This review considered the evidence offered by the surface spectroscopies on the nature of the layers formed on metals and alloys of industrial importance by atmospheric exposure, *i.e.*, the layers which might be expected to be present after routine preparation of the surface for coating. It took the form of a gradual reconstruction of the layer-by-layer structure which owes its origin to the steady reduction in the surface free energy available on the original, totally clean, surface. The surface free energies of liquids and solids involved in adhesion science are given in Table 1 and the correlation of this with the hierarchy given in Fig. 1 is quite apparent.

TABLE 1 The Hierarchy of Surface Free Energies Corresponding to the Layers Shown in Fig. 1

Surface of	Surface free energy (mJ m^2)
Liquid air	20
Organic hydrocarbons	*ca.* 20
Organic polymers	*ca.* 20–30
Epoxides	*ca.* 50
Water	73
Metal oxides	200–500
Metals	1000–5000

THE METAL SURFACE

The metal surface is the basal plane of the surface layers and, to some extent, the base plate, which guides their structure by virtue of the phenomenon of epitaxy. Interest in its structure, studied by low energy electron diffraction (LEED), predated the ability to analyze it chemically. A useful review of surface structural defects, as understood at this time, was given by Rhead [7] and monolayer segregation, to the surface, of a large number of impurity and alloying elements was reviewed by Seah [8]. The investigation of sulphur and chlorine on un-oxidized metal surfaces has a history as long as AES itself [9,10]. It is now beyond doubt that they arise from the metal and their concentration depends on its thermal history, as shown in Fig. 2, in which sulphur segregates to the surface of iron during vacuum annealing [11]. The segregation of non-metallic and metallic elements to free metal surfaces [12] and to grain boundaries [8] in high vacuum is of immense importance in our understanding of metallurgical phenomena such as temper brittleness and of some types of stress corrosion cracking. Although their effect on the formation of an oxide layer may be minimal, sulphur is believed by some to influence the adhesion of oxides to metal surfaces and, thus, has a great influence on spalling of oxides. Interface segregation, however, does not appear to have been implicated in any case of coating disbondment. This may be because segregants are trapped at the alloy/oxide interface in much the way that they are trapped at grain boundaries, as shown in Fig. 3 taken from Reference [8], and, hence, do not reach the oxide/polymer interface. Nevertheless, the work showed that segregation to the interface between oxide and metal is quite likely to occur during processing of coatings by stoving operations.

ADSORPTION FROM THE GAS PHASE

The uptake of monolayers of oxygen by clean metal surfaces at low or ambient temperature had been a favoured topic of study [13]. Figure 4 gives data for the binding energy of the O1s electron. It is constructed in the form of a chart to illustrate the relationship between the binding energy and the position of the element or molecule within the hierarchy of layers given in Fig. 1. At the base of the chart is gathered together some of the data for adsorption of oxygen at the monolayer level. At the top of the chart are values derived from the outer surface and contamination material. In this paragraph we consider the adsorption stage. The chart shows that the earliest stage of adsorption from the atmosphere, that of the undissociated oxygen molecule, can

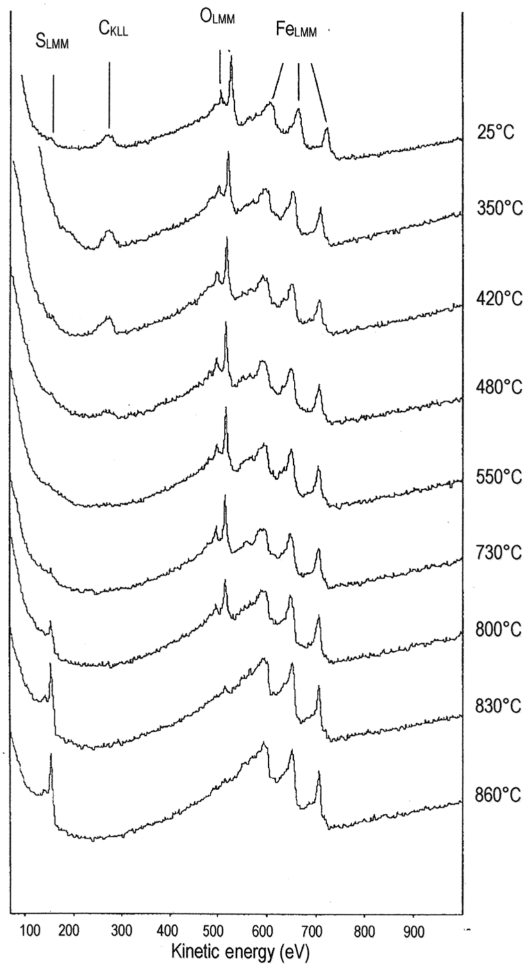


FIGURE 2 Segregation of sulphur on the surface of iron, as studied by AES. Note that loss of oxygen precedes the S segregation (A. Brooker, [11]).

be recognised by the high binding energy, *ca.* 533 eV. On dissociation, the binding energy of oxygen moves closer to that of true oxide at *ca.* 530 eV. Much of the work of this period had the aim of elucidating the reactivity of metal surfaces and, thus, of the mechanism of adsorption. Useful reviews of the work in this period were given by Joyner [14] and by Roberts [15]. The work of the 2007 Nobel Prize laureate, Gerhard Ertl, was well established at this time, providing an insight into the interactions of molecules on surfaces [16]. Considerable success had

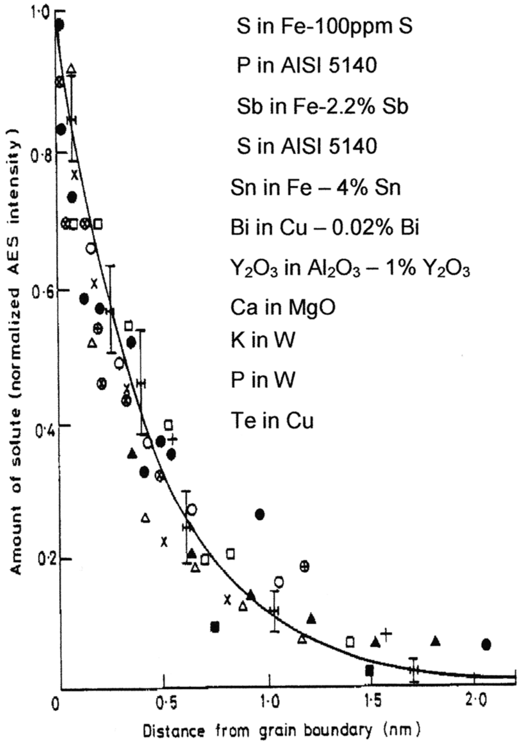


FIGURE 3 An illustration of the manner in which many minor elements in metals and non-metals segregate to the surface and to grain boundaries. (After Seah *et al.* [8], Copyright John Wiley & Sons. Ltd., 1990. Reproduced with Permission).

been had in distinguishing dissociative from non-dissociative adsorption of molecules. However, from the viewpoint of adhesion, the extent to which "back-bonding" stabilized adsorption by donation of electrons from the metal to the bonding orbitals in the adsorbed molecule was of greatest interest. Figure 5, taken from the work of Joyner and Roberts [14], shows how back-bonding gives rise to a relationship between the heat of adsorption of CO on various metals and the binding energy of the O1s electron. This class of adsorption is likely to be important in determining the most suitable molecules for use as adhesion promoters or corrosion inhibitors. Bailey and Castle [17], for example, examined butylamine chemisorbed on clean iron and discussed back-bonding. Kishi and Roberts found, however, that back-bonding was unimportant in the adsorption of a number of nitrogen-containing

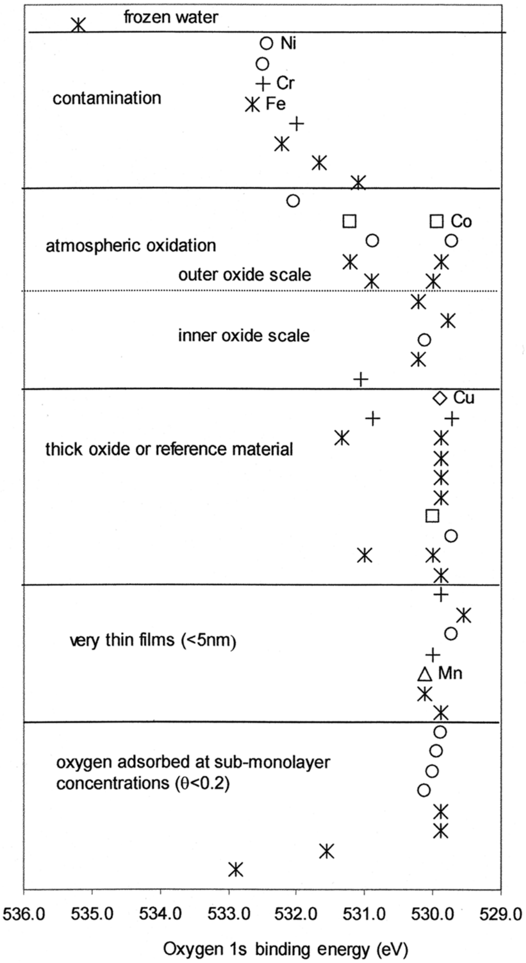


FIGURE 4 Chart giving the positions of the oxygen 1s peaks on a number of metal surfaces. The data are arranged in the order of the hierarchy depicted in Fig. 1. At the bottom are the values obtained by a number of workers (cited in the text) for the early stages of adsorption. Moving upwards the data represent greater coverages until the point is reached when thin oxide films form. The next section gives values obtained for thick oxide or reference materials. Beyond this are given values actually obtained on metal surfaces exposed to atmospheric oxidation. The upper sections detail the values obtained from contaminated surfaces and finally for frozen water. The symbol used for a given metal is indicated for one of each of the data points.

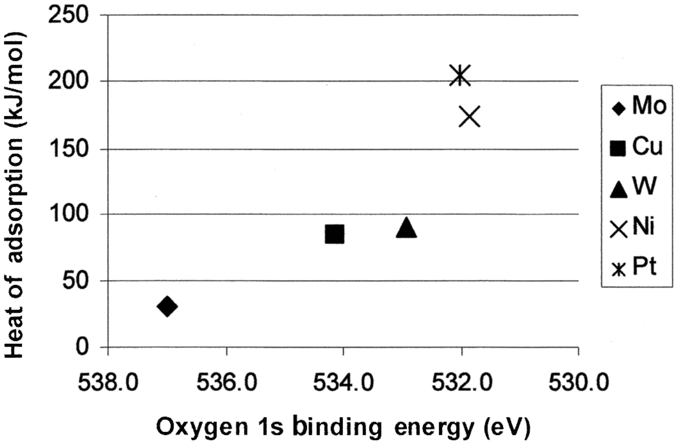


FIGURE 5 Data taken from Joyner and Roberts [14] illustrating the relation between O1s binding energy and the heat of adsorption of CO on various surfaces. (Copyright Elsevier, 1974. Reproduced with Permission).

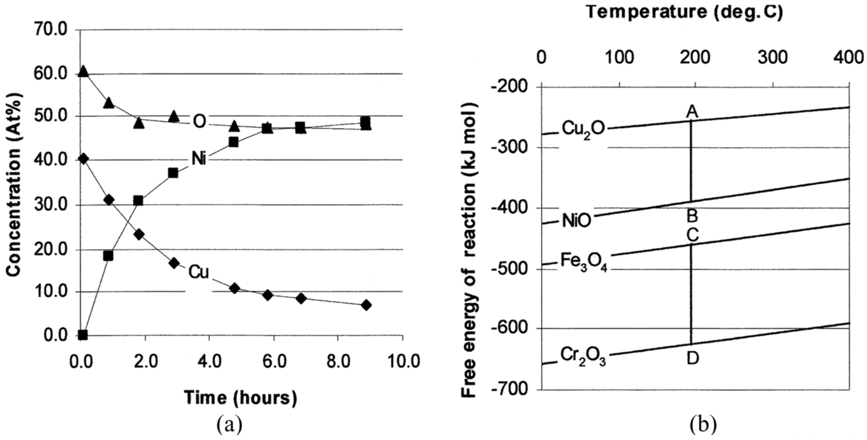
molecules [18]. This latter study brought to light one further fact of importance in the establishment of surface layers: that the strength of the N-metal bond is lowered by subsequent adsorption of the more electronegative oxygen molecules.

THE OXIDE LAYER

The further growth of adsorbed monolayers into 3-D oxide has now received considerable study by way of *in situ* oxidation of clean metals. Figure 4 includes the peaks positions for the oxygen 1s binding energy for the principal steel forming and non-ferrous alloying elements. As will be seen, the binding energy is close to 530 eV for most oxides. This enables the true oxides to be easily distinguished from, *e.g.*, hydroxides or oxy-hydroxides but distinguishing one oxide from another depends on examination of the metallic peaks themselves. At room temperatures and in dry oxygen or air at atmospheric pressure, the surface passivates on reaching a thickness of *ca.* 2 nm with growth kinetics not markedly different from those described by the Cabrera and Mott [19] equations for very thin films, *i.e.*, a rate of growth showing an inverse exponential dependence on time. At the time, Fromm and Mayer [20] dissented strongly from the use of Cabrera and Mott's equations in which the limiting thickness is determined by the quantum mechanical tunnelling limit for electrons and pointed out that the same limit is reached in the nitridation of metals even though many of the nitrides are metallic conductors. They attempted to classify the oxidation of 13 transition metals into five groups. Recent work has, in fact, shown that films grown slowly under much reduced pressure may reach a limiting thickness that is much less than the tunnelling limit [21]. For whatever reason, the oxide thickness on most metals exposed in dry air at room temperature reaches a limit at *ca.* 2 nm.

All told, there is probably little of surprise to the coating technologist from the work on pure metals. The films reach a limiting thickness when they are exceptionally thin but that was well established prior to the use of surface analysis. Surface and interface energies appear not to have greatly disturbed thermodynamic equilibria. For example, FeO is not found as a surface phase as had once been considered possible and the nickel oxide (NiO) layer is probably oxidized to Ni_2O_3 at the oxygen interface [22,23]. However, there is relatively little change in the spectra on heating to moderate temperatures, *i.e.*, 400–500°K.

There has been very much less work on the early stages of oxidation of alloys but here the particular advantage of XPS of recognising the oxidation state of each alloying component in addition to monitoring the uptake of oxygen had given useful results. For example, the surface oxide formed on 70/30 Cu/Ni alloy is exclusively nickel oxide [24], whilst the surface layer on 80/20 Cu/Zn alloy is cuprous oxide [25]. Oxidation of the cupro-nickel at only a moderate temperature (473 K) promotes diffusion of copper and the formation of a thick outer layer of cuprous oxide which is reduced by nickel on subsequent heating in vacuum. The reduction stage is illustrated in Fig. 6a. The thermodynamic driving force for reduction comes from the difference in the free energy of reaction between the alloys elements and oxygen. This can be predicted from the Ellingham diagram, a simplified version of which is given in Fig. 6b. The line for the oxidation of nickel lies below that of copper, indicating that nickel oxide is the more stable. Thus, in a situation in which there is insufficient oxygen for both oxides to form, then nickel will remove the oxygen from copper oxide. The line AB shows the situation for the process occurring in Fig. 6a. The interval AB is a measure of the free energy available for the reduction step and the gradual replacement of nickel oxide on the surface of the alloy, followed by XPS, gives a measure of the kinetics of the process. Notice that an analogous situation arises for iron-chromium alloys, represented by the line CD. For many steels at room temperature the oxide has a composition closely similar to that of the steel itself [26–28]. However, chromium will diffuse to the surface of a steel under the driving force available from reduction of magnetite, Fe_3O_4 [29,30], as



(a) (b)

FIGURE 6 (a) XPS data showing the conversion of a surface oxide (Cu_2O) to the more stable NiO on heating in vacuum; (b) Diagram illustrating the free energy of oxidation and its dependence on temperature. The lower the line in this chart the more stable the oxide. The line AB represents the free energy change for the process given in 6a.

represented by CD. The line for the oxidation of manganese lies below that of chromium and, sometimes, it is manganese oxide that eventually terminates the steel surface after vacuum heat treatment. Such reactions might well be important when stoving a coating onto a metal surface and have even been observed to occur at room temperature over periods of a hundred days or so.

In distinguishing oxides from each other and from their parent elements, standard spectra of well defined surface compounds are obviously necessary. These are now available for many metals [31]. The oxides of iron are most conveniently distinguished by means of the shake-up satellites (Fig. 7) [30,32].

EXPOSURE TO WATER VAPOUR

By the end of the 1970's there had been several well documented investigations into the behaviour of metals in water vapour [33,34]. These, of course, hold special interest because of the adverse effect of water vapour on coating adherence. Fuggle *et al.* [34], Roberts [35], and Wood and Dwyer *et al.* [36] have shown that the oxidation of iron is arrested at a much smaller layer thickness (0.2 nm) in water vapour than in oxygen. In all cases, oxygen and water vapour exposures were carried out with the same materials and in the same equipment

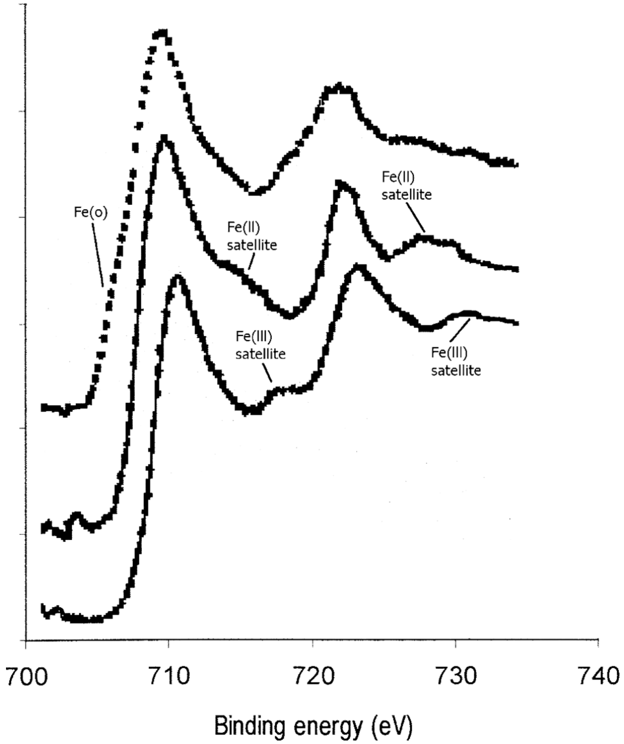


FIGURE 7 Photoelectron spectra of iron. The lower spectrum is that of the ferric state, the centre, the ferrous state, whilst the upper spectrum is that frequently seen on technological surfaces and contains both ferric and ferrous states.

and the contrasting results in the gases cannot be explained by differences in technique. Roberts concluded that the unusual passivation arises from the formation of FeOOH because of the stoichiometric growth of two oxygen peaks. Fuggle *et al.* suggests the formation of an oxide, Fe_3O_4 or Fe_2O_3, with less than full (approximately 90%) release of hydrogen. This group found no difficulty in observing the growth of AlOOH on aluminium which made the different result on iron the more significant. The formation of the (OOH) group is a feature of oxidation when water vapour is available and is easily recognised by the double oxygen peak. Values are given for reference compounds in the chart of Fig. 4 and it will be seen that this signature is frequently observed in metals exposed to the ambient atmosphere.

Neither of the groups led by Roberts or Fuggle found oxygen peaks corresponding to adsorbed water. Fabian *et al.* found the O1s peak in frozen water to be 535 eV but even at temperatures as low as 123 K this peak converted, for water on an iron substrate, to 530.3 eV ($O^{=}$) plus 532.5 eV (OH^{-}). A low temperature peak at 534 eV was ascribed to physisorbed molecular oxygen but Asami *et al.* [37] ascribe a peak at 533 eV to adsorbed water molecules. Norton *et al.* [22] made the interesting and significant observation that films of NiO formed in oxygen convert completely on exposure to water vapour for periods of several days to a hydroxide form (O1s = 531.3 eV) although the thickness does not increase.

ATMOSPHERIC EXPOSURE

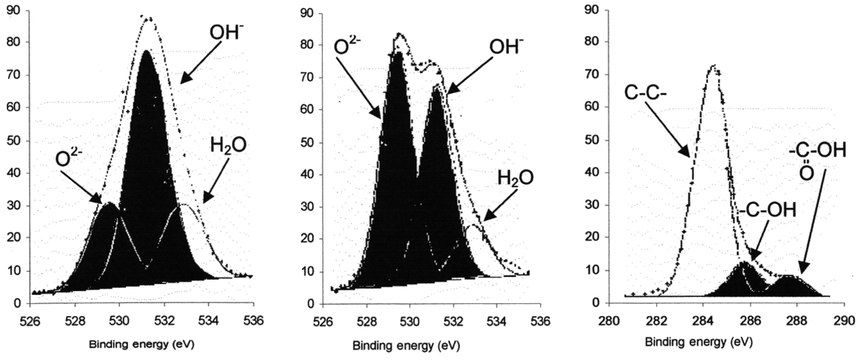
Apart from the initial, almost inadvertent, exposure to the atmosphere there have been few reported studies of the effect of atmospheric oxidation. Norton *et al.* [22] showed that exposure of preformed oxides to the atmosphere led to the formation of hydroxides with little change in total layer thickness. Barr [38], however, reported an investigation of the surface layers formed on a large number of metals after atmospheric exposure. The metals were each etched back to the zero valence state and then exposed to air (relative humidity 35%) for as long as was necessary to produce a passivating or "terminal" layer. The film thickness varied from *ca.* 2 nm (Cu) to 10 nm (Zr) and were, thus, not dissimilar to those found by other workers in pure oxygen. However, the outermost layers were, as might be expected from work in water vapour, rich in hydroxides. The most interesting observation was that the behaviour of the metals could be described in two groups which had close parallel with the groupings used by Fehlner and Mott [39] to describe network modifiers and network (glass) forming elements. Bolger and Michaels [4] gave a diagram showing the importance of surface hydroxyl groups in allowing the retention of bound water and the consequent formation of an extensive network of H-bonded water molecules. In the context of understanding passivation of metals, Okamoto [40] demonstrated the important presence of bound water on chromium-containing steels by use of tritiated electrolytes, and so the fact that water molecules are present, and strongly bonded, on the surface of many metal oxides was well established. Table 2 reproduced from Barr's study shows his results. Group A metals, which include iron, cobalt, nickel, and copper, formed an oxide in their lower normal valence states with a terminal layer of a higher valence state. Group B metals, including aluminium, tin, and molybdenum, formed surface hydroxides or hydrated oxides as a terminal

TABLE 2 Classification of Surface Oxides Formed by Atmospheric Exposure [38]

Group	Metal	Bulk oxide/hydroxide	Skin oxide/hydroxide
A network modifiers	Ce	Ce_2O_3, $Ce(OH)_3$	CeO_2, $CeO(OH)_2$, $Ce(OH)_4$
	Pt	PtO	PtO_2, $Pt(OH)_4$
	Pd	PdO	PdO_2, $Pd(OH)_4$
	Fe	FeO	Fe_3O_4, Fe_2O3, $Fe(OH)_3$, FeOOH
	Co	CoO, $Co(OH)_2$	Co_3O_4, Co_2O_3, CoOOH
	Ni	NiO	Ni_2O_3, NiOOH, $Ni(OH)_2$
	Cu	Cu_2O	$Cu(OH)_2$, CuO
B network formers	Si	SiO_2	SiO_2, $Si(OH)_4$
	Al	Al_2O_3, AlOOH	Al_2O_3, $Al(OH)_3$
	Zr	ZrO_2	ZrO_2, $Zr(OH)_4$
	Sn	SnO_2	SnO_2, $Sn(OH)_4$
	Mo	MoO_3, Mo_2O_5	MoO_3, Mixed oxide-hydroxide
	W	WO_3	WO_3, Mixed oxide-hydroxide
	Y	Y_2O_3	Y_2O_3, YOOH
	La	La_2O_3, LaO	La_2O_3, LaOOH
	Rh	Rh_2O_3	Rh_2O_3, RhOOH

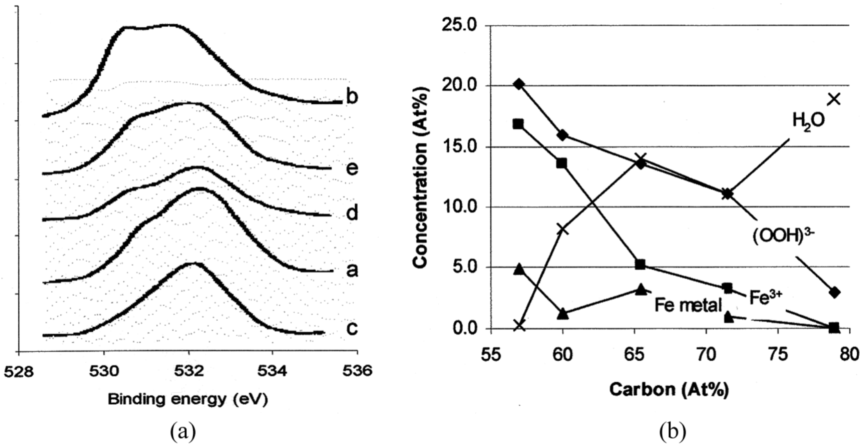
layer. The division is based on the final state but also on the fact that the Group A oxides grew in the lower valence condition and only oxidized to the higher state when the growth had virtually ceased. Many of the metals in Group B, however, do not naturally form two valence states and the oxides of SnO and SnO_2 are very difficult to distinguish [41]. Iron in Group A apparently had a rather thick Fe outer layer. Thus, the division into groups is not exact but the concept is useful and was in line with current thinking concerning the role of high valence ions, chromate and molybdate for example, on the formation of passive oxides [42]. Barr noted the presence of hydrocarbon contamination on the surface and also the occasional formation of carbonate ($<5\%$) but paid no special attention to these. In subsequent work, the slow accumulation of hydrocarbon layers from exposure to laboratory air has been the subject of a special study in the context of the stability of standard weights manufactured from a stainless steel [43]. Chromium was apparently not included in the study by Barr. This important steel forming element could perhaps be found in either group but curiously it alone in Fabian's study [34] did not form a hydroxide. The atmospheric oxidation of iron chromium alloys and stainless steels had been commented on by Asami *et al.* [26], Olefjord and Elfstrom [44], Storp and Holm [28], Castle and Clayton [45], Castle [46] and McIntyre *et al.* [47]. At ambient temperature none of the authors found selective oxidation of chromium relative to iron in either dry or moist air. However, in the experience of all authors, the presence of hydroxide was very noticeable on both alloy and plain carbon steels. Chromium-rich steels frequently terminate in a layer of hydroxide, whereas, in the absence of this element steels frequently show the oxy-hydroxide. Examples are given in Fig. 8.

The characteristic signature of carbon contamination is also shown in Fig. 8. An association between accumulation of organic contamination and water retention on the surface was shown by the results of a study of surface preparation carried out by D.C. Epler in the author's laboratory. Coupons of plain carbon steel were prepared by five methods: (a) abrasion under water within 600 grade silicon carbide, (b) dry abrasion with 400 grade energy, (c) wire brushing, (d) ultrasonic cleaning in water containing "Decon" detergent, and (e) ultrasonic cleaning in acetone. These were left in the atmosphere for 70 h. A further five samples were then prepared by the same methods and all ten loaded together into the spectrometer. The iron peaks of both sets show features from metallic iron and the ferric iron: clearly surface preparation had far more effect on total film thickness than environmental exposure. The oxygen peaks were reproducible from set to set (Fig. 9a) showing that the different methods are consistent in their effect on the surface, and have two components in



(a) (b) (c)

FIGURE 8 Oxygen and carbon spectra from the surface of metallographically polished surfaces of (a) stainless steel and (b) plain carbon steel illustrating the difference in their surfaces. Stainless steel is dominated by the OH groups in the network created by the presence of Cr ions; plain steel has the signature state of the OOH structure. The organic contamination on both surfaces is similar and is represented by (c) the carbon spectrum.



(a) (b)

FIGURE 9 Typical information showing the influence of surface preparation on the surface condition of a steel. (a) The oxygen spectra are stacked with the cleanest at the top. As less effective methods are used the high energy (right hand) component increases at the expense of the oxide component illustrating the increased enrichment of OH ions and water molecules in the surface. (b) The plotted data show how the water content increases with the carbon peak and the manner in which the growth of this contamination layer gradually obscures the signal form the oxide and metal that lie beneath it.

the oxygen spectrum which bear a close resemblance to those found from oxy-hydroxides.

On the emery prepared surface, which had the most intense iron peak, the two components of the oxygen are of equal intensity. All other samples have an excess intensity of the higher binding energy peak and when this excess is included in a plot of normalized peak intensities (Fig. 9b) there is a correlation with the carbon intensity. There is also a steady shift in the peak position from 531.2 (Cls = 285) 285) to 532.4 eV. At low carbon coverage (dry emery) the peak is principally due to that of the hydroxyl ion (531.5 eV), whereas the peak (BE > 532.4 eV) found on the more contaminated surface (high carbon concentration) represents adsorbed water associated with the organic molecules on the surface. Figure 9b summarizes the findings: as the carbon signal increases, so does that from water; these increases stem from an increase in the thickness of the contamination layer that then attenuates the signals from the base, Fe metal, Fe^{3+}, and $(OOH)^{3-}$ all decreasing as the contamination builds. We have found this characteristic association of a high binding energy oxygen with organic molecules on many samples. It is removed by the lightest ion etch.

Because of its lightly bonded state the ion etch profile underestimates its thickness, and analysis of XPS spectra suggest that its thickness is similar to that of the underlying oxide.

INTERACTION WITH LIQUID ENVIRONMENTS

Water

Although this article deals with the atmospheric formed layers, some mention of their response to water and its solutions should be made. Several authors [37,45,48] have found that chromium steels lose the iron constituent in their oxide by selective solution of Fe^{++} ions. Similarly, zinc is leached from brass [49,50]. However, the oxide formed on aluminium brass (4 at% Al in 68Cu/30Zn brass) in sea water retains zinc and incorporates magnesium from seawater as a mixed hydroxide with aluminium [51,52]: This mixed hydroxide, known as hydrotalcite, has ion exchange properties which act to protect the brass from sea water by a chemical buffering action [52]. Attempts have been made more recently to incorporate hydrotalcite pigments in organic coatings to exploit this buffering action. XPS results (Fig. 10) for brass exposed to seawater show how a metal surface can change in composition in response to an applied electropotential [53]. This response was not

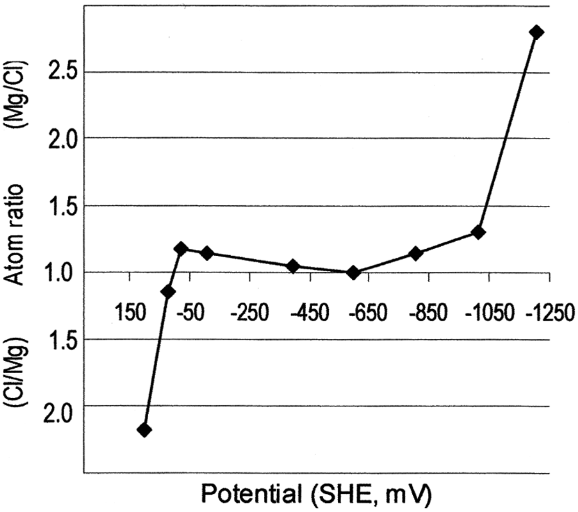


FIGURE 10 The reversible response of a surface to an applied electropotential. In the presence of ions found in seawater there is a change from an acidic surface (high chloride) at anodic potentials to a basic surface (high Mg) at cathodic potentials.

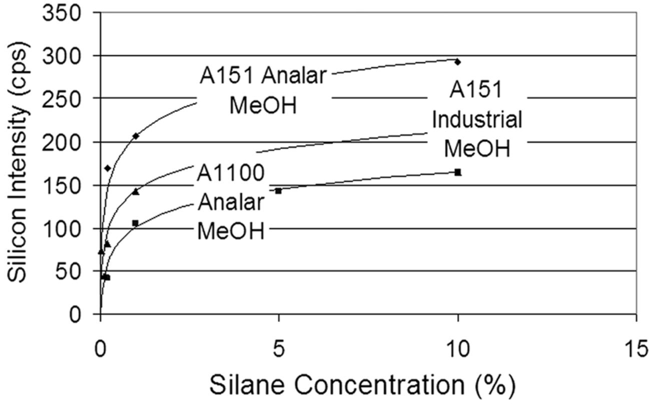


FIGURE 11 The uptake of silanes as a function of their concentration in solution. The surface concentration is shown by the count rate of the Si2p photoelectron peak. The use of industrial grade methanol as a solvent led to a marked reduction in adsorption.

due to any visible corrosion: the total charge passed through the surface was chosen to be that necessary to modify only the outer 5 nm and the composition changed rapidly to match the applied potential. Uhlig [53] suggested on the basis of electrochemical data that the oxy-hydroxide layer on steel may behave in the same way.

Non-Aqueous Systems

The interaction between the fully passivated metal surface and solutes in organic solvents is typified by the adsorption of adhesion promoters such as the ethoxysilanes. Studies of their adsorption on iron [17] showed that a Temkin isotherm could be obtained using pure solvents, indicative of a non-uniform heat of adsorption (Fig. 11). Notice, however, that when industrial solvents containing impurities were used to apply the silane the uptake was lower because impurities competed with the silane for the same range of adsorption sites.

CONCLUSIONS

Could we, after one decade in the use of surface analytical techniques, paint a characteristic picture of the passivated metal surface which advances on that of 1968 and is typified by Fig. 1? Much of what had been deduced by use of indirect techniques had been confirmed by surface analysis but there had been some surprises, notably in

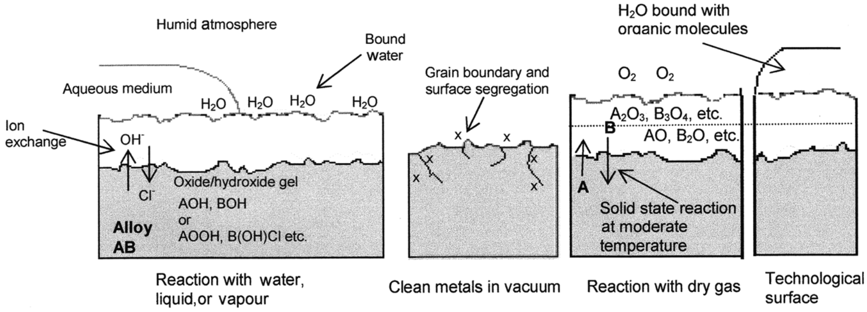


FIGURE 12 A composite diagram illustrating the dynamic nature of surface reactivity—work detailed in this review has shown the importance of ion exchange, solid state reactions and segregation to interfaces—in addition to the more widely appreciated modes of surface adsorption.

the dynamic response of the surface towards the environment. The composite diagram in Fig. 12 summarises some of the processes which, from the results cited above, we now know to be important. In the centre of the diagram is placed the clean metal as a reminder of the possibility of impurity segregation to this surface and associated interfaces. To the left is indicated the likely surface to form in the presence of water vapour or aqueous media. We can note the formation of hydroxides and oxy-hydroxides and that these compounds are likely porous or gel-like and may participate in ion exchange reactions with any surrounding electrolyte. The composition may change in response to any applied electropotential. The surface layer is rich in bound water and the metallic interface is likely to be rugged. Selective dissolution of alloying elements may have left this surface enriched in one or another of the alloying elements, depending on solubility criteria. Right-of-centre is shown the influence of a dry atmosphere. In the presence of oxygen the oxidizable components of the alloy form an oxide in which little structural differentiation can be made—but which may be terminated by a higher oxide. The interface between oxide and metal probably breaks up into a zone across which the oxygen potential of the oxide drops to that of the alloy and within which segregated impurities would be lost by dispersion over the many boundaries. In the presence of water vapour, the oxide converts to hydroxides yet not necessarily with increases in thickness. On heating, solid state reactions between the oxidized material and the underlying metal occur at quite low temperatures (*ca.* 200°C). These lead to surface films enriched in the more stable oxide of the given alloying elements, even if these are at a very low concentration. For example, manganese oxide forms on heating steel in vacuum. Organic molecules, especially those derived from the aqueous phase, stabilize an extended structure of water molecules with a thickness similar to that of the oxide. This may be pierced by strongly adsorbing organic molecules but it is not readily removed by preparative techniques such as abrasion or wire brushing. This is indicated on the far right of the diagram.

This structure has fewer formal layers than that envisaged in 1968. Water, in particular, extends in some form continuously throughout the structure and probably accounts for its reactivity in terms of bulk adsorption. Because of its lack of sharp divisions, it seems unlikely that the extended bound water structure can be displaced by polymer application and, in the absence of direct interfacial evidence, we must assume it to be present as a discontinuity in most organic coating applications. This is clearly the most important area for further work using the power of XPS although ingenuity will be required to expose the region for analysis.

This last sentence was written in 1978! In the intervening decades surface studies have moved from metallic surfaces to those of semiconductors, intermetallics, fibres for use in composite materials, biomaterials, and now are increasingly focused on nano-tubes and nano-fibres. Although each different type of surface poses its individual type of challenge the sequence of layers and their interactions has remained broadly the same as described in this review of metallic surfaces. The dynamic nature of surfaces, and the importance of the adsorbed films found on technological surfaces, has been vividly illustrated by the recent finding that the surface conductivity of single crystal diamond results from electrochemical interaction with the adsorbed film of water [54].

Returning to the context of adhesion to metallic surfaces, surface preparation prior to coating is easily monitored using XPS [55] and now widely used: a better understanding of the role of primers and the inclusion of bonding agents has become possible by use of the technique [56]. It is now taken for granted that, following failure of a coating, the locus of failure will be examined by XPS [57,58] and the presence of any possible weak boundary layers identified [59–61]. XPS studies of the interface have, in fact, given much information on interfacial bonds [62–64], especially from the use of adsorption isotherms to examine the uptake of individual components of complex protective systems [56,65]. What was not envisaged at the time of writing the original notes was the exceptional power that static SIMS would bring to the study of the interfacial chemistry of adhesion [66]. It will not have escaped attention that these final references are all to the work of Prof. John Watts. They are but a selected few of the huge publication list representing his contribution to the subject of adhesion since this article was first prepared some thirty years ago. He is surely to be congratulated on his fine achievement.

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