

Techniques for the examination of corrosion products

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The examination of products of aqueous and non aqueous corrosion is carried out to obtain information about one of a combination of aspects such as composition, hardness, stress level, adhesion to basis metal and other mechanical properties (figure 1). A number of techniques are available to investigate corrosion products and some of these techniques have found greater application with products of aqueous corrosion and some with products of gaseous corrosion. This paper presents the techniques available for obtaining information about the various aspects mentioned above and discusses the main characteristics, nature of data obtainable, advantages and limitations of some of the less known techniques.

Identification-composition

Identification studies of corrosion products include, the determination of composition, structure, concentration profiles of elements and the presence if any of contaminants from the environment. The techniques generally used for the identification of bulk specimens like stripped oxides are the various forms of chemical analysis (wet analysis, ignition analysis, colorimetry, polarography, gas chromatography and others), mass spectroscopy and less frequently, thermogravimetry. In

most of these methods, although elements present in very small quantities can be determined, local compositional changes are difficult to detect.

Other techniques that can be used to identify corrosion products are listed in Table I. In all these techniques, some particles or species are incident (or probing) on the surface, and information is obtained from analysis of the emitted species. Some important parameters of these analytical techniques are also given in Table I. Among these, electron probe micro-analysis (EPMA), energy dispersive analysis, back scattered electron spectroscopy and Auger electron spectroscopy as well as some other techniques such as transmission electron microscopy and electron diffraction analysis have basis in the interaction between incident electrons and materials. Techniques 1, 2, 4 & 5 of table I have been extensively used in corrosion studies and will not be discussed here. Back scattered electron spectroscopy has recently been used to study the distribution of elements. The intensity of the back scattered electrons from elements with high atomic number is higher and produces a brighter image. Also, depending on elemental distribution, the images have higher contrast and are in relief as compared to secondary electron images in a scanning electron microscope. Neutron Activation

TABLE I — TECHNIQUES OF ANALYSIS AND SOME OF THEIR PARAMETERS

No.	Techniques of analysis	Incident species	Emergent species	Elements detected	Detection Limit (ppm)	Lateral resolution (μm)	Depth of Information (\AA)
1	Electron probe micro	Electrons	Charac.X-rays	$\geq \text{Be}$	100-1000	1	~ 5000
2	Energy dispersive	Electrons	Charac.X-rays	$\geq \text{Na}$	~ 1000	10	~ 10000
3	Back scattered electron spectroscopic	Electrons	Back scattered electrons	$\geq \text{Li}$	~ 1000	1	10-50
4	Auger spectroscopic	Electrons	Auger Electrons	$\geq \text{Li}$	~ 1000	0.05-30	5-20
5	X-ray fluorescence	X-rays	Charac.X-rays	$\geq \text{Mg}$	atomic number 12-22 > 1000 > 22 ~ 1	300	10-80
6	Neutron activation	Neutrons	δ -rays	$\geq \text{Na}$	~ 0.1	~ 1000	Complete specimen upto 1 cm
7	Electron spectroscopic	Fotons	Electrons	$\geq \text{He}$	~ 1000	~ 1000	5-20
8	Secondary ion mass spectroscopic	Ions	Secondary Ions	$\geq \text{H}$	0.1-100	1-3000	3-10
9	Ion scattering spectroscopic	Ions	Ions	$\geq \text{Li}$	~ 1000	100	3-10
10	Rutherford backscattering spectroscopic	Ions	Ions	$\geq \text{C}$	~ 100	1-3	3×10^4
11	Elastic recoil detection	Ions	Ions	H to F	~ 100	1-3	$\sim 10^4$
12	Nuclear reaction	Ions	Deuterons, δ -ray Protons, He^+	Specific elements	~ 50	~ 5	5×10^6
13	Mossbauer spectroscopic	X-rays	δ -rays, X-rays electrons	Mossbauer elements	~ 5000	—	$\sim 10^4$
14	Laser Raman spectroscopic	Mono chromatic (laser)	Scattered Light	Raman active molecules	> 1 mono layer	~ 1	$\sim 10^3$

analysis consists of exposing specimens to thermal neutrons in a reactor facility, followed by δ -spectrometry and is useful in qualitative analysis of corrosion products.

Electron spectroscopy is classified as photo-electron spectroscopy (PES) if the ionizing process is achieved by ultraviolet radiation or electron spectroscopy for chemical analysis (ESCA) if a monoenergetic X-ray source is used. The growth of protective films from sub-monolayer coverage on different metals can be studied by ESCA^{1,2}. Although this technique is not suited to the determination of small deviations in stoichiometry, compounds such as oxides can be distinguished from the parent elements of the basis metal by analysing chemical the parent elements of the basis metal by shifts. The oxygen shift is helpful in distinguishing oxide, hydroxide and bound water forms³.

Is secondary ion mass spectroscopy (SIMS), surface and interior microanalysis of solids materials for all elements in the p.p.m. range and below, are possible. Microcompositional data on a three dimensional basis can be obtained since the technique utilizes ion sputtering to remove surface material. In an ion microprobe mass analyser, a focussed ion beam is swept across the surface to give an ion micrograph, while in a Cameca ion microanalyser, ion micrographs are obtained by direct imaging.

Ion scattering spectroscopy consists of bombarding the specimen surface with inert gas ions such as $^4\text{He}^+$, $^{20}\text{Ne}^+$ or $^{40}\text{Ar}^+$ with 200-5000 eV and energy analysing the scattered inert ions at a specific angle. Peak resolution decreases if the difference in mass between the surface atom and the inert gas increase. Also, to make an entire elemental scan, different gases are required⁴. A monoenergetic ion beam, usually $^4\text{He}^+$ is also used to bombard specimens in Rutherford back-scattering spectroscopy (RBS), but at much higher energies (2 MeV), to yield information about the mass, the absolute amount and the depth profile of elements present upto a few microns. RBS is quick, quantitative and does not require calibration. The main limitation of RBS is the inability to separate elements of similar mass. Elastic recoil detection analysis (ERDA) uses even higher energy incident ions (10-40 MeV and typically chlorine) to probe the surface. ERDA differs from, but is complementary to RBS, in that ERDA is particularly sensitive to light elements in heavy substances⁵. In the nuclear reaction technique a high energy probe beam is used to produce nuclear reactions with impurity atoms. This technique also overcomes the difficulty of measuring light elements in a heavier matrix. For example, carbon and oxygen can be detected using the reaction $^{12}\text{C}(d,p)^{13}\text{C}$ and $^{16}\text{O}(d,p)^{17}\text{O}$ respectively, where "d" refers to a deuteron, "p" the emitted proton, and the latter is detected. A combined technique of RBS and ERDA or RBS and nuclear reactions is effective for obtaining the concentration profiles of both metallic species and oxygen in a thick surface film⁶.

Mössbauer spectroscopy is a form of δ -spectroscopy where in δ -rays penetrate the specimen and due to de-excitation, produce the emission of δ -rays, X-rays and electrons. These are counted by a detector. From a Mössbauer spectrum (count rate vs Doppler velocity) three parameters viz., the centre shift, quadrupole splitting and magnetic splitting can be derived, and used for unambiguous identification of one or more chemical species of a given Mössbauer atom. Only a limited number of tracers are suitable for Mössbauer spectroscopy, the major one being ^{57}Fe . The three parameters mentioned above are sensitive to the oxidation state of iron. Mössbauer spectroscopy has been used to determine the composition of rust on steel surfaces and

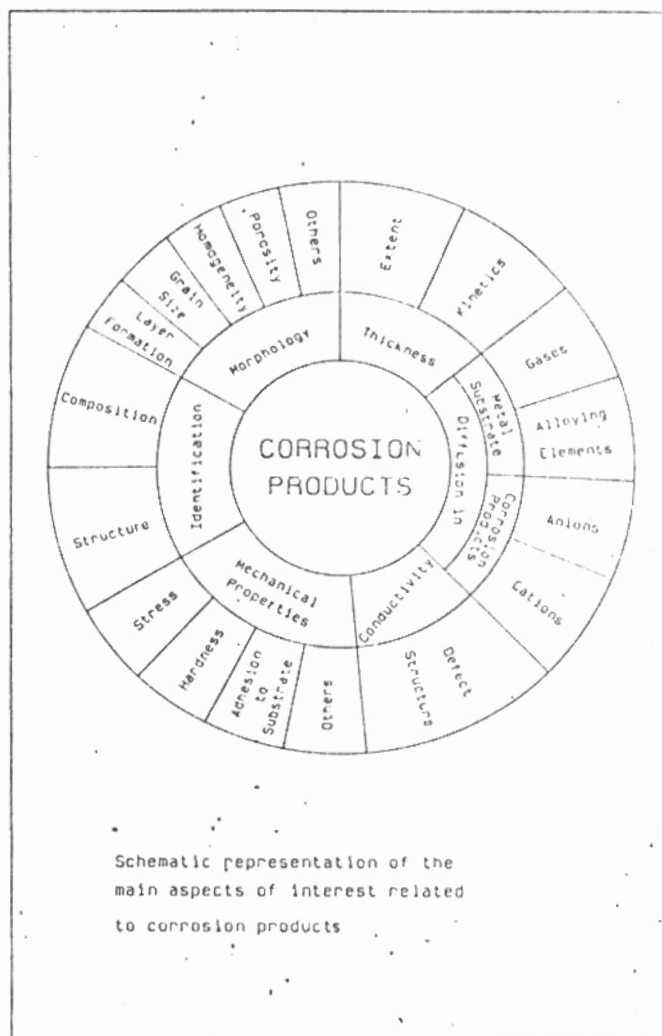


Fig 1. Schematic representation of the main aspects of interest related to corrosion products

to provide information about the relative concentrations of the different species⁷. Compared to X-ray diffraction, this technique is sensitive to both crystalline and amorphous constituents. Laser Raman spectroscopy can be used for insitu analysis of corrosion product films in gaseous and aqueous environments, since water and most of the gases give very weak Raman spectra and hence produce little interference. This technique provides quick and nonambiguous identification of corrosion products present in surface films as thin as 50 Å. In order to identify compounds, it is necessary to have spectra of the pure compounds for reference⁸.

Identification-structure

Information about the structure of corrosion products also help in their identification. The techniques widely used for structure determinations are X-ray diffraction and electron diffraction. Besides identifying compounds, these techniques also yield information about the crystal size, orientation and lattice parameters. X-ray diffraction has been extensively used to study both detached oxides with the aid of Debye Sherrer powder cameras and oxides insitu using glancing angle or back reflection techniques. Electron diffraction is similar to X-ray diffraction in many respects, but the depth of penetration of electrons is small and of the order of several 100 Å. In low energy electron diffraction, (LEED), electrons with energies as low as 100 V are used to identify oxidation products on an atomic scale, enabling the study of the early stages of oxidation⁹. Transmission electron dif-

fraction can be used to study both oxides attached to metals and detached oxides^{10,11}.

Morphology

Morphological information about corrosion products generally includes data such as form, homogeneity, grain size, presence of porosity, cracks, layers and others. The techniques often used are various forms of microscopy (optical, electron, ion) and mercury porosimetry. The most common technique for studying thick corrosion products in plan or in section is optical microscopy. Table II summarizes the information that can be obtained from optical microscopy of corrosion products. Other special optical techniques which can be used for morphological studies include interference microscopy, phase contrast microscopy, infrared and ultraviolet microscopy and chemical microscopy¹². The use of polarized light helps identify layering in corrosion products¹³.

Scanning electron microscopy (SEM) is a widely used technique for studying corrosion product morphology, as it combines high resolutions, improved depths of field and simple specimen preparation. Transmission electron microscopy (TEM) of corroded specimens includes the study of (a) replicas of corroded surfaces (b) replicas of thick oxide sections, (c) stripped oxides and (d) thin metal films with oxides on them. Information about pore structure in aluminium oxides was obtained by studying oxide replicas¹⁴. The study of stripped oxide films by TEM calls for special handling and specimen preparation techniques¹⁵. The study of thick oxides has been made possible with the high voltage electron microscope (HVEM), which eliminates tedious specimen preparation steps. The scanning transmission electron microscope (STEM) helps reveal besides specimen morphology, secondary electron image, selected area diffraction patterns, microbeam diffraction patterns, electron channelling patterns and elemental analysis.

TABLE II. INFORMATION OBTAINED FROM OPTICAL MICROSCOPY OF CORROSION PRODUCTS

OBSERVATION	INFORMATION OBTAINED
in plan	(a) uniformity of corrosion (b) colour (c) grain size (d) spalling (e) edge effects (f) presence of protuberances
in section	(a) uniformity of thickness (b) local or general loss of adhesion (c) porosity (d) layer structure (e) cracking (f) grain size and distribution (g) grain boundary penetration (h) precipitation phenomenon (i) presence of internal oxides
with polarized light	(a) presence of complex oxides (b) layer structure
with oblique illumination	(a) with greater depth of focus (b) with increased contrast

Field emission microscopy (FEM) has been used to study the early stages of oxidation of refractory metals and oxide morphology¹⁶. In field ion microscopy, (FIM) magnifications in the 10⁶ range and resolutions of the

order of 1-2 Å are possible and thus enable the detailed study of surface topography at the atomic level. FIM has been used to study oxide epitaxy on iron oxidised in the range 25-800°C in oxygen¹⁷. Oxide interfaces of nickel, cobalt and iron have also been studied with the aid of FIM¹⁸.

The conventional mercury porosimeter has often been used to characterize bulk ceramic oxides. A modification of this has been used for investigating pores down to 10 Å in thin oxide films on zirconium¹⁹.

Thickness measurement

Corrosion product thickness measurements are usually carried out to throw light on the extent or rate of corrosion. Table III lists a number of techniques that can be used for measuring corrosion product thickness. A number of surface analytical techniques coupled to ion bombardment apparatus are also often used for film or scale thickness measurement.

Other information

Information about self diffusion coefficients and concentration gradients of cations and/or anions in thermally oxidized films is also often sought. The EPMA and other analytical techniques coupled to ion bombardment apparatus can be used to measure metal concentration profiles. Some of the latter also give information about anion profiles. The diffusion rates are subsequently deduced from the profiles. Radioactive tracers can also be effectively used to determine the diffusion coefficients. Autoradiography of newly cut oxide — metal sections containing radioactive isotopes have been used to estimate the self diffusion coefficients and activation energies, to help identify the predominant diffusion mechanism, whether bulk or grain boundary²⁰. Oxygen ion profiles in oxides have been studied by proton activation of oxides, which give radioactive isotopes by nuclear transformation ¹⁸O(p,n)¹⁸F. The location of the isotope ¹⁸F is subsequently determined by autoradiography of sections²¹.

A number of metals dissolve substantial quantities of certain gases, hence the determination of the gas content in the underlying metal is also often carried out. Oxygen profiles in metals are usually determined by microhardness measurements, X-ray diffraction or vacuum fusion analysis²². In microhardness measurements, the orientation dependence of hardness has also got to be taken into account. The X-ray diffraction method relies on the influence of oxygen on the lattice parameter to give information about the oxygen content. Internal friction techniques also give diffusivity data at definite oxygen levels. The EPMA although less sensitive than the above methods, can also be used to determine the oxygen concentration in metals.

Electrical conductivity measurements on metal surface oxides throw light on the type of defects in the oxide. Caution is necessary during data interpretation as surface oxide layers have quite different grain size, grain size distribution and impurity distribution as compared to bulk oxides. Information about defect structure in oxides can also be obtained from a.c. impedance measurements and is sensitive to impurities and cracks in the oxide as well as to heat treatment effects.

Among the various mechanical properties of surface oxides (a) stresses (b) hardness and (c) adhesion to metal substrate constitute the more important ones. A number of techniques have been used to measure stresses in oxidizing specimens. The most common techniques for measuring stresses involve the measurement of the extent of bending of a foil or the angular deflection of a helix masked with an inert substance on

TABLE III — TECHNIQUES FOR MEASURING CORROSION PRODUCT THICKNESS

TECHNIQUE	FILM/SCALE THICKNESS AND OTHER FEATURES	REFERENCES
<i>A. Optical techniques</i>		
1. Optical microscopy	>1 μ and also > 100 Å	20
2. Differential reflection spectroscopy	< 7 Å°	21,22
3. Differential reflectometry	~ 50 Å° and insitu measurements	23
4. Two beam or multiple beam interferometry	~ 5 Å°	24
5. Interference colour measurement	$\lambda/4$ to few λ with 10% accuracy where λ is wavelength	25
6. Spectrophotometric measurements	250 Å° to 15 μ	26
7. Ellipsometry	< 100 Å° and insitu measurements	20
<i>B. Non-optical techniques</i>		
8. Coulometric reduction	~ 5 Å°	20
9. X-ray diffraction	0,1 μ — 100 μ	27
10. Capacitance measurement	Ion conducting anodic films > 10 Å°-1 μ	28
11. Electrical resistance measurement	Suitable for rapidly oxidising thin specimens	29
12. Film forming voltage measurement	Requires calibrated forming voltage vs thickness curves	30
13. Radioactive tracers	upto several 1000 Å°	31
14. Thermogravimetric measurements	Thickness determined as a function of weight gain	32
15. Surface analysis techniques coupled to ion bombardment apparatus.	examples: AES, SIMS, Activation analysis and others	—

one side during oxidation. Other techniques include (a) the measurements of stress relaxation during reduction of the oxide (b) measurement of restoring forces with electromagnetic systems to prevent stress induced deformation during oxidation and; (c) the use of X-ray diffraction. The microhardness of single phase oxide films is influenced only by grain size, whereas in mixed oxides, hardness gradients exist, requiring caution in the choice of spot for indentation. To measure the adhesion of oxides to basis metals, there is no standardised method. A crude method consists of attaching the oxide to a support with a resin and pulling it off using tensile machines. The limitations of this technique are obvious. Other mechanical properties such as tensile strength, elongation, loss of ductility and creep of corrosion products can be measured using conventional techniques but adaptations are necessary depending on the specimen, type of oxide, temperature and so on.

Concluding remarks

The characteristics of the techniques, whether it is to analyse the surface, obtain morphological information, measure thickness or any other parameter, differ. Some techniques give more information than others. A synergetic approach has often been found to be quite useful, especially for confirming results. The influence of high vacuum on data obtained should be borne in mind, since most equipment used in surface analysis and structure determinations operate under high vacuum and could affect corrosion products. More sophisticated equipment are continuously being developed and tested. However, many of the traditional techniques still continue to render relevant and meaningful information.

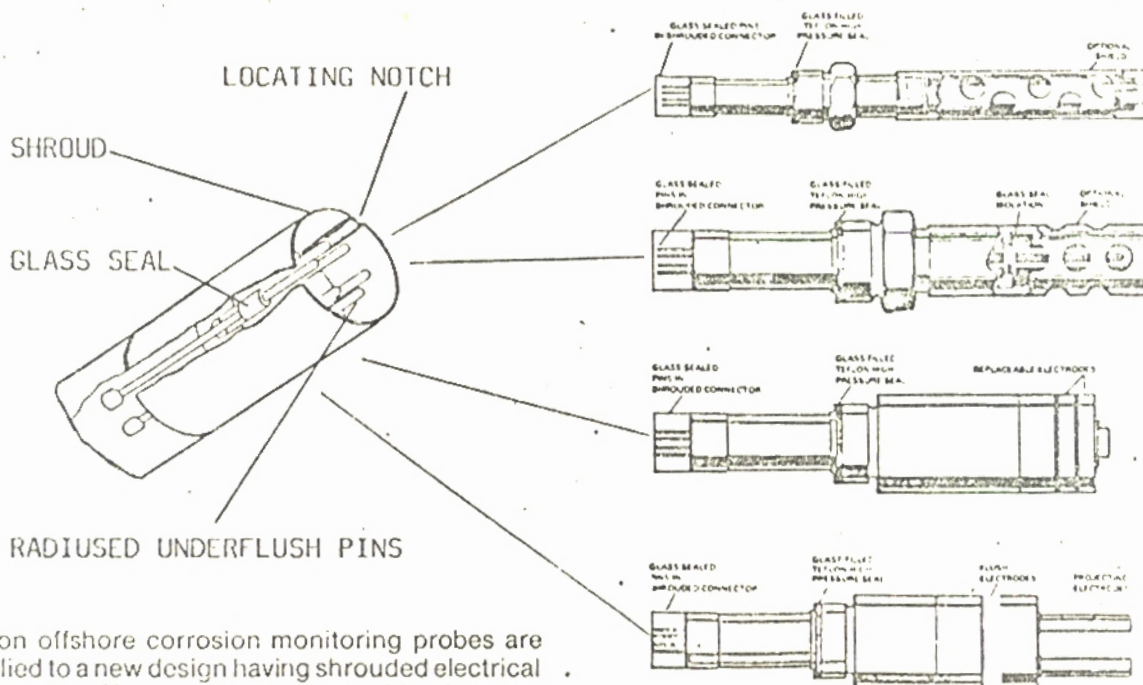
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